LA-UR-23-21437

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Title:	Small Angle X-Ray Scattering and Polymers
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Intended for:	Report
Issued:	2023-03-29 (rev.1)

Small Angle X-Ray Scattering and Polymers

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Abstract: Polymers are some of the most versatile and useful materials on this planet. Properties of polymers are a result of their processing history, chemical makeup, and physical structure. Therefore, characterization is necessary to develop new polymer formulations and processes. Many established techniques for polymer characterization are destructive, and alternative methods that don't destroy samples are in high demand. Thermal analysis techniques such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) yield important characteristic information for polymer samples while destroying the sample. Non-destructive strategies such as X-ray diffraction (XRD) or small angle X-ray scattering (SAXS) can also find polymer characteristics while preserving a sample's attributes. Sample preservation is desirable when investigating novel formulation and processing methods. SAXS analysis will be done on two different polymers: polyethylene, and a triblock copolymer. Using these two polymers allows for confidence between tests as polyethylene is very common, and well understood. Polyethylene analysis will be done first, and when methods have been refined so that the SAXS data matches accepted thermal analysis values for HDPE, there will be confidence to use the same analysis on block copolymers. Block copolymers remain relatively unexplored, so SAXS data will yield valuable information on their characteristics. Understanding the mechanical properties of these polymers is paramount to their application in upcycling, a process by which waste plastic can be converted into a higher value commodity. For this project, the upcycling process will be done via 3-dimensional (3d) printing.

1. Introduction

In the last 50 years, technology used to examine material properties has improved dramatically. Techniques have changed from using small samples that are ruined after testing (i.e., destructive techniques) to use of neutrons and photons to do nondestructive analysis. Additionally, new techniques allow for increased capacity, giving room for the study of larger samples. This may seem inconsequential, but in polymer characterization experiments, a small sample (millimeter scale) means that many tests from different parts of the original specimen must be done. For this project, analysis will be done on HDPE samples and polymer filament using SAXS. The block copolymer filament can be analyzed after 3d printing and while polymer is being printed because of the increased capacity and accessibility of SAXS instruments. Previously, to investigate the crystalline structure of polymers, DSC would have been used.

1.1 Differential Scanning Calorimetry

DSC probes how polymers respond to heating. The response describes many of the physical properties of the polymer. These include heat capacity ($q/\Delta T$), where q is heat energy and ΔT is the change in temperature, glass transition (the point where mechanical properties change from elastic to brittle), crystallization (the point where the polymer chains are energetic enough to form ordered crystals), and melting point (where the chains move freely and lose any structure). A differential scanning calorimeter will find these quantitative values by "heating two pans, one with sample, and the other without to be used as a control. The calorimeter monitors the temperature and regulates the rate at which the temperature of the pan s change." [1] Developed by E.S. Watson and J.J. O'Neill in 1962 [2], DSC has been one of the primary methods of investigating polymer properties ever since. One issue with DSC is that it uses a small sample of polymer. These small samples may not represent the bulk material, as crystalline domains occur on the micrometer scale. Therefore, many samples will be necessary to account for variation across a large sample. Additionally, DSC is destructive to samples, so specimens cannot be modified and tested again. These disadvantages push the upcycling project to use photons instead, as they aren't destructive and larger samples can be used.

1.2 X-Ray Diffraction

Diffraction is a fundamental principle that pervades all optics. Described as the process by which a beam of light or other system of waves is spread out as a result of passing through a narrow aperture or across an edge," and shown in Figure 1A, diffraction and should be a familiar concept demonstrating how light behaves as a wave.

