Mechanism of Micro-Crack Propagation in Semicrystalline Polymers

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Abstract: The development and propagation of cracks is the principle reason for premature mechanical failure of polymeric materials. The well known and widely accepted fracture theories, namely the Griffith fracture theory and the Irwin model, both assume that fracture takes place through the presence of preexisting cracks in the polymer. These minor preexisting cracks, or micro-cracks, are practically present in most polymeric samples. The Griffith approach assumes that for any particular material, the fracture stress is controlled by the size of the flaws present in the structure.

The control and minimization of micro-crack size during polymer processing requires an understanding of the inherent micro-crack propagation mechanism.

The present research reveals a mechanism of internal stress-induced micro-crack propagation in semicrystalline polymers and describes the effect of the intricate crystalline morphological interactions on the extent and direction of intra-spherulite and inter-spherulite micro-crack propagation. In conclusion, a method for minimizing inter-spherulite micro-crack propagation is presented in this article.

INTRODUCTION

The principle reason for premature mechanical failure of polymeric materials and composites is the development and propagation of cracks. The crack development and eventual failure of polymeric materials, due to externally applied static and dynamic stresses, is an extensively researched subject which is crucial for assessing the performance of polymeric materials and composites [1,2].

There are two principle theories, or models, that attempt to describe the process of brittle fracture, the Griffith fracture theory and the Irwin model. Both models assume that fracture takes place through the presence of preexisting cracks in the polymer and are concerned with the phenomena occurring near the cracks when a load is applied [3-5].

These minor preexisting cracks, hereafter termed as micro-cracks, are practically present in most polymeric samples. The Griffith approach assumes that for any particular material, the fracture stress is controlled by the size of the flaws present in the structure. Accordingly, the breaking stress σ_B is given by the equation $\sigma_B = [4\gamma E/(\pi a)]^{1/2}$, where γ is the free energy per unit area of surface, E is the Young modulus and the crack length is a. The Irwin model has shown that the stress (σ) near the tip of a crack can be written in terms of the applied stress, crack length (a) and a quantity K, called the stress intensity factor. Accordingly, the breaking stress σ_B can be written as $\sigma_B = K_c[2/(\pi a)]^{1/2}$, where K_c is the critical stress intensity factor, at which fracture stress is reached [5].

The relevance of these models with respect to the present research is in the fact that both Griffith and Irwin relate to the presence of inherent micro-cracks as the basis of their theory and the fact that both models show a decrease of the breaking stress with the increase of the crack length.

Thus, the strength of any particular sample can be increased by reducing the size of these flaws [4-7].

The following research presents a mechanism of micro-crack propagation in semicrystalline polymers and describes the effect of the polymer crystalline morphology on the extent and direction of micro-crack propagation.

EXPERIMENTAL

Materials

DuPont Sclair 2909 high-density polyethylene (HDPE); Polyethylene oxide (PEO) MWs 6000 and 10000, purchased from Sigma.

Instrumentation

Polarized light microscopy studies were performed on an Olympus CX31 optical microscope, fitted with a polarizer and analyzer and a digital camera.

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Electron microscopy studies were performed on a SEM JOEL 6510LV instrument, equipped with a SE (secondary electron) detector, with a resolution of 3nm at 30 KV. Acceleration voltage was 10KV. The crystallized samples were viewed with Au sputter coating.

Reflectance microscopy studies were performed on a Zeiss Axiolab reflect light microscope, equipped with a Canon A80 digital camera. Crystallized samples were viewed after Au sputter coating.

Sample Preparation

The samples were melted on clean microscope glass slides and kept at above melting temperature for 2 minutes in order to erase crystalline memory and then crystallized by either quenching or by cooling at room temperature. Cooling at room temperature (at 30°C) was performed by removing the samples from the heating plate and holding the samples in the air until completion of the crystallization process. Sample quenching was performed in two stages: samples were removed from the heating plate and held in the air at room temperature until initial crystallization occurred, which was observed as a very slight loss of sample transparency, after which the samples were promptly cooled to 0°C, by ice-water.

