Chemical Etching Technique Makes Possible SEM Investigation Of Polyolefin Microstructures

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Although scanning electron microscopes (SEM) have been used to study the polyolefin polymer morphology as it relates to the development and modification of the commercial products, it has seldom been used to study polyolefin microstructures such as spherulite and lamellae morphology. Rather, transmission electron microscopes (TEM) have been used for such morphology studies because they provide the resolution necessary for observation of polymer microstructures. Unfortunately, TEM studies require the microtome-sectioning of the bulk samples to produce suitable test samples after unloading. In contrast, we have shown that, if suitable sample preparation techniques are employed, the surface morphology of bulk polyolefin samples, such as the thick test pieces and commercial products, can be characterized using the SEM. In this article we introduce our chemical etching technique that is suitable for the investigation of the polyolefin microstructures. The polyolefin morphologies acquired using this technique have shown good reproducibility and agree well with other works, most of which have been produced by TEM.

Chemical Etching Technique for SEM

The schematic diagram of permanganic etching sample preparation procedure used for SEM observation of polyolefin microstructure is shown in Figure 1.

The etchant is composed of potassium permanganate ($KMnO_4$), concentrated phosphoric acid (H_3PO_4) and/or concentrated sulfuric acid (H_2SO_4). The final etchant formulation for each polyolefin type is determined by adjusting the relative amount of the each material. In addition, various etching times, from 10 minutes to more than 7 hours, were necessary in order to get an optimum etching time. To avoid any dangerous condition, all of the etching procedures were performed at room temperature.

The permanganic acid solution selectively etches the amorphous part of the polyolefin in such a way that the lamellae appears clearly. Subsequently, the specimens were carefully washed with distilled water, hydrogen peroxide and acetone sonication, in order to avoid any artifacts.

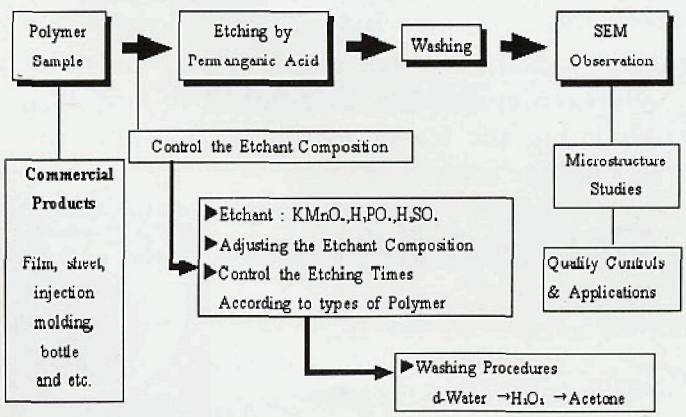

Figure 1: Sample Preparation Procedures for SEM Observation of Polyolefin Morphology.

Polyethylene Applications

When polymers crystallize from the melt, they generally start from single lamellae. These lamellae rapidly branch to more complicated structures and then form a spherulite. Polyethylene spherulite often shows a series of outward growing rings having concentric shells of spherulite in the center. In polyethylene, these screw-shaped dislocations form regularly and the daughter lamellae, formed on outward growth, do so at a continually increasing angle. This dislocation formation is an incremental process and not a continuous spiral. Figure 2 shows the SEM images of polyethylene banded spherulite after etching. As shown, polyethylene banded spherulite morphologies, having either surface or cross section of melt crystallized polyethylene, can be reproduced by this method. SEM cross sectional morphology is generally observed after the fracture of specimen when it is hard to investigate the surface morphology. But surface morphology of polyethylene