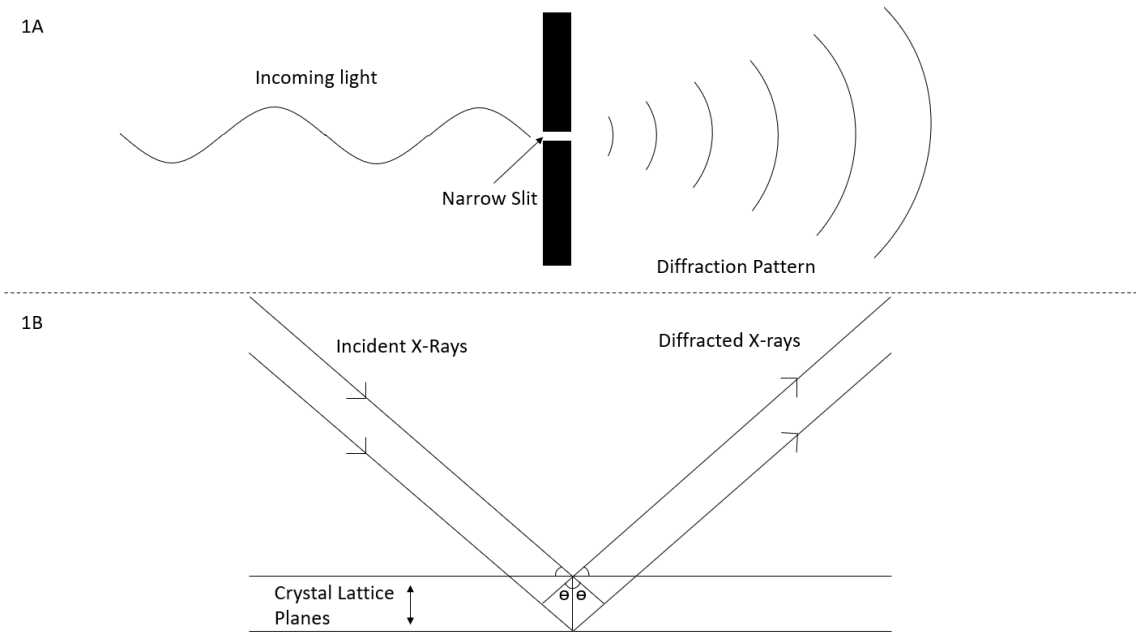

Fig. 1A. Diffraction illustrated as light waves passing through a single slit and then spreading out, demonstrating the wave nature of light. Fig. 1B. A schematic view of X-rays entering a sample and diffracting out [1]. The diffracted X-rays would then enter a detector for further analysis.

Diffraction is important because it can be used to analyze polymer structure. X-ray diffraction (XRD) is like DSC in the sense that crystallinity can be observed. It differs by being nondestructive and uses a larger range of sample sizes. Additionally, DSC can only get crystallinity percentage by weight, where XRD acts like a microscope, allowing for observation at the atomic level. In XRD, "X-rays are sent through a sample to determine composition, crystallinity, and phase purity. The X-rays change direction when they impact atoms in the structure, which changes the angle of the beam. This change in angle is the angle of diffraction. Some beams constructively interfere and produce a greater signal for specific angles. Bragg's law is then used to find the difference between atomic planes." [3] Bragg's law is given by $sin\theta = n\lambda/2d$ where λ is wavelength, θ is the angle of diffraction, and d is the distance between atomic planes. Solving for d gives the distance between the sheets of atoms with some simple algebra. Every other factor in Bragg's equation is known and will be a parameter of the experimental setup. A visualization of XRD can be seen in Figure 1B. X-rays have a wavelength similar to the spacing between atoms in a sample, making them the ideal candidate for atomic-level analysis. This means that "the angle of diffraction will be affected by the spacing of the atoms in the molecule." [3] Another way to look at polymer structure via photons is by using SAXS. This technique is for slightly different applications than X-ray diffraction and will be the focus of this project.

2. Small Angle X-ray Scattering

X-rays were first used in scattering observations in the 1930s. [4] This was no easy task, as primitive X-ray sources were used, and scattering measurements must be done close to the incident beam. While X-ray diffraction investigates the sub-nanometer scale, SAXS is best suited for 1-100 nm measurements. [5] Scattering happens mostly within two regimes, elastic and inelastic [6]. Elastic scattering, also known as Rayleigh scattering, occurs when "the wavelength of the scattered light is not changed apart from a possible doppler shift due to movement. This implies that the inner energy of the scattering particles is not change; there is no electronic excitation of deexcitation involved." [6] Inelastic scattering or Raman scattering happens when "the inner energy of the scattering particles changes. For Raman scattering of gas molecules, "the vibration and rotation states of the molecules change. Typically, the molecules have a higher energy after the scattering process, implying a correspondingly lower photon energy." [6] Since the first SAXS observations, many changes have been made to SAXS instrumentation. These changes include better X-ray sources, such as synchrotron generators instead of copper/molybdenum targets, fine collimation systems, and monochromator crystals. These advancements have made for more accurate measurements as well as better resolution. [7] Additionally, there have been advances in interfaces, software, and data analysis capabilities, making SAXS instruments much easier to use, and allowing for a greater range of data to be taken. These changes have led to fascinating systems with impressive optical capabilities.