All microscopy observations were performed without removal of the samples from the microscope glass slides, thus samples were undisturbed following treatment. For both SEM and reflectance microscopy, samples were Au-coated, since both these methods observe the sample surface and this can be best observed after Au sputter coating.

RESULTS AND DISCUSSION

The vast majority of polymeric materials are melt processed and are consequently subject to development of internal stresses during the cooling and hardening process. This phenomenon is particularly pronounced in polymeric materials due to their low thermal conductivity and thus uneven cooling process.

The materials chosen for this research were high-density polyethylene (HDPE) and polyethylene oxide (PEO). HDPE is one of the most used and researched polymers for a vast variety of applications and products and PEO is extensively researched and used in the biomedical field.

These polymers differ in all aspects, including crystal system (orthorhombic vs. monoclinic, respectively), molecular weights (50000 vs. 10000 and 6000, respectively) and average crystal sizes (100 μm vs. millimeters to centimeters, respectively).

Figure **1** exhibits SEM scans of high-density polyethylene (HDPE) and polyethylene oxide (PEO) films, air-cooled at 30°C. Both polymers exhibited micro-cracks within the spherulites. These micro-cracks were predominantly in the radial directions of the spherulites, indicating a stress-induced interlamellar cleavage of the crystals. In Figure **1a**, the stress-induced radial lamellar splitting resulted in splitting the spherulite, revealing the radial symmetry of the lamellar structure.
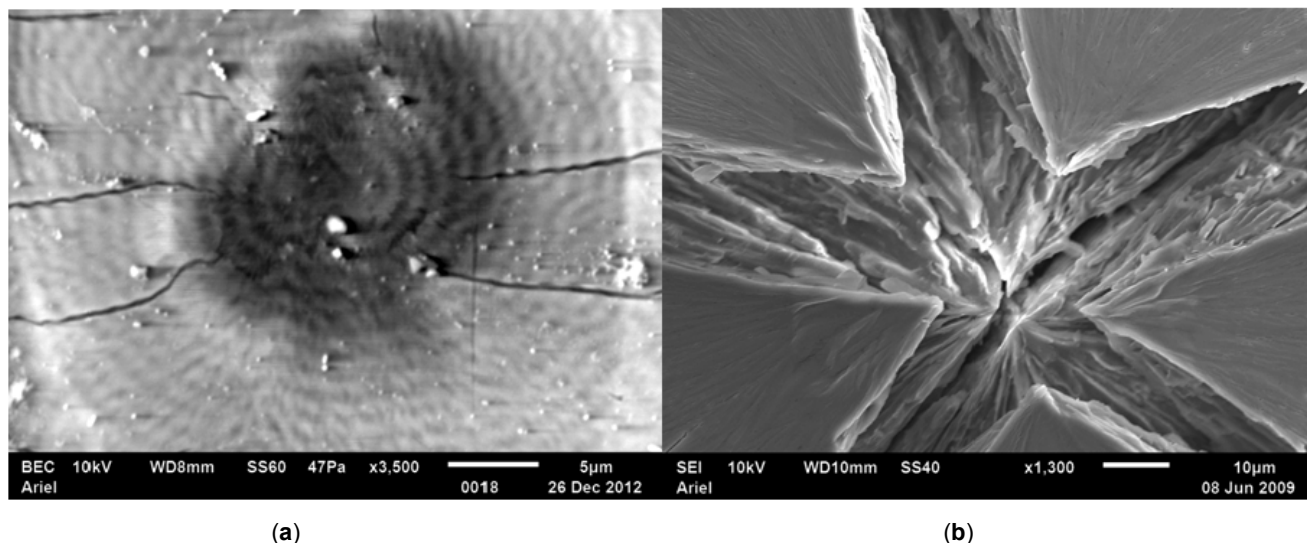