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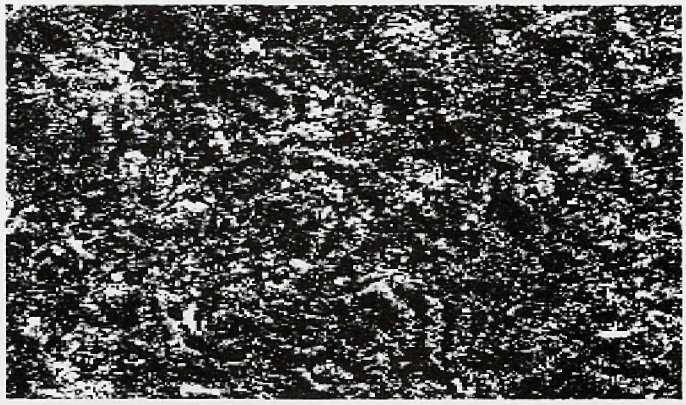
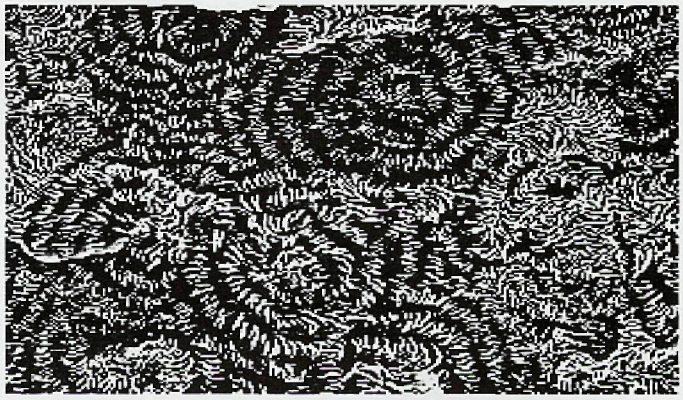
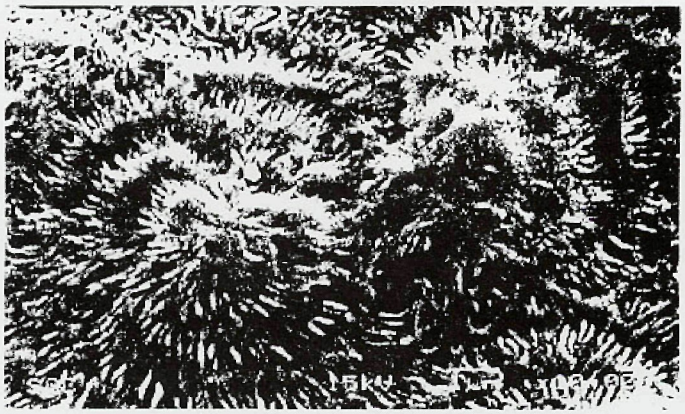


A. Surface morphology of HDPE



B. Crossectional morphology of MDPE.



C. Crossectional morphology of LLDPE.

Figure 2: SEM photographs of Polyethylene Banded Sperhulite.

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can be observed easily by introducing this chemical etching technique, as seen in Figure 2-A.

Because the orientation is induced during film processing, the epitaxy growths of lamellae are observed on the surface of film. The lamellae are oriented in the processing direction, so it is possible to correlate the lamellae morphology and processing information by this morphology. It is also possible to investigate the relation between this morphology and long period of lamellae.

Polypropylene Applications

In general, varying the crystallization conditions can produce at least three different crystal structures of isotatic polypropylene (iPP). The first is the monoclinic α-form that was characterized by Natta *et al.* The second form, which crystallized over a particular range of crystallization temperature and/or under specific rheological conditions, is the hexagonal β-form. The third, with a triclinic γ-form, can be isolated by solvent fractionation from low-molecular-weight iPP samples, but the yield of product using this process is very low. So the crystal structure of γ-form is very particular one. Consequently, the α- and β- phases dominate in the crystal structure of the iPP used in the most industrial applications.

Figure 4, which shows the results from the 160°C isothermal crystallization of iPP, illustrates the typical fibrous texture and dendrite growth of iPP spherulite. In this figure the bright region is the crystalline part of iPP and the dark area represents the amorphous part.

Figure 5 shows β-spherulite morphology of iPP. Because of strong negative birefringence and highly luminous character of β-form, β-spherulite region is brighter than α-spherulite regions. Figure 5-B is an enlarged image of a specific region which is identified as a circle on A. In the etched iPP surfaces, it is clear that the relief of the surface is much more pronounced at the β-spherulites than Figure 4. IPP spherulite morphology and its lamealla structure, the α-spherulite. This is because the twisted β-phase lamellae are preferentially revealed by the acid etching, whereas the interlocked network of parallel α-lamellae is more resistant to attack by the etchant. Consequently, for a sample in normal orientation, the 'wavy' surfaces of the β-lamellae will release more secondary electrons to the detector and the corresponding spherulites will appear brighter than the α-species.