2.1 Optics Behind SAXSD

Designing a SAXS system is no easy task. A common design for a SAXS instrument uses pinholes to guide a beam of X-rays to a sample. Figure 2 shows a transmission geometry setup for a SAXS measurement. This setup "consists of an X-ray source and a set of optical devices that define the beam energy and shape the beam geometry and direction. A sample is placed in the incident beam and the scattering profile is recorded on a 2D detector." [3]

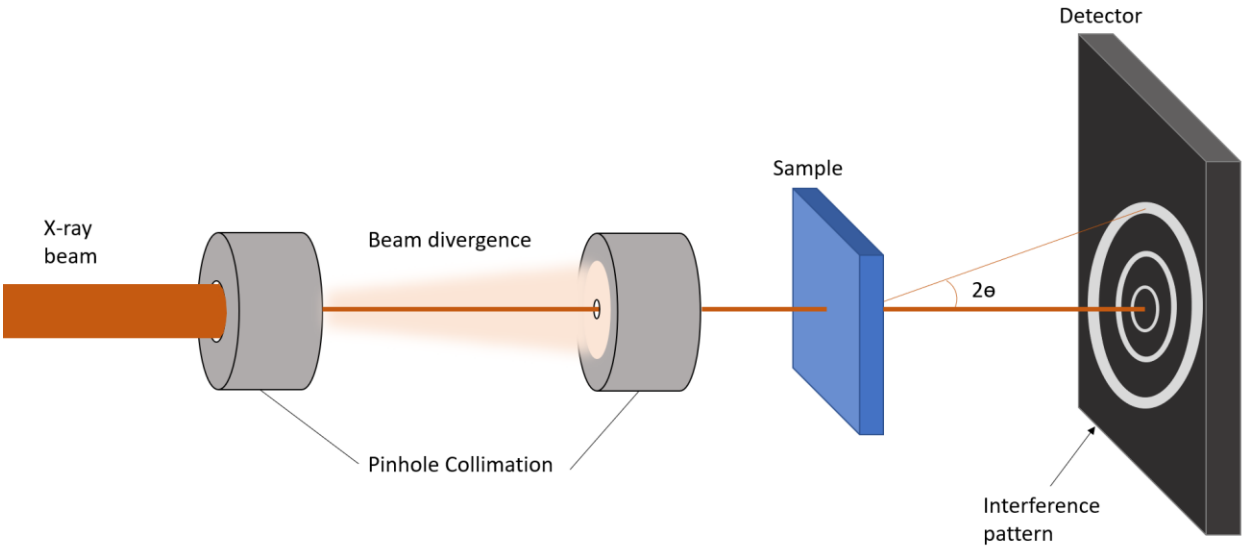

Fig.2. A basic Transmission Geometry set-up for SAXS done by "delivering a collimated beam through a sample. As the beam travels through a sample, a small portion of it interacts with the atoms to create scattering events. The intensity of the scattered radiation is collected on the detector." Adapted from [3]

To determine the energy at which the X-rays should be sent, it is important to know how scattering works. Every atom has a chance to scatter or absorb an incident X-ray. When averaged over time, a value known as the "differential scattering cross section" is determined. This cross section "describes the magnitude of the interaction between an atom and an applied X-ray field that yields a particular type of scattering event, taking into account the flux and energy." [8] Once sufficiently powerful X-rays are generated, they need to be monochromatic. This is done with the use of a double mirror or crystal monochromator system. Mirror monochromators can "produce adequate energy resolution on the order of 0.1-1% and can increase the power density of the incident X-ray beam by a factor of 10-100 compared to crystal monochromators." [5] Once all the photons are the same wavelength, accurate measurements can be made, as the intensity received at the detector will not be a function of the incoming X-rays. The next task is detecting the X-ray photons. There are many ways to detect the scattered photons, with advantages and disadvantages for each.

