Polarizing Optical Microscopy: Birefringence Analysis and the Effect of Different Crystallization Temperatures on the Spherulitic Microstructure

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203

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Abstract

The purpose of this experiment was to analyze birefringence and spherulitic microstructure characteristic of semicrystalline polymers using the OLYMPUS BH-2 polarizing optical microscope. The interactions of polarized light with a birefringent sample and none birefringent sample were observed and analyzed. The effects of different crystallization temperatures on the spherulitic microstructure were determined. The samples being examined were polyethylene (PE) and poly (ethylene oxide) (PEO). The oriented region of the PE sample produced a "Maltese cross" pattern, indicating that birefringent materials have the optical property of a refractive index that depends on the polarization and propagation direction of light. However, no light was observed in the unorentied region of PE. The average densities for the PEO samples were determined to be 67.87, 407.2 and 2539 spherulite/cm^2 at crystallization temperature of 25, 0 and -196 ˚C, respectively. it was found that as the crystallization temperature increases, the size of decreases and the density of spherulites increases. The experiment implied that the size and the density of the formed spherulites affect crystallinity, which in turn influences other mechanical properties of polymers. Crystallinity increases with the increase in spherulite density and decreases with the increase in the spherulite size.

Introduction

When non-branched linear polymers such as polyethylene (PE) crystallizes from the melt, formation of sphere-shaped semicrystalline areas occurs.[1] These ordered regions, just like the grains in metals and ceramics, inside non-branched linear polymers are called spherulites.[2] A spherulite has a diameter ranging from 1 to 1000 micrometers.[2] It is composed of nucleus, lamellae, and interlamellar regions, as shown in Figure 1. Nucleus is the center part where the formation begins to grow. Lamellae is the crystalline part of spherulite with ribbon-like, which grows radially from center.[2] The amorphous part of the material is contained in the interlamellar regions.[2]

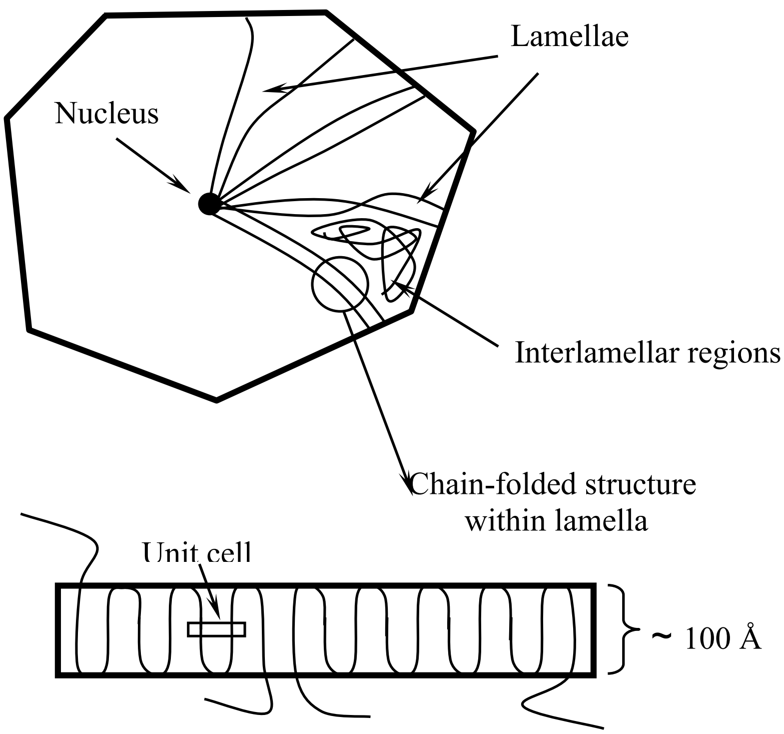


Figure 1. The internal structure of a spherulite, showing the arrangement of the polymer molecules.[2]

Formation of spherulites influences many properties of the polymer material. In term of optical properties, alignment of the polymer molecules within the lamellae results in birefringence producing a variety of colored patterns, including Maltese cross. In a birefringent material, the index of refraction (n) is different in one direction compared to another (usually perpendicular). Birefringence, and therefore the presence of polymer chain orientation, can be observed in the polarizing microscope, where the beam of light is directed in one orientation by passing it throw the polarizer. In the polarizing microscope, the sample is placed between the polarizer and the analyzer. The polarizer is below the microscope stage, and the analyzer is in the column.