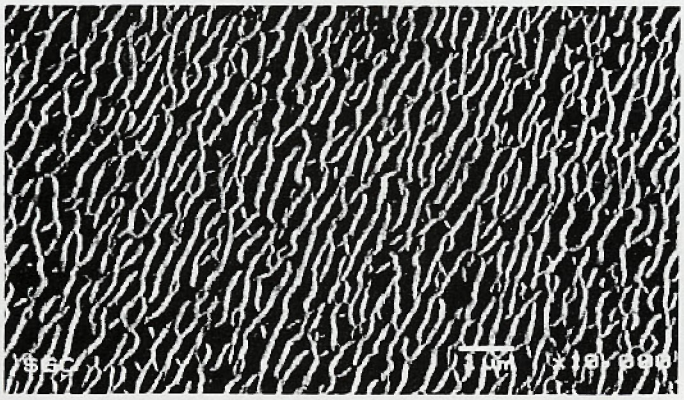

Figure 3: Surface morphology of polyethylene stretch wrap film.

Applications to Polypropylene block copolymer and its blend

Block PP has been widely used in industrial products such as automobile products, electronics, toys, etc. Impact polypropylene has been produced as toughened grades of iPP. Also blending a block of PP with an additional elastomer is used in the manufacture of high impact polypropylene. Recently, such blends have been obtained by polymerizing the monomers directly in the reactor. This kind of reactor-made iPP blend is polypropylene block copolymer (block PP). Generally, block PP has two different phases. First phase is the matrix PP. Next phase is the dispersed phase, which consists of two regions. One is polyethylene in the center of dispersed phase and the other is ethylene-propylene rubber (EPR) in the outer region of dispersed phase.

The physical properties of block PP are largely influenced by the dispersed phase composition, size and shape. Therefore, the investigation and characterization of the dispersed phase in block PP is very important in manufacturing the good commercial products. Figure 6 shows the etched morphology of block PP. The center of dispersed phase is polyethylene domain and the outer vacant region is rubber domain, which had been removed during etching. The characteristic properties and morphologies of block PP can be investigated easily using this chemical etching technique.

Figure 7 shows the morphologies of post reactor blends of polypropylene. As seen in the figure, the dispersed phase morphologies can be easily characterized and the basic physical properties can be predicted by this morphologies. The domain size of dispersed phase is from about 0.5 μm to 1.0 μm. In block PP blends, the dispersed phase size was increased by incrementally adding rubber and/or polyethylene. Figure 7 shows the morphology of block PP/HDPE blend (A) and that of block PP/EPR rubber