2.2 Detectors for SAXS Measurements

Many different detectors are available for use in SAXS experiments. For photon counting, photodiodes are used, and are cooled to reduce thermal noise. Photodiodes are great for counts in a two-dimensional system; however, linear position-sensitive detectors increase efficiency of experiments and make time-resolved measurements feasible. For weak scattering measurements, Gabriel-type detectors have been used [5]. These detectors act like photomultiplier tubes, as they apply a high voltage to a wire in a gas chamber. As ionization events occur in the gas chamber, photoelectrons are accelerated in the wire, causing an avalanche effect, providing amplification. Additionally, two types of photodiode array (PDA) detectors have been used. These include directly exposed X-ray photodiodes, and

phosphor scintillators coupled to PDAs. Direct exposure photodiodes have a higher gain, but a narrower detectable range. Because of radiation damage, they also have a higher dark current and lower sensitivity. For phosphor scintillator – PDA type detectors, a phosphor with a short lifetime is needed, not only between the X-ray to visible conversion but for the conversion to visible photons inside the intensifier (via fiber optics) for acceptance by the PDA. [5] The instrument that will be used for this project (Xenocs Xeuss 3.0) has two detectors: A Pilatus 300K reverse biased photodiode and an Eiger 2 R 500K reverse biased silicon diode array [9]. Correctly picking up the scattered light is very important, which is why detectors play such a significant role in SAXS.

2.3 SAXS and Polymers

Using the same principles as X-ray diffraction, SAXS will be used to analyze polymer structure. The main difference is that SAXS is meant for larger scale structures. SAXS can still get some diffraction information in large lattices but is "better suited to distances between 10s and 1000s of interatomic distances, but also scattering by perturbed or nonperiodic structures." [5] This is significant for the polyethylene project because it will not be necessary to peer all the way down to the atomic level. A broader look at crystalline and non-crystalline regions is needed instead. To investigate polyethylene and block copolymers under different conditions, understanding the difference between the regions will provide useful information on internal structure. Knowing the internal structure gives insight to mechanical properties, which can be modified as needed. To gather this information, the Xenocs Xeuss 3.0 SAXS instrument will be used. Unfortunately, information on the inner workings of the Xeuss instrument is not publicly available. Regardless, the fundamentals of SAXS apply and will be the driving force for data collection on this project.

3. Polymers and Upcycling

As plastic use continues to grow, global production is expected to accelerate in the coming decades as seen in Figure 4. About 40% of this plastic is single use in nature and will end up as waste [10]. Additionally, according to a recent report by Beyond Plastics, a project based at Bennington College (Bennington, VT), only 5% of plastics that are sent to recycling are recycled, as most are not in the correct condition. [11] The other 95% ends up in the landfill or incinerator, damaging the environment [12][13]. Most of this plastic is HDPE, which is a material currently under the spotlight of polymer research. Because of its many uses, research is being done to investigate how manipulation of the polymer at the molecular level changes its physical properties. This leads to upcycling, a strategy that allows for waste plastics to be converted back to useful implements. This can be done by blending a block copolymer with a homopolymer. The resulting blend can be extruded into a filament, which can be three dimensionally (3D) printed into useful objects.

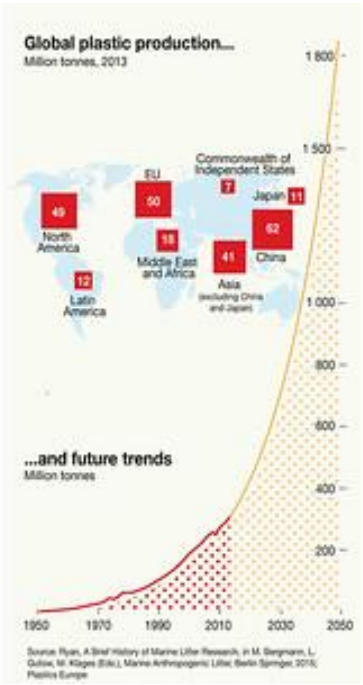

Fig. 4. Projected acceleration of global plastic production rates from Marine Litter Vital Graphics. This is an approximation based on current production rates, the trend toward more plastic is important, the qualitative numbers less so. [10]

3.1 Polyethylene and block copolymers

Polyethylene is incredibly versatile. It is strong, resistant to chemicals, and can be a sterile way to transport food and water. It is made by forming a long linear chain of hydrocarbons via the creation of free radicals at the end of hydrocarbon chains. The resulting polymer is purified into a powder, which can be machined into pellets. Through a process called compression molding, the pellets are heated and compressed into a slab of polyethylene. HDPE has large regions of crystallinity and low regions of branching polymer (~90 % crystalline). This means that there are strong intermolecular forces, increasing the toughness of the material. [14] Low density polyethylene (LDPE) has smaller crystalline regions (30-50% crystalline) and larger branching regions, as seen in Figure 1. This decreases the strength of the material and increases its flexibility. LDPE is commonly seen in plastic bags, while HDPE can make underground water pipes.