BEC 10kV WD8mm SS60 47Pa x3,500	5μm
0018	26 Dec 2012
Ariel	

SEI 10kV WD10mm SS40 x1,300	10μm
	08 Jun 2009
Ariel	

(**a**) (**b**)

Figure 1: SEM micrograph of a HDPE spherulite (magnification x3500) (**a**) and a PEO 10000 spherulite (magnification x1300) (**b**), exhibiting internal micro-cracks.
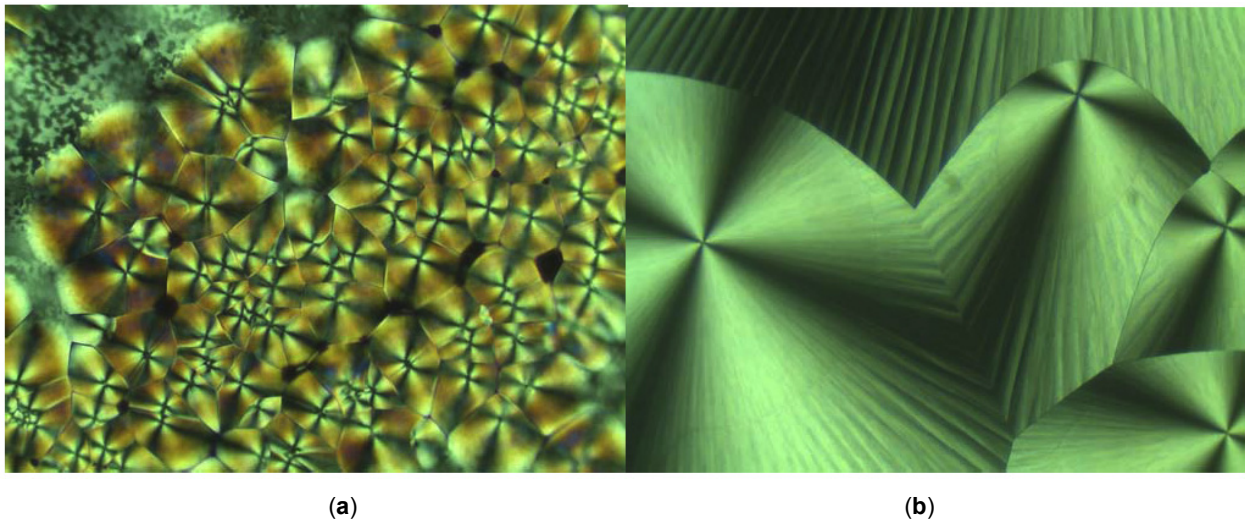
(**a**)   (**b**)

Figure 2: Pollarized light microscopy photographs of HDPE (small spherulites) (**a**) and PEO 10000 (very large spherulites) (**b**), both magnified x100.

As it is known, with increasing applied stress, internal or external, cracks gradually grow and propagate within the material. Thus it is reasonable to assume that at significant levels of internal stresses, the micro-cracks originating within the spherulites will propagate beyond the boundaries of these spherulites. The question that arises is in which direction the micro-cracks will propagate and what mechanism determines the propagation extent and direction.

The polarized optical microscopy (POM) pictures of the same polymers (Figure **2**) reveal the overall spherulitic crystalline morphology of these polymeric films, with distinct borders separating adjacent spherulites, which create an apparent honeycomb-like pattern. The morphology and crystallography of the

same HDPE under various crystallization conditions were published earlier [8,9].

