

BALANCING TEAR STRENGTH AND MODULUS OF MACHINE DIRECTION ORIENTED FILMS CONTAINING HIGH MOLECULAR WEIGHT POLYETHYLENE

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Abstract

This paper presents a newly formulated machine direction oriented (MDO) film that utilizes unique polymers that balance machine direction (MD) tear with the enhancements seen in other properties, such as modulus. By combining the suggested film and the MDO process, films with an unparalleled balance of physical properties can be manufactured.

Introduction

Machine direction orientation (MDO) is a solid-state post-extrusion process that has been practiced commercially for more than 40 years. In this process, a polymer sheet or film is preheated to an appropriate temperature and drawn in the machine direction to a fixed ratio. The orientation is typically induced through a narrow gap (one to 100 mm radial distance between the rollers) between two heated rollers rotating at varying speeds. After orientation, the film can be annealed to control specific film properties, such as shrink, and is then cooled to ambient conditions and rewound. Figure 1 is a schematic of an MDO process.

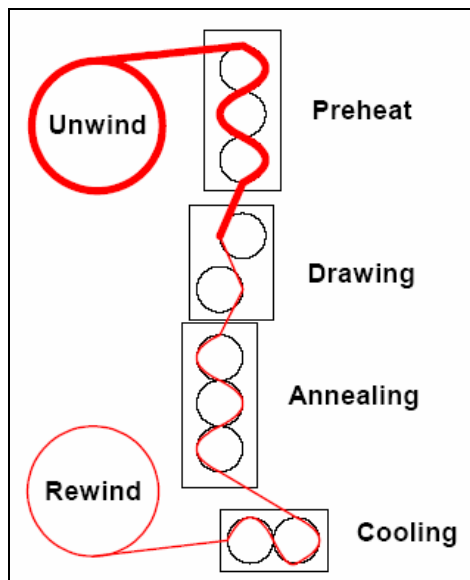


Figure 1. A Schematic Drawing of an MDO Process [1]. The film enters the top of the unit, passes through a preheating section before the orientation stage, and is annealed and cooled to ambient temperature before exiting the process.

BACKGROUND

The solid state orientation of semi-crystalline polymers has been studied extensively for the past four decades, with great focus on understanding the mechanisms associated with the deformation of the crystalline and amorphous domains. Upon orientation, the gloss, tensile strengths, moduli, and barrier properties increase while machine direction tear strength and dart drop decrease [2]. A similar relationship is seen in blown film when comparing machine direction tear strength and the draw-down ratio of the blown film process [3] and frost line height [4].

Significant research has been conducted to understand the relationship between crystallographic deformation and orientation with respect to polymer film tear properties. Lee et al. observed a linearly decreasing relationship between machine direction tear strength and increasing Herman's orientation function of the (110) plane, relative to the machine direction measured via wide angle x-ray scattering (WAXS), with an apparent limit of 0.4 for the Herman's orientation function. They also noted that the Herman's orientation function for the (110) plane increases linearly with decreasing blow-up ratio, i.e. increasing machine direction orientation [5].

Additional work has shown that during the MDO process, transformations occur in the crystallographic architecture of the polymer. As the draw ratio increases, the C-axis of the unit cell aligns in the machine direction; the lamellar normals align in the machine direction, then tilt to a specified angle, and fracture; and tie molecules become taut [1, 6-9]. In relation to previous studies [5], WAXS was utilized to measure the orientation of the unit cell of high density polyethylene after the MDO process [1]. In this work, a strong linearly decreasing correlation was observed between the machine direction tear strength and the Herman's orientation function of the (110) plane, relative the transverse direction, shown in Figure 2.