In the polarizing microscope, the phase of the light entering the sample is the same for both components. This means that the ratio of the electric vector magnitudes of the two components stays constant before the light enters the sample. The path lengths of the light as they exist the sample can determine of a sample is birefringent.[1] If a sample is birefringent, a Maltese cross pattern will be observed due to the difference of the path length for the two components as shown in Figure 2. These components will not be in phase when they exit the sample. This indicates that the ratio of the electric vector magnitudes for the two components changes. On the other hand, if a sample is not birefringent, no batter will be observed due to the fact that and no phase difference between the two components as the light propagates through the sample exists. The light exiting the sample remains vertically polarized and no light gets through the analyzer.[2]

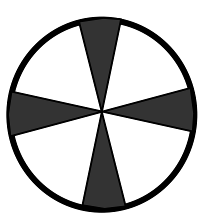


Figure 2. “Maltese cross” pattern produced by a birefringent materials.[2]

The purpose of this experiment was to analyze birefringence and the spherulitic microstructure characteristic of semicrystalline polymers using polarizing optical microscopy. The interactions of polarized light with a birefringent sample and none birefringent sample were observed and analyzed. The effects of different crystallization temperatures on the spherulitic microstructure were determined. The samples being examined were polyethylene (PE) and poly (ethylene oxide) (PEO).

Experimental Procedure

The equipment used in this experiment was the OLYMPUS BH-2 polarizing optical microscope. The software used with the equipment was Axiovision 4.7.2. For analyzing polymer crystallization, a total of six PEO samples were prepared at three different temperatures, 25, 0 and -196 ˚C. For analyzing polymer orientation, two PE samples were obtained from a plastic soda bag.

In order to prepare the six PEO samples, a small quantity of PEO was placed on each of six glass slides. Then, the slides were placed on a 75 ˚C preheated hotplate, which enabled polymer samples to melt. After melting was complete, each slide was covered with a cover glass, allowing the polymer to spread uniformly between the slide and the cover glass. Using a pair of tweezers, two samples were quickly transferred into liquid nitrogen. Two were transferred in an iced water, and the other two were simply allowed to air cool. Any condensation that had formed on the liquid nitrogen-quenched sample was allowed to evaporate. The samples were allowed to crystallize.

The light at the base of the microscope was turned on, and the polarizers were set at a 90˚ angle. This was achieved by looking into the eyepiece and rotating one of the polarizers until the field was as dark as possible with no sample on the stage. Each sample was first placed on the microscope stage, between crossed polarizers. Then, the lowest power objective lens was selected.

The image of sample was focused while it was observed through the eyepiece. Focusing with other objective lenses in place was accomplished by moving the stage down. A caution of moving the stage up while looking into the eyepiece was taken into consideration. Such a practice can damage the lens if the sample is brought into contact with it. [2] After the image was fully focused, two representative micrographs of each PEO samples were taken. The software was used to add a calibration bar to each micrograph. The effect on the "Maltese cross" pattern was observed in two scenarios. The first one was after the sample stage was rotate. The second scenario was that the sample was left stationary and the polarizers were rotated together (maintaining a 90˚ angle). For polymer orientation analysis: a piece of polyethylene (PE) retainer ring was carefully stretched until a necked region about an inch long formed. The sample was obtained by cutting out the necked region and including a portion of the unreformed regions on each side of the neck. The sample was flattened by clamping it between two microscope slides. The necked and the unreformed regions were compared in the polarizing microscope. The effects were noted when the sample was rotated through 360˚. [2]

Results

A PE retainer ring sample was observed before and after stretching. Before starching, the observed pattern as it was rotated through 360º between crossed polars was completely dark. After starching, the observed pattern as it was rotated through 360º between crossed polars was found to follow the pattern in Figure 2, where it produced dark at the crossed polars. No light got through the analyzer when the first index was parallel to the polarizer where all the light propagated down the first index axis. When the sample was rotated 90º, 180º and 360º, the sample appeared dark as well. The sample appeared thicker to the light beam in the high index direction, and thinner in the low index direction.