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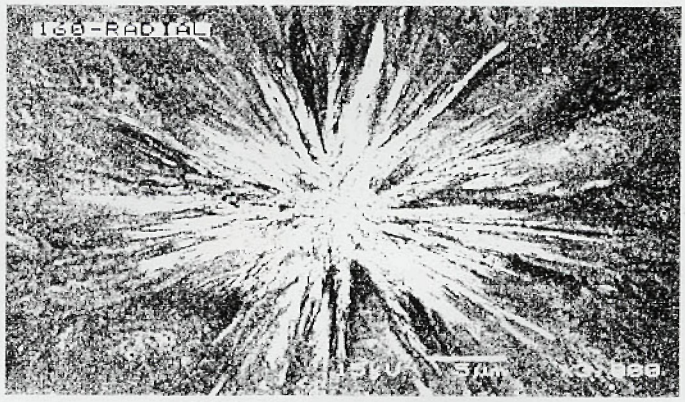
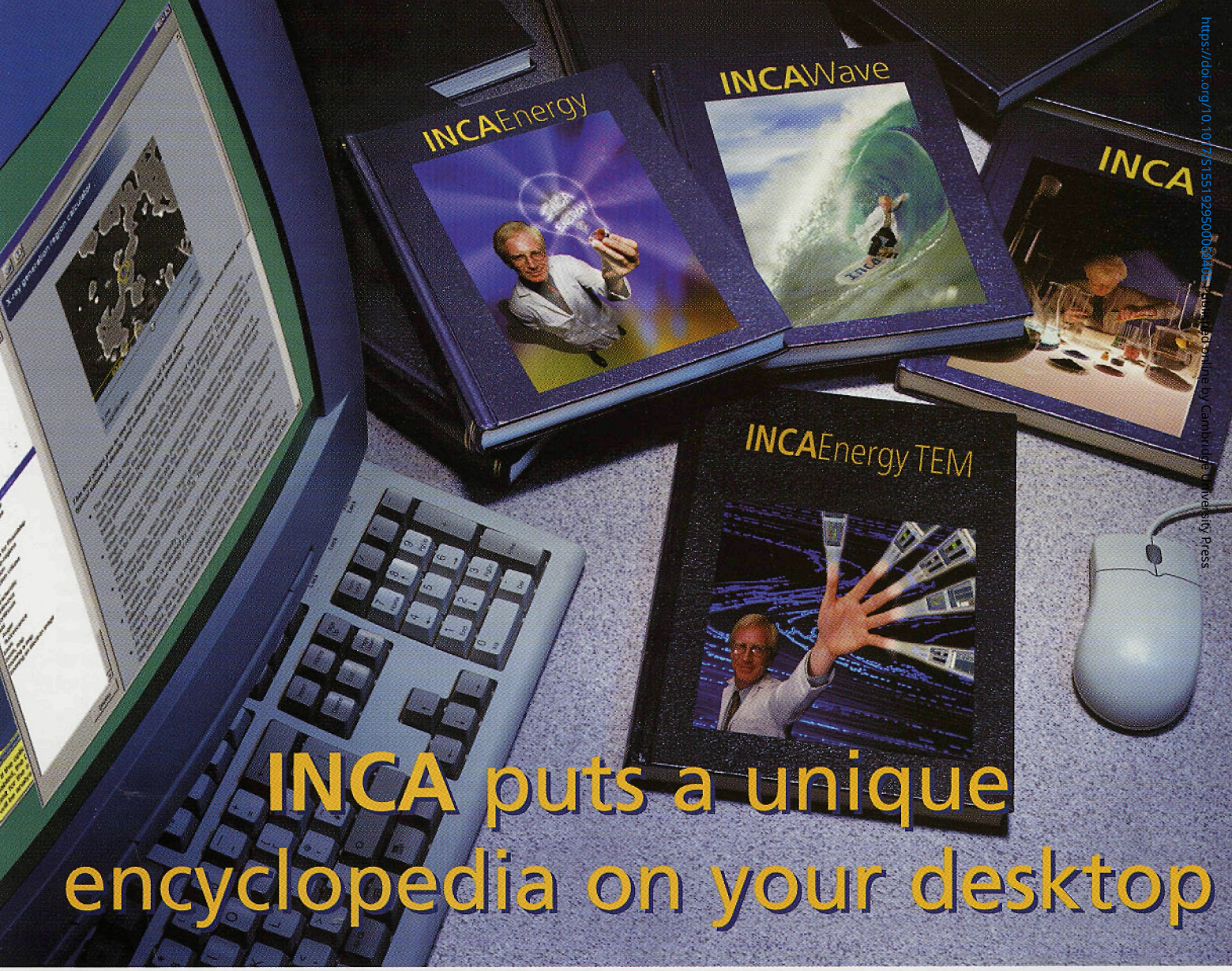


A. Spherulite gowth pattern of iPP.

B. Magnification of circle on A. (detailed morphology)

Figure 4: IPP spherulite morphology and it's lameallar structure.



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(B). The dispersed phase of Figure 7-A is enlarged because of the high contents of polyethylene and it can be easily distinguished by the characteristic morphology of polyethylene without any electron diffraction study. Meanwhile, the high rubber content region, Figure 7-B, can be also characterized by the vacant morphology of dispersed phase, which is selectively removed during etching.

In addition to the example in this article, the Research Center of Samsung General Chemicals has applied this chemical etching technique to other fields such as the skin/core morphology of injection molding compounds, film application and various kinds of polyolefin blends.