Thus it may be possible to reason that a micro-crack growing beyond the spherulite boundaries, would continue to propagate along the inter-spherulite boundaries, rather than propagate into the adjacent spherulite. Nevertheless, by viewing the SEM scans of a relatively wide area of the polymeric films (Figure **3**), it may be clearly recognized that the micro-cracks that propagate beyond the spherulite of origin, consistently propagate in practically the same direction into the adjacent spherulite. More so, in areas in which the internal stresses were higher, these cracks continued further into the next spherulite and beyond into the next and so on. This phenomenon persisted consistently
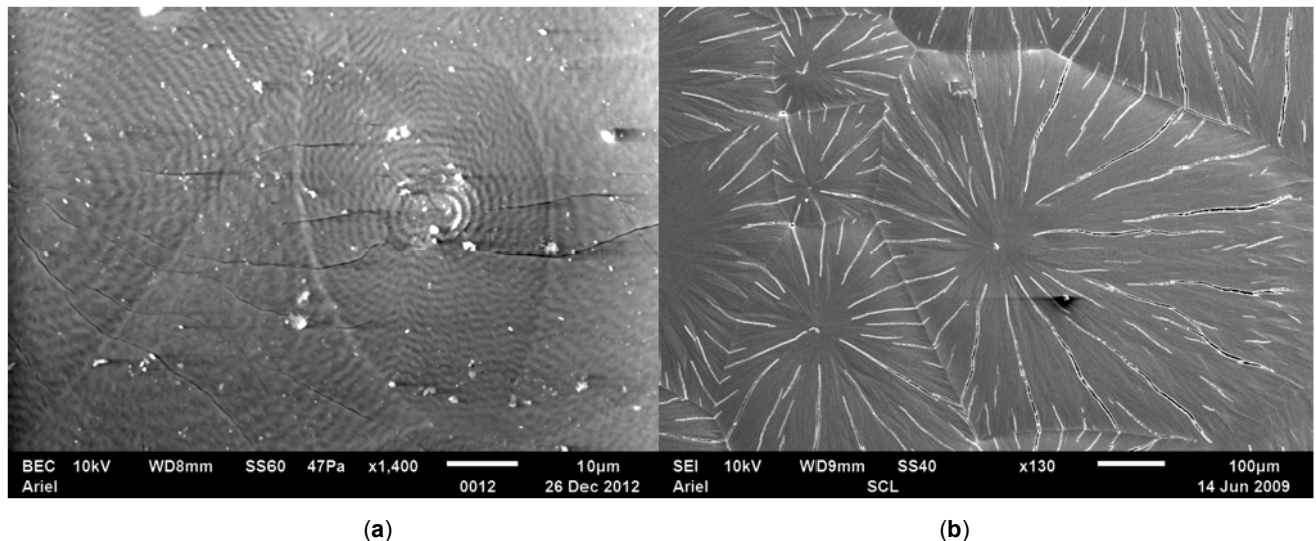

(**a**)   (**b**)

Figure 3: SEM micrograph of HDPE (magnification x1400) (**a**) and PEO 6000 (magnification x130) (**b**), exhibiting micro-cracks propagation pattern.
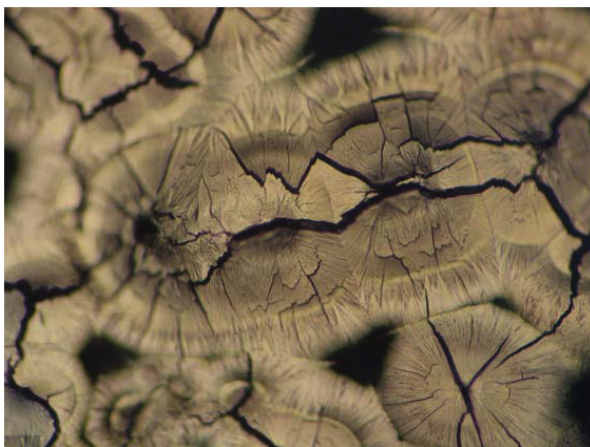
Figure 4: Reflectance microscopy photograph of Au-coated PEO 10000, magnified x100, exhibiting micro-cracks propagation pattern.

would continue to propagate at the weaker inter-spherulite bondaries rather than penetrate into the next spherulite and propagate through it.