In all of the PEO samples, linear boundaries were observed to form between adjacent spherulites, and within each spherulite appears a “Maltese cross”. Rotation of the sample through 360º had no effect on the pattern, while Rotation of the polarizer and the analyzer, with the sample fixed, caused the “Maltese cross” pattern to rotate.

The spherulites of PEO at crystallization temperature of 25 ˚C were found to be uniform with low density, as shown in Figure 3. The spherulites of PEO at crystallization temperature of 0 ˚C were found to be less uniform with moderate density, as demonstrated in Figure 4. The spherulites of PEO at crystallization temperature of -196 ˚C were found to be uneven with large density, as seen in Figure 5.

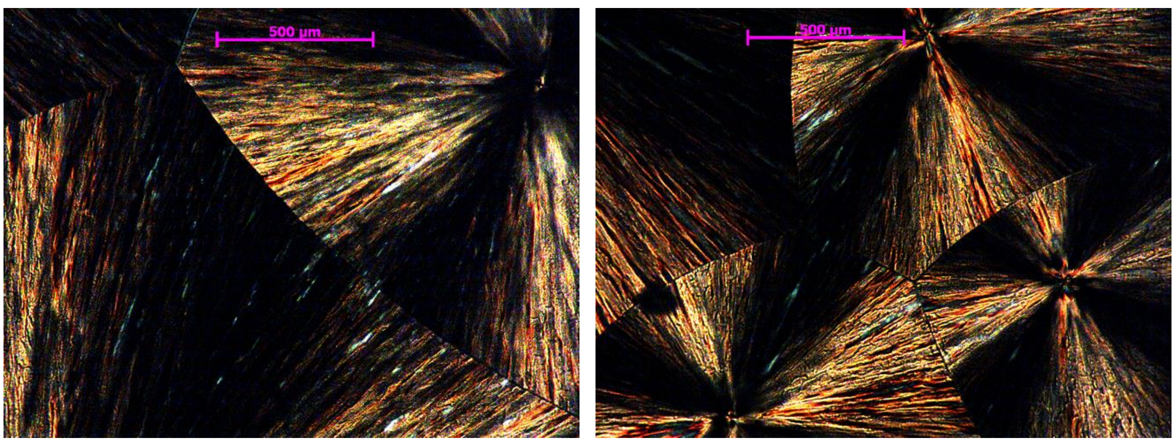


Figure 3. A transmission photomicrograph (using cross-polarized light) showing the spherulite structure of poly (ethylene oxide) at crystallization temperature of 25 ˚C.

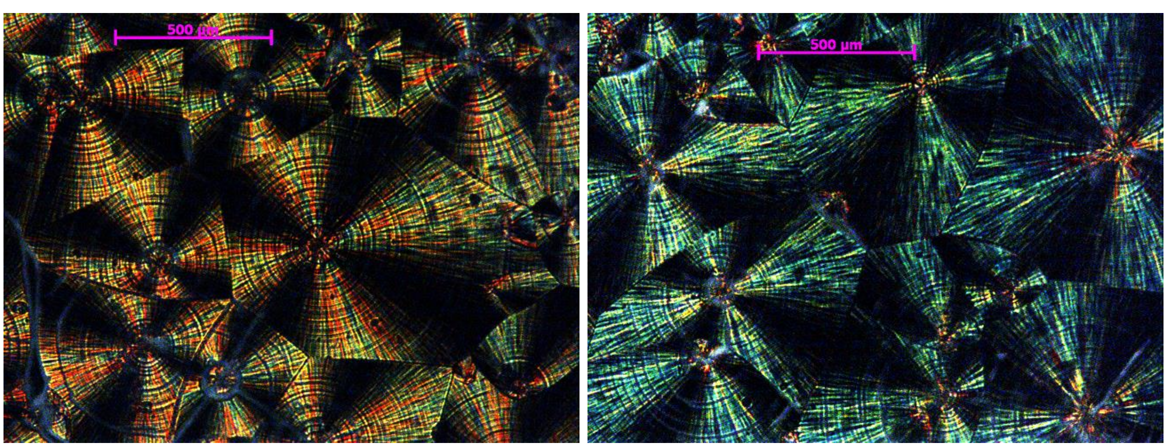


Figure 4. A transmission photomicrograph (using cross-polarized light) showing the spherulite structure of poly (ethylene oxide) at crystallization temperature of 0 ˚C.