By itself, HDPE is quite useful, but alternative materials called block copolymers will be investigated as well. These copolymers are useful for compatibilizing polymer blends, especially in recycling applications. Compatibilization is important because homopolymer blends are often difficult to use. [12] Block copolymers, when combined with a homopolymer, yield an increased break and tensile strength and are much easier to work with than homopolymer blends.[12] For the upcycling project, it will be necessary to use a block copolymer that will pair well with waste plastic to create a more robust material [15].

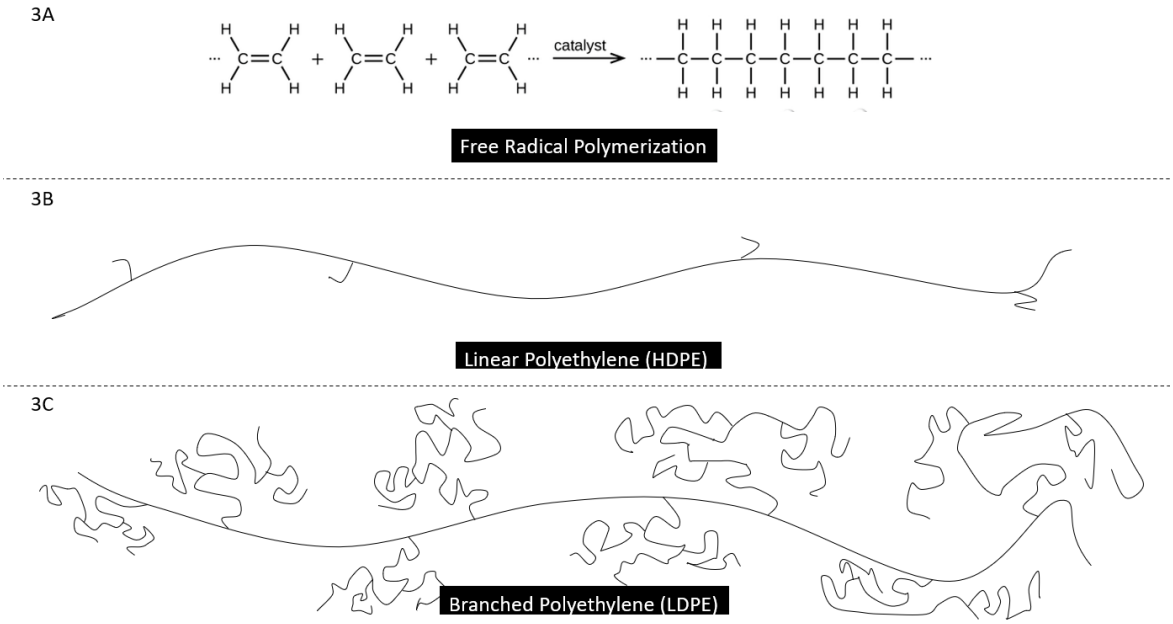

Fig. 3A. A visual description of free radical polymerization, the method by which polyethylene is made. From [16], License: https://creativecommons.org/licenses/by/4.0/deed.en . Fig. 3B. A linear chain of polyethylene, the structure that would make up most HDPE (Ex. water pipes). Fig. 3C. An example of branched polyethylene, which would make up LDPE (Ex. plastic bags)

4. Conclusion

Polymer science is a fascinating field that is still very young. Because of widespread plastics use, it is becoming more important to understand the properties of polyethylene and block copolymers to help with global recycling/upcycling efforts. To make material that can by upcycled, block copolymers can be used to change the mechanical properties of recycled material. Once the material has been "upgraded" it can be 3dprinted into any desired shape, completing the upcycling process. Once the samples are printed, small angle X-ray scattering measurements will be taken to gain information on the internal structure of the printed polymer. Additionally, SAXS data will be taken on polyethylene samples. This is done by sending a beam of collimated, monochromatic X-rays at a sample, and measuring the scattered light using a complex detector system. The measurements will then be used to characterize the nano-scale structure of the polymer which will then be correlated to mechanical properties.

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