The reflectance microscopy pictures taken of the Au-coated samples accentuate very clearly this micro-crack propagation pattern (Figure **4**).

Observation of the spherulites and the inter-spherulite boundaries at much larger SEM magnifications (Figure **5**), reveals, that there is no clear-cut and defined boundary between adjacent spherulites. Rather, lamellae from each spharulite penetrate into the adjacent spherulite and vice versa. These lamellae are also branched, thus creating an interlocked zipper-like interaction between the adjacent spherulites.

throughout the samples in both polymers although it would be reasonable to expect that the micro-cracks

Thus if an internal stress causes an inter-lamellar splitting that propagates to the edge of the initial
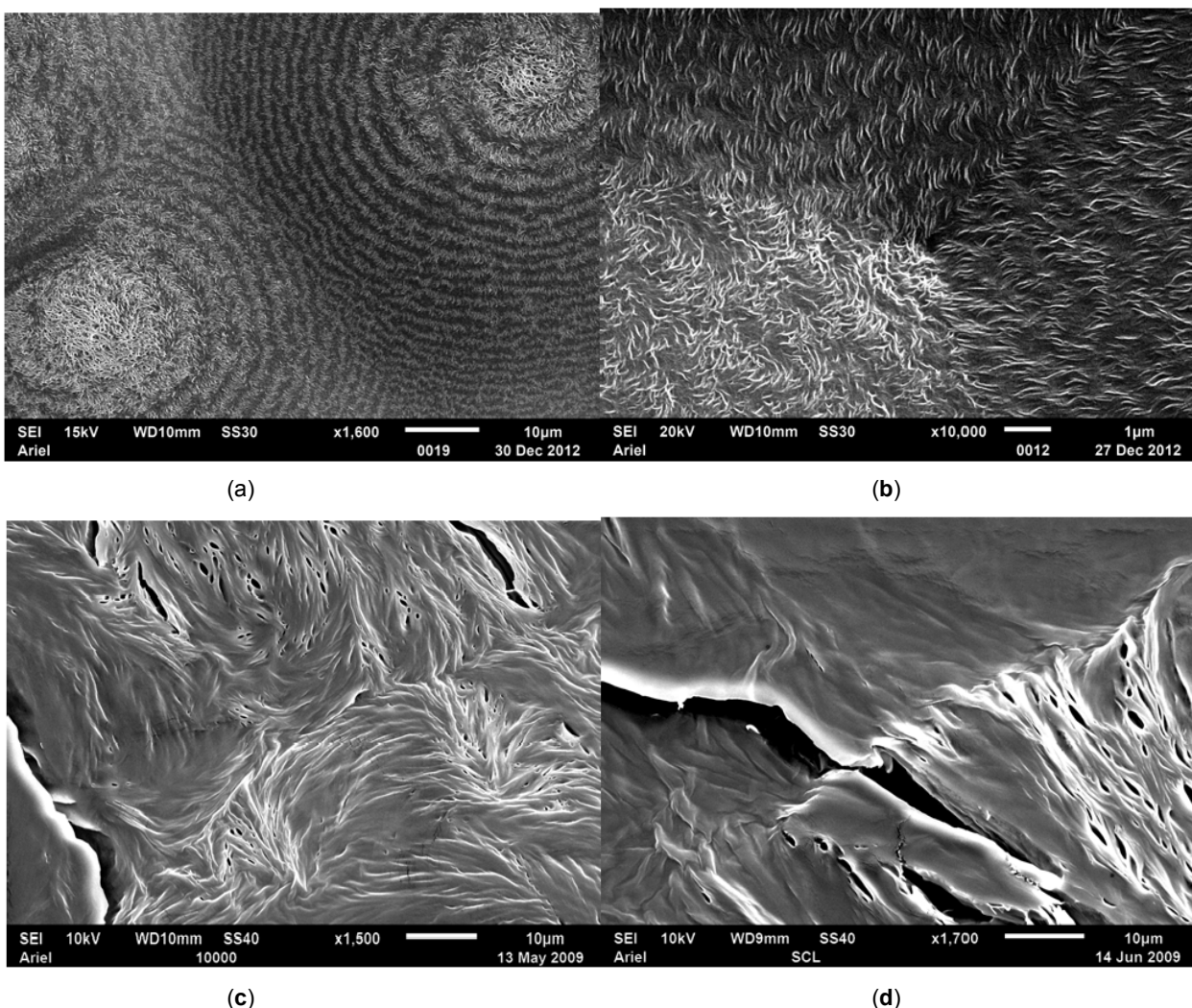