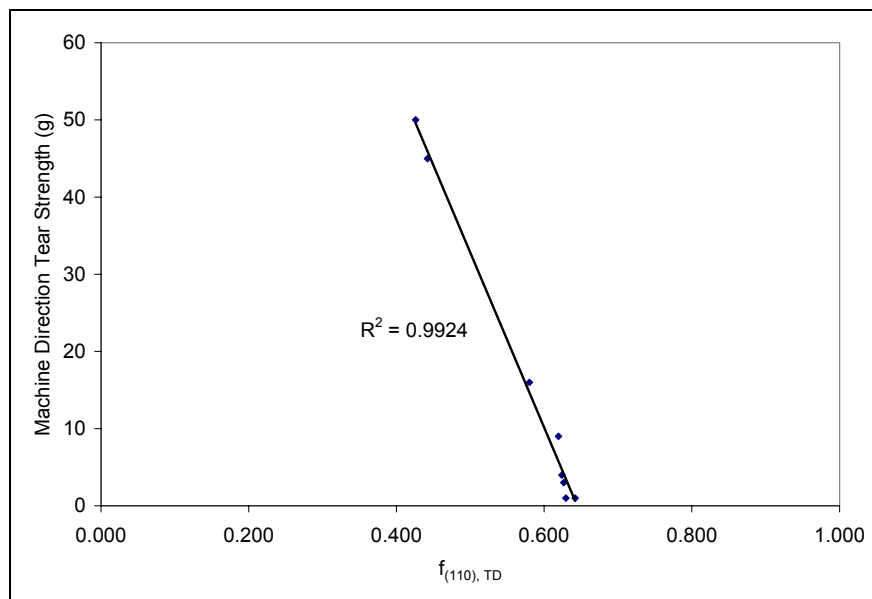


Figure 2. Plot of Machine Direction Tear Strength Versus the Herman's Orientation Function of the (110) Plane, Relative to the Transverse Direction of the Film.

A consistent observation made in highly oriented polymers is the formation of anisotropic fibrous structures having large aspect ratios that favor the long direction of the fiber parallel to the machine direction [6, 7]. Of specific interest is the model proposed by Peterlin, which

discusses the effects of defects, primarily inter-lamellar entanglements, mosaic boundaries, and chain ends incorporated into lamellae and cilia, on the presence of intra- and inter-fiber tie molecules [8, 9]. The relationship shown in Figure 2 supports Peterlin's model, which states that during solid-state deformation, the lamellar crystalline domains break into crystalline blocks, separated by mosaic boundaries. Tear of a bulk sample would likely propagate along these boundaries. The packing of the chains in the lamellae in the (110) plane are held by weaker van der Waal forces, resulting in the fracture of the crystalline domains along this plane.

DISCUSSION

The intent of this paper is to discuss the effects of drawing, primarily as a result of MDO processing, on the machine direction tear and modulus properties of oriented semicrystalline polymer films. From the aforementioned structural model, one expects polymers with high levels of branching and a large amount of an amorphous component to have a higher concentration of intra- and inter-fibrous tie molecules. Such a comparison can be made between homopolymer high density polyethylene (HDPE) and linear low density polyethylene (LLDPE). Since film failure occurs at the fibrous interface, greater energy is necessary to tear films with higher concentrations of intra- and inter-fiber tie molecules, resulting in higher machine direction tear strength. While producing oriented films from lower density polymers increases the machine direction tear strength of the film, it lowers both the machine and transverse direction moduli of the film. In many cases, a certain modulus value is necessary to satisfy the needs of a given package, resulting in a compromise in machine direction tear strength. A film with both high modulus and high tear strength, relative to an incumbent film, would be desirable to the packaging industry. Such a film would allow for the production of innovative packaging and possibly the elimination of more costly structures, such as laminated polyethylene terephthalate (PET) PET and nylon (PA).

In previous work [1], 6 mil (150 micron) monolayer films of five different grades of bimodal high molecular weight polyethylenes were blown, utilizing typical extrusion conditions as seen in industry. The thick blown films were then oriented to various draw ratios until they failed. Figure 3 shows that the machine direction tear strength decreases significantly with increasing draw ratio for the five sets of oriented monolayer polyethylene films. Films produced with lower density (HD 4 and HD 5) had slightly higher tear strength than the higher density grades (HD 1 through HD 3) at moderate draw ratios. At high draw ratios, the tear strength of all of the monolayer films converge at a relatively low value.