Conclusion

If proper sample etching technique is employed, polyolefin microstructure can be revealed by use of the SEM. The observed morphologies of various kinds of polyolefin using our techniques agree well with those from TEM observation. Because the sample preparation method is useful and simple, this technique easily applies to the industrial area for the purpose of developing, manufacturing and modifying the new commercial products.

Acknowledgement

The authors appreciate the kind assistance of Dr. Xawquan Zhang, during the study. ■

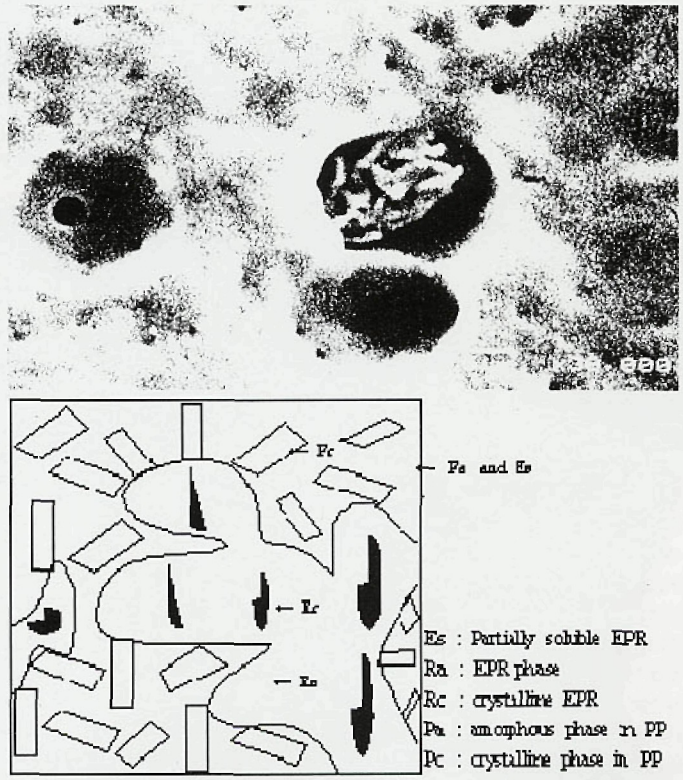
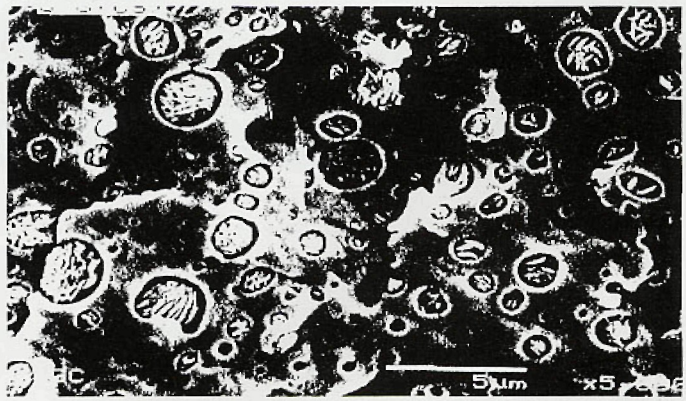


Figure 6: Characterization of Block PP morphology (Detailed morphology of dispersed phase and schematic diagram of block PP morphology)

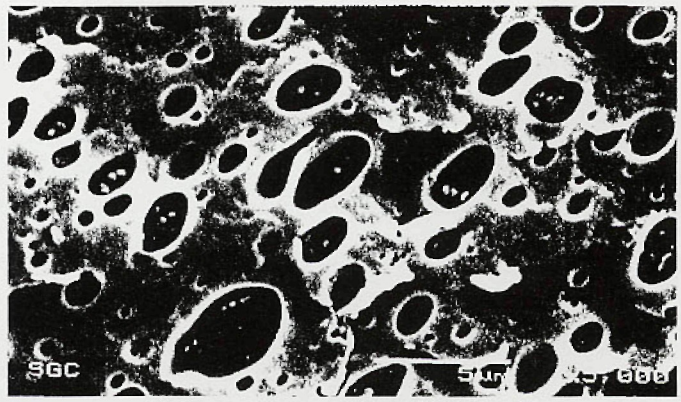
A: IPP β-spherulite region.