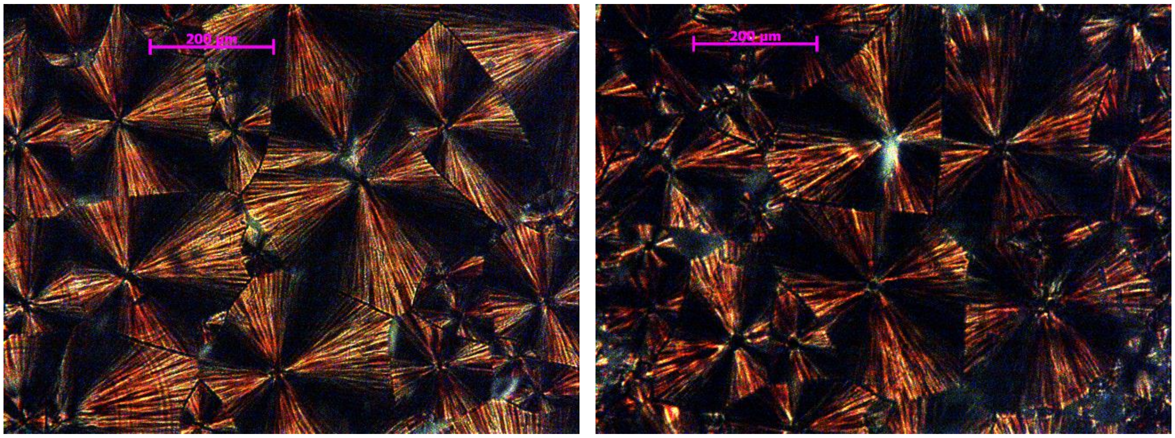


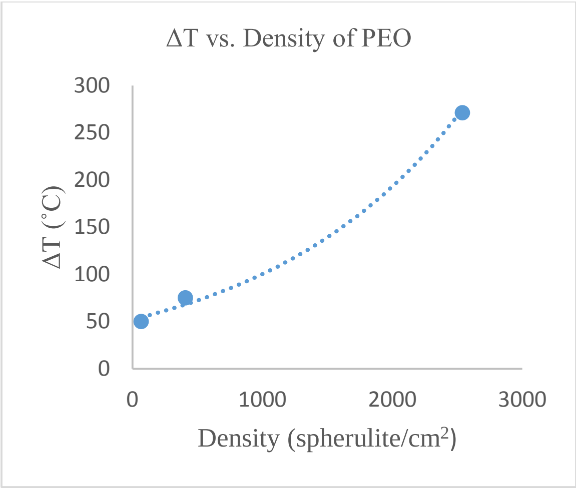
Figure 5. A transmission photomicrograph (using cross-polarized light) showing the spherulite structure of poly (ethylene oxide) at crystallization temperature of -196 ˚C.

The average densities for the PEO samples, as shown in Table 1, were determined to be 67.87 spherulite/cm^2 at crystallization temperature of 25 ˚C, 407.2 spherulite/cm^2 at crystallization temperature of 0 ˚C, and 2539 spherulite/cm^2 at crystallization temperature of -196 ˚C.

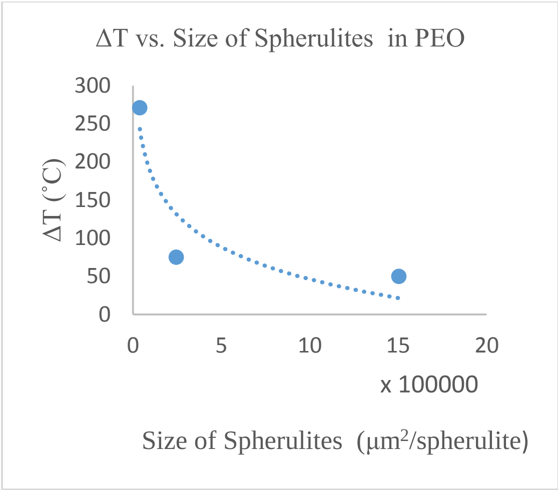
Table 1. The calculated density of spherulites in spherulite/cm^2 and the size of spherulites in mm^2/spherulite.