(a)

(b)

(c)

(d)

Figure 5: SEM micrographs of HDPE (**a**, **b**) - (magnification x 1600 – a; (magnification x 10000 - **b**) and PEO 10000 (**c**, **d**) (magnification x 1500 c; magnification x 1700 -**d**), exhibiting the inter-spherulite borders in detail.

spherulite, this in turn will exert a splitting force on the adjacent spherulite, due to the interlocked lamellae, thus prying it open similar to the action of a crowbar. The direction in which the micro-cracks will propagate inside the adjacent spherulite is governed by the radial lamellar symmetry directing the micro-crack propagation towards the center of the spherulite and away again towards the edge, splitting open the next spherulite and so on. This propagation pattern is very clearly seen in Figure **4**. Also, Figure **5d** exhibits at a high SEM magnification the propagation of the micro-crack tip into the adjacent spherulite.

Since according to the existing mechanical models, the inherent micro-crack size will influence the eventual fracture of the material, it is beneficial to inhibit micro-crack propagation from one spherulite to the next due to internal stresses. This may be achieved during material processing by quenching the melt at lower temperatures, thus creating a more amorphous or less ordered region between spherulites, which can absorb the internal stress energy and minimizing the ability of an initiated micro-crack to propagate into the neighboring spherulites. For this purpose, HDPE samples were cooled at room temperature until initial crystallization occurred, which was observed as a very slight loss of sample transparency, after which the samples were promptly cooled to 0°C, by ice-water. The rationale of this procedure was to allow initial spherulite development and than quench the remaining melt around the spherulites formed in the initial stage of the process.

Figure **6** exhibits the POM with crossed polarizers of a HDPE film quenched at 0°C as described above. The bright-appearing spherulites are surrounded by dark zones of relatively high extinction.
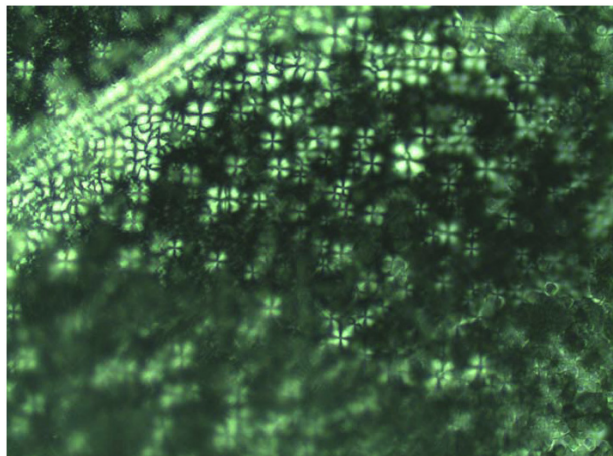

Figure 6. Pollarized light microscopy photographs of HDPE, quenched at 0°C (magnification x100).