B:Magnification of circle on A.(detailed morphology

Figure 5: IPP β-spherulite morphology and it's characterization.

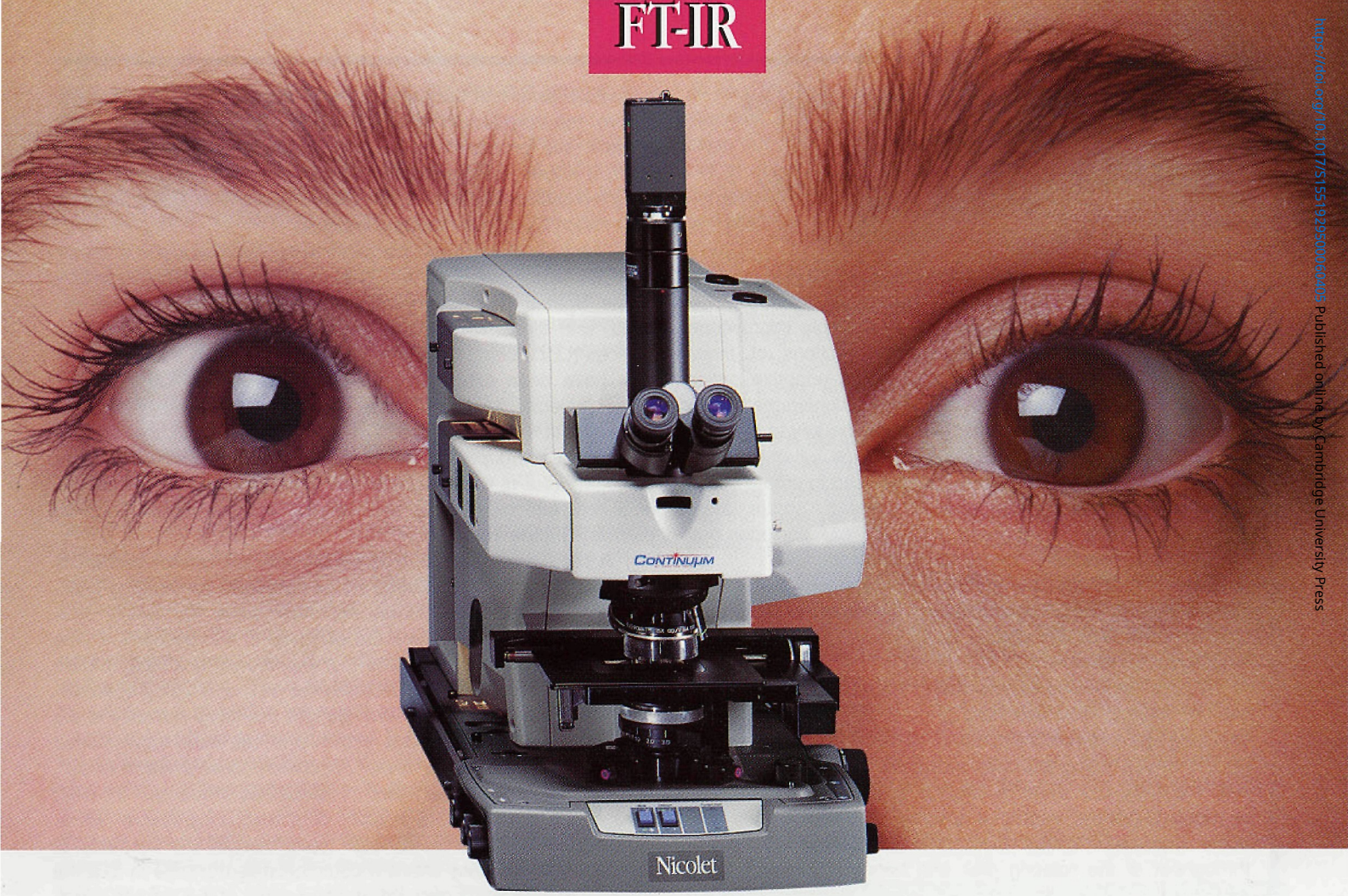


A: The morphology of block PP/HDPE blend



B: The morphology of block PP/EPR rubber

Figure 7. The morphology of polypropylene block copolymer post reactor rubber blends.



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