Cryst. Temp.	spherulite/cm^2			mm^2/spherulite		
(˚C)	Sample 1	Sample 2	Average	Sample 1	Sample 2	Average
25	58.18	77.57	67.87	1.72×10^6	1.29×10^6	1.50×10^6
0	426.6	387.8	407.2	234×10^5	257×10^5	2.46×10^5
-196	2698	2380	2539	3.71×10^4	4.20×10^4	3.95×10^4

It was observed that as the crystallization temperature decreases, the density of spherulites increases whereas the size of spherulites decreases. The relationship between ΔT (˚C) and density of spherulites were determined to exponential and the reciprocal of it for the size of spherulites, as shown in Figure 6.



(a)



(b)

Figure 6. Graph (a) shows an exponential relationship between ΔT (˚C) and density of Spherulites in PEO. Graph (b) shows a reciprocal relationship of the density of Spherulites in PEO.

Discussion

No light passed through the unstretched PE sample as it was revolved through 360º because there was no phase difference between the two components of light. In more details, the light exiting the sample remained vertically polarized and no light got through the analyzer. Thus, there was no rotation of the plane of polarization observed, indicating that the indices of refraction were equal to one another. [1,2] The stretched PE sample exhibited a "Maltese cross" pattern as it was revolved through 360º, which indicates that the sample was uniaxially oriented, birefringent. It appeared dark at the crossed polars because one of the indices was parallel to the polarizer where all the light propagated down the index axis, preventing any light to get through the analyzer. [3] The "Maltese cross" pattern observed was due to the difference in the speed of light when it propagated in one direction compared to the other. This phenomena happens when the indices of refractions are not equals to each other. It is worthwhile to note that the smaller the index of refraction is, the faster the waves of light will propagates through it. [2]

In the PEO samples, all rotating angles were concurrently existing due to the many lamellae and their radial orientation. Lamellae parallel to the polarizer or the analyzer stubbed out vertically polarized light, while lamellae with intermediate orientations rotated the plane of polarization and allowed some light to pass through the analyzer. A "Maltese cross" pattern was observed as shown in Figure 3, Figure 4 and Figure 5. The rotation of the polarizer and the analyzer, with the sample fixed, caused the Maltese cross pattern to rotate because the location of lamellae was changed taking into consideration its new location to the polarizer or the analyzer. As demonstrated in Figure 5, the ununiformity of spherulites existed in the PEO sample crystallized at -196 ˚C was caused by not maintaining a constant temperature at the time of crystallization. [3] It was observed that as the crystallization temperature decreased, the density of spherulites increased whereas the size of spherulites decreased, as indicated in Table 1 and Figure 6. This is due to the fact that as Tc declines, the nucleation rate grows exponentially; number of nuclei forming increases sharply as temperature is dropped below melting point. [2, 3]

Conclusions

The purpose of this experiment was to analyze spherulitic microstructure characteristic of semicrystalline polymers using polarizing optical microscopy. The interactions of polarized light with a birefringent sample and none birefringent sample were observed and analyzed. The effects of different crystallization temperatures on the spherulitic microstructure were determined. The samples being examined were polyethylene (PE) and poly (ethylene oxide) (PEO).

Overall, the experiment succeeded in showing that birefringent materials have the optical property of a refractive index that depends on the polarization and propagation direction of light, producing a "Maltese cross" pattern. Furthermore, the experiment succeeded on demonstrating the dependency of spherulites microstructure on the crystallization temperature. It was concluded that the number of spherulites in the sample and their size depend on the degree of supercooling, fewer nuclei form when the crystallization temperature increases. The experiment also asserted that no light to passes through when the lamellae is parallel to the polarizer or the analyzer, while lamellae with intermediate orientations rotates the plane of polarization and allows some light to pass through the analyzer. The experiment implies that the formation of spherulites affects crystallinity, which in turn influences tensile strength and Young's modulus of polymers. [3] The size and the density of the spherulites has a great impact on changing the mechanical properties of polymers upon formation of spherulites. Crystallinity increases with the increase in spherulite density and decreases with the increase in the spherulite size. [3] Tensile strength and Young's modulus follow the same trend. The increase is a resulted from the lamellae portion within the spherulites, where the molecules are more closely packed than in the amorphous region. [1]

References

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[3] W.D. Callister Jr., Materials Science and Engineering: An Introduction, Seventh Edition (Wiley, New York, 2007).