Scanning electron microscopy (SEM) views of the quenched samples (Figure **7**), clearly exhibit the spherulites formed during in the initial stage and the very significant less ordered micro-crystalline regions between the spherulites. In these samples, no visible micro-cracks were observed, indicating that the less ordered interspherulite regions more efficiently absorbed the internal stress energy created during the cooling process.
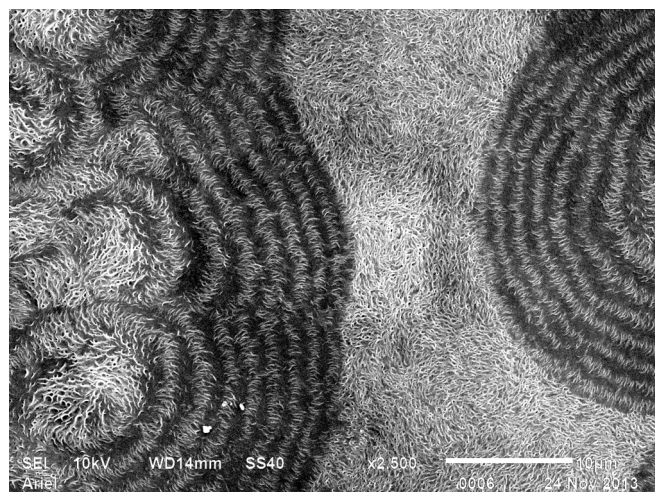

Figure 7. SEM micrograph of HDPE, exhibiting spherulites and the less ordered micro-crystalline inter-spherulite regions obtained during the two-stage process (magnification x 2500).

CONCLUSIONS

The initiation and propagation pattern of inherent micro-cracks in semicrystalline polymers was investigated in the present research. It was demonstrated that micro-cracks, due to internal stresses, are mostly initiated inside spherulites. Within each micro-crack-containing spherulite, the micro-crack direction is in most cases in the radial direction, splitting the spherulite according to the interlamellar crystal cleavage.

It was demonstrated that when a micro-crack propagates to the edge of the spherulite, causing it to split, further propagation of the micro-crack will consistently continue into the adjacent sepherulite and not along the inter-spherulite borders. This observation is in contrast to the fact that the inter-spherulite borders are usually regarded as weaker regions.

It was further demonstrated here, that there is no clear-cut and defined boundary between adjacent spherulites. Rather, lamellae from each spherulite penetrate into the adjacent spherulite and vice versa. These lamellae are also branched, thus creating an

interlocked zipper-like interaction between the adjacent spherulites. Thus, it is concluded here, that if an internal stress causes an inter-lamellar splitting that propagates to the edge of the initial spherulite, this in turn will exert a splitting force on the adjacent spherulite, due to the interlocked lamellae, thus prying it open similar to the action of a crowbar. Also, the direction in which the micro-cracks will propagate inside the adjacent spherulite is governed by the radial lamellar symmetry directing the micro-crack propagation towards the center of the spherulite and away again towards the edge, splitting-open the next spherulite and so on.

Although the two polymer types chosen for this research differ in all possible aspects, including chemical composition, crystal systems, molecular weights and average crystal sizes, the observed micro-crack propagation mechanism was very similar in both polymers. This emphasizes the significant relevance of the observed mechanisms to semicrystalline polymers in general.

As a conclusion of the present research, a method of minimizing the inherent micro-crack propagation from one spherulite to the next was presented here. The polymer melt was quenched the melt at lower temperatures in two stages (as described in the experimental and the results & discussion sections), thus creating a less ordered micro-crystalline region between spherulites, which can absorb the internal stress energy and minimizing the ability of an initiated micro-crack to propagate into the neighboring spherulites. The results have shown that samples treated under these conditions exhibited mostly isolated spherulites surrounded by dark zones of relatively high extinction. SEM views of the quenched samples, clearly exhibited the spherulites formed during the initial cooling stage and the very significant less ordered micro-crystalline regions between the spherulites created during the second quenching stage of the process. In these samples, no visible micro-cracks were observed, indicating that the less ordered interspherulite regions efficiently absorbed the internal stress energy created during the cooling process.

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