

Step Change Improvements in EVOH Barrier Using MDO

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ABSTRACT

This paper presents the effect of draw ratio in the machine direction orientation (MDO) process on the oxygen permeability of ethylene vinyl alcohol (EVOH). It also discusses the effect MDO has on the oxygen barrier of EVOH at higher relative humidities (RH). Data is presented on how film gloss and haze are enhanced by draw ratio for the EVOH coextrusion in question.

INTRODUCTION

Ethylene vinyl alcohol (EVOH) is usually used in packaging for high gas barrier applications. It is most often used to provide high oxygen barrier. When the relative humidity increases, the oxygen barrier properties decrease. At higher relative humidities (RH) (greater than 50%), the oxygen barrier of EVOH degrades very quickly.

Machine direction orientation (MDO) involves uniaxially stretching film in the machine direction to improve the physical and barrier properties of the films. Past work¹ has shown that orienting and annealing EVOH at elevated temperatures (140 °C) can improve the oxygen barrier.

EXPERIMENTAL

The film samples studied were made on a 10-inch, seven-layer blown film line at approximately a 2.0:1 blowup ratio (BUR). The basic structure was as follows:

LLDPE / LLDPE / Tie / EVOH / Tie / LLDPE / LLDPE

The LLDPE was hexene-based. The EVOH was a standard grade with 38% ethylene content. The following layer distribution was used to produce the coextruded film. The EVOH layer was an average thickness of 8%. The tie layers averaged 4% each. The LLDPE skins were 17% each, and the inner LLDPE layers were each 25%. The average gauge of the undrawn film was 8.0 mils.

This film was then MDO on a Collin lab scale MDO unit. The MDO unit had the ability to dual draw (stretch twice in a