

Resolving Difficult Multilayer Film Structure by Transmission Electron Microscopy

Shuang Qin¹, Hu Duan¹, Wei Dai¹

¹. Material Science and Characterization, Avery Dennison Corporation, 8080 Norton Parkway, Mentor, OH

Multilayer films are widely used in the packaging and labeling industries. The layer thickness and chemical compositions are rationally designed to meet the stringent customer requirements including conformability, printability and transparency etc. The challenges to analyze the structure of new generation multi-layer film products primarily are 1: the layers have very similar chemical compositions, usually polypropylene/polyethylene blends are used due to low cost, 2: advanced extrusion and stretching technologies can produce very thin layer down to 1 μm or less.

In this study, a commercial multi-layered polyolefin film was examined to identify its layer construction. Optical microscopy of Olympus BX51 identified an overall film thickness of approximately 50 μm (Fig. 1A). The chemical compositions of the film layers were analyzed by Horiba XploRA One Confocal Raman spectroscopy (Fig. 1B). The results show that all layers consist of polypropylene (PP) and polyethylene (PE) blends. The thin skin layer on one side contains higher ethylene content than the core layer and the other-side skin layer. The latter two layers have nearly the same chemical compositions. However, the thickness of each layer could not be accurately measured using Raman microscopy due to relatively large Raman spot size. Optical microscopy and scanning electron microscopy are not successful either in distinguishing the layer structure due to the lack of contrast between layers. Therefore transmission electron microscopy (TEM) was utilized with aid of appropriate contrast enhancing staining technique.

The trimmed samples, which were embedded in Eponate 12, were polished at ambient temperature using a Leica EM UC6 ultramicrotome. The blocks were stained in RuO_4 vapors [1][2] before being re-polished. Ultrathin sections of 100-120 nm in thickness were collected from the stained blocks at ambient temperature. TEM images were captured using a FEI Tecnai G2 TEM operating at an accelerating voltage of 300 keV with an energy filter of 30 eV. In order to verify the feasibility of this method, two monolayer reference films with known PE and PP ratio were examined along with the commercial multi-layered polyolefin film. The TEM image of the reference sample comprising 70% PE (Fig. 2B) shows darker contrast due to higher degree of staining/absorption on PE domains compared with the reference sample comprising 20% PE (Fig. 2A). The multilayer polyolefin film was examined to determine its layer structure and thickness. There is significantly different morphology between the core layer (Fig. 3B) and the skin layer (Fig. 3A). The skin layer has more severe staining indicating higher PE content. The staining is much less inside the core layer, where discrete crystalline PE domains from fiber-like lamellae are observed. With relatively sharp boundary between the skin and core layer, the thickness of the skin layer is determined to be approximately 1.3 μm . No interface was observed between the core layer and the skin layer on the other side (Fig. 3C), which was consistent with the Raman results.[3]

References:

[1] J. Blackson, *et al*, *Microscopy and Microanalysis* **13** (Suppl 2) (2007) 323

[2] D. Montezinos, *et al*, Journal of polymer Science, Polymer Letters Edition, **23** (1985) 421
 [3] The authors acknowledge Dr. Midori Hitomi from Cleveland Clinic Foundation for sample preparation and Dr. Danqi Wang from Case Western Reserve University for TEM imaging.

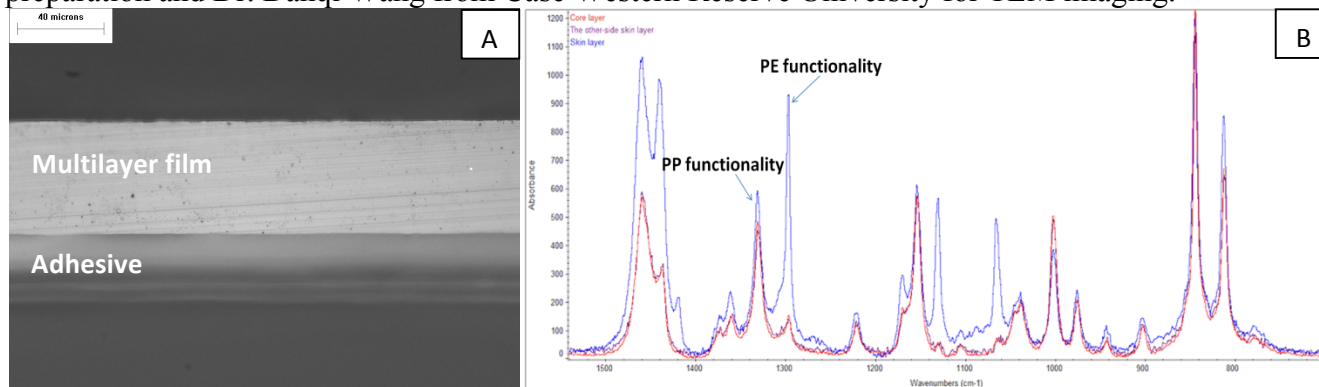


Fig. 1 (A) Optical micrograph of the cross-section of multilayer film facestock laminated with adhesive; (B) Raman spectra of the skin layer, the core layer and the other skin layer of the multilayer film.