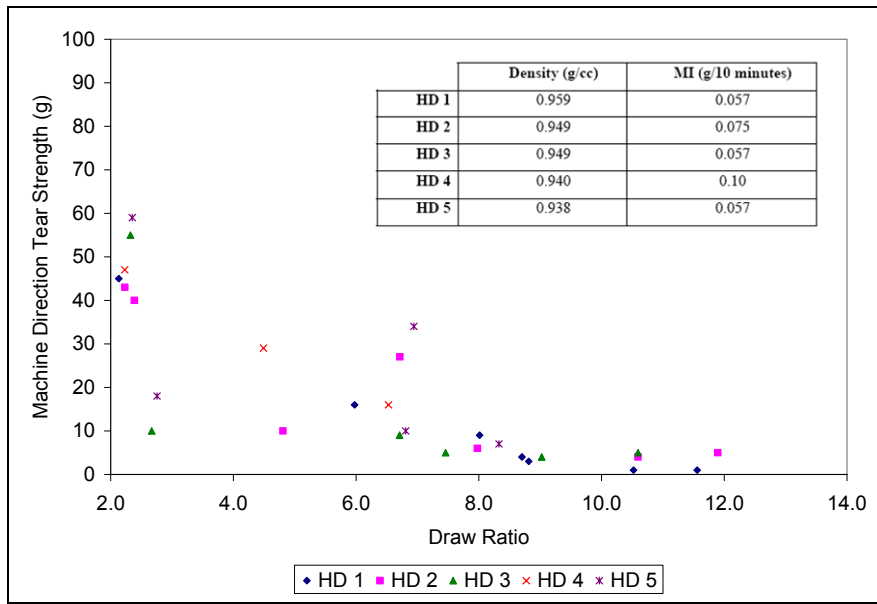


Figure 3. Plot of the Machine Direction Tear Strengths of Monolayer Blown Film Produced from Five Different Bimodal High Molecular Weight Polyethylenes, Relative to Draw Ratio.

In comparison, the machine direction modulus increases exponentially and the transverse direction modulus increases logarithmically with increasing draw ratio [1], as shown in Figures 4 and 5. As expected, the film’s moduli, regardless of the direction, is greater for films produced with polymers of higher density.

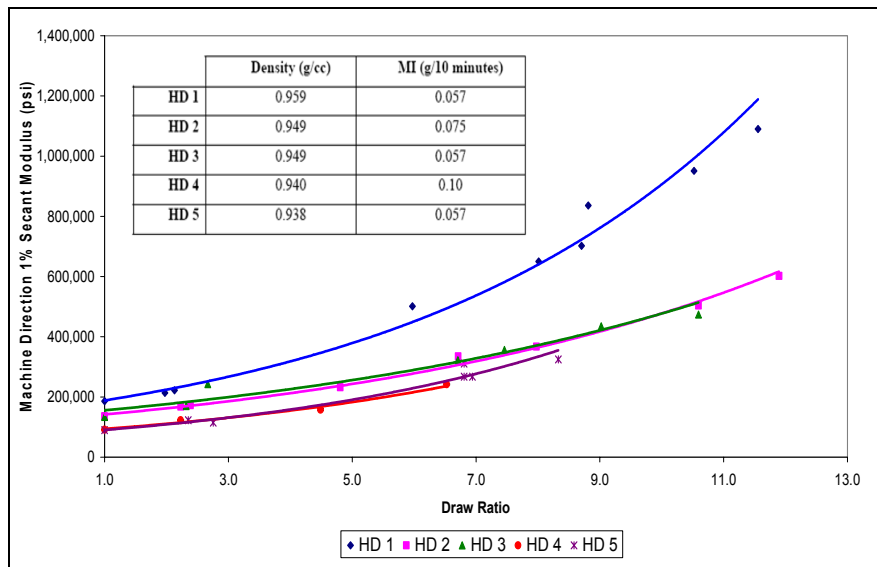


Figure 4. Plot of the Machine Direction Modulus, Relative to Increasing Draw Ratio.

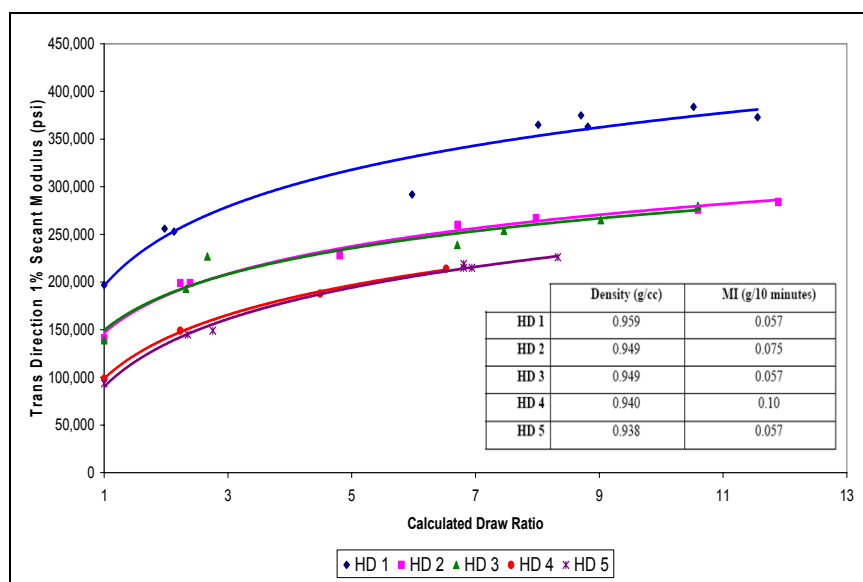


Figure 5. Plot of the Transverse Direction Modulus, Relative to Increasing Draw Ratio.

By understanding that increasing the draw ratio in the MDO process decreases the machine direction tear strength and increases the modulus of the polymer film, optimizing the balance between the two properties can be achieved through proper polymer and film structure selection. As described in previous work [1], the inherent properties of bimodal high molecular weight polyethylenes allow them to process well in the MDO. This, coupled with the well known fact that LLDPE has exceptionally high tear strength (as evident with its use in high strength applications, such as heavy duty shipping sacks [10, 11]), warrants the consideration of using the two polymers in combination to balance the tear strength and modulus of the film.

Williams has shown that when a film produced from an equal percentage blend of bimodal high molecular weight polyethylene and a superhexene linear low density polyethylene is oriented, the machine direction modulus increases while the tear strength decreases until the maximum draw ratio, at which the machine direction tear strength unexpectedly increases [2]. By blending the two polymers, the modulus and tear properties could be balanced, but not maximized, meaning that the highest modulus obtained was approximately 113,000 psi. Whereas with monolayer high molecular weight polyethylene (HMW-PE) films, a modulus of approximately 1,100,000 psi is possible [1], therefore, an opportunity exists to produce a film with a higher modulus and similar tear properties as current HDPE films.

To achieve this goal, an equilayer, three-layer coextruded film of HMW-PE skins and a superhexene LLDPE core that utilized the same polymers as Williams [2] was produced at varying thicknesses and drawn to a uniform final thickness of 0.5 mil (12.5 micron). Figure 6 is a plot of the machine direction tear strength and machine direction modulus of the MDO films, relative to draw ratio.

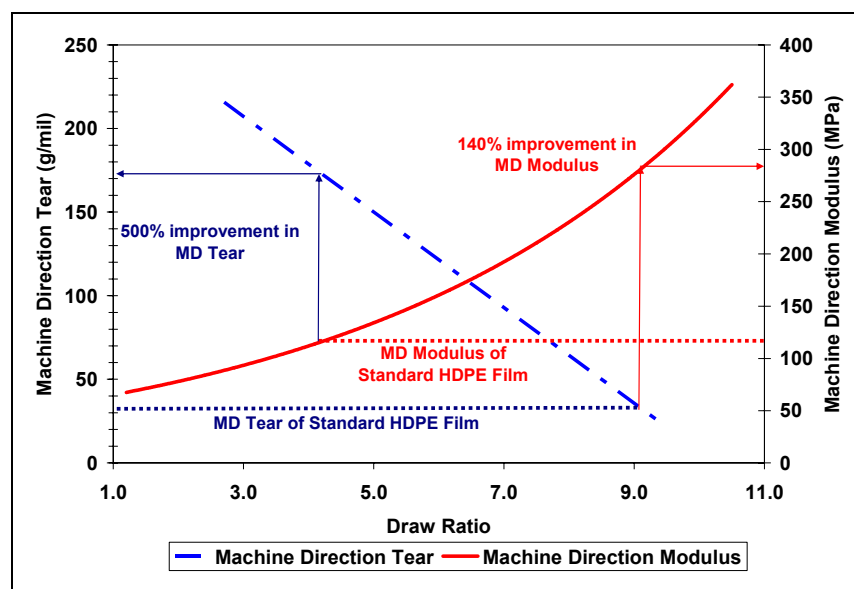


Figure 6. Plot of the Machine Direction Tear Strength and Machine Direction Modulus, Relative to Draw Ratio for Equilayer, Three-Layer Coextruded HMW-PE/Superhexene LLDPE/HMW-PE MDO Films with a Final Gauge of 0.5 mils.

To produce an MDO film that has the current machine direction tear strength as an incumbent HDPE film of the same gauge, this structure can be oriented to a draw ratio of approximately 9:1, resulting in a film with an improvement in machine direction modulus of nearly 140% (280,000 psi). Contrarily, if the modulus of a standard HMW-PE film is acceptable for a given application, the proposed structure can be drawn to a ratio of approximately 4:1 and achieve an improvement of approximately 500% (170 g/mil) in machine direction tear strength, relative to standard HMW-HDPE film of the same gauge. As one can see, utilizing a coextruded structure in the MDO process provides a means of retaining a film of high machine direction modulus, which, for a given set of film property requirements, can result in an MDO film with a significantly higher tear strength.

Conclusions

MDO has traditionally been utilized to increase the moduli, tensile strength, and barrier and optical properties of polymer films. Unfortunately, these improvements have come at the cost of lower machine direction tear strength. By properly selecting the polymers and film structure to be utilized, MDO can be used to produce films with a unique balance in properties.

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Key Words: MDO, machine direction orientation, bimodal high molecular weight polyethylene, tear, modulus