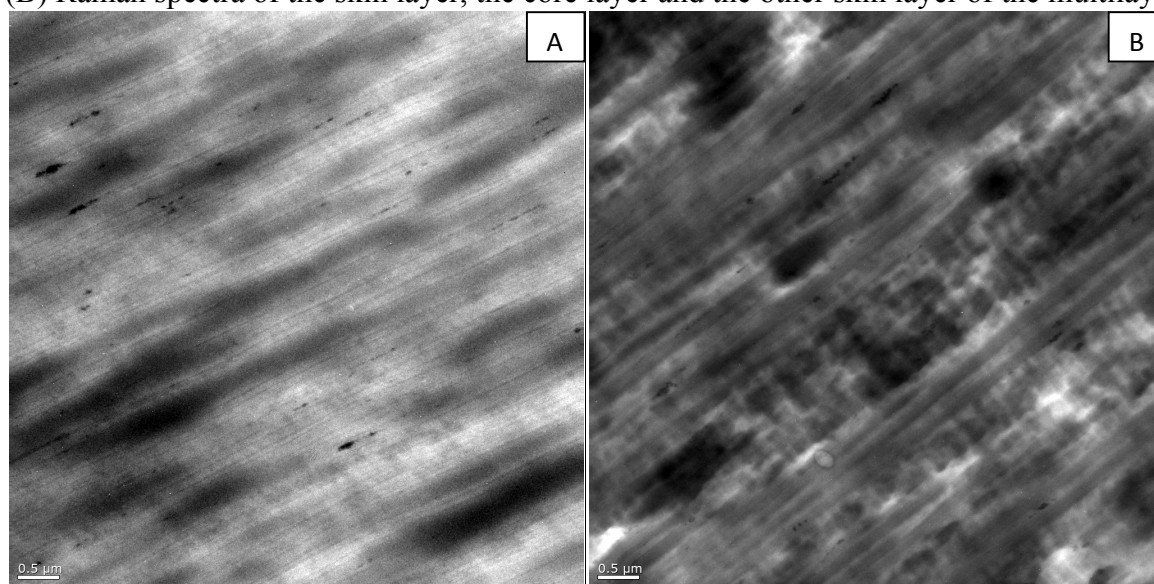


Fig. 2 TEM micrographs of the monolayer polyolefin films comprising (A) 20% PE; (B) 70% PE.

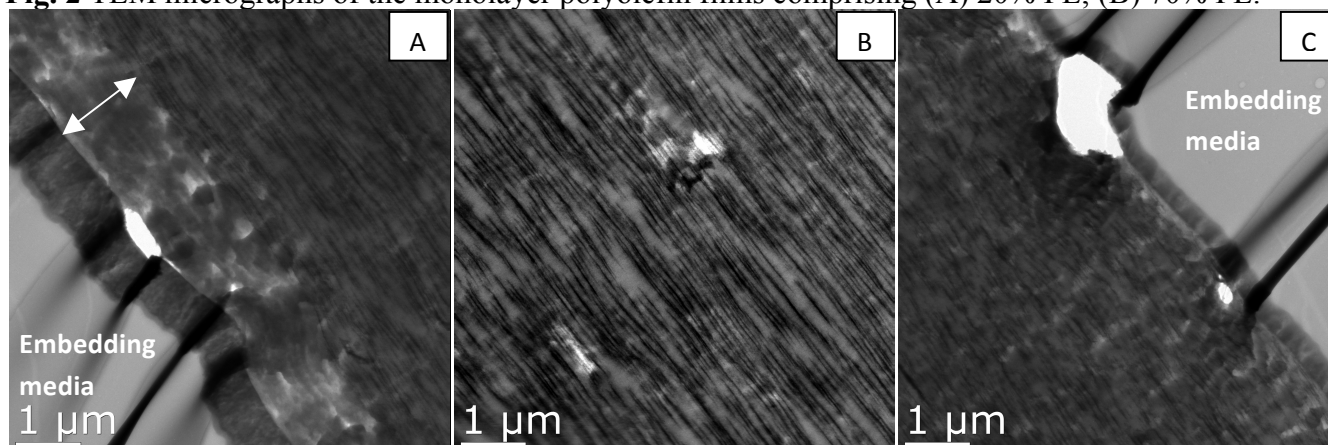


Fig. 3 TEM micrographs of the multilayer polyolefin film (A) the skin layer (arrowed); (B) the core layer; (C) the skin layer on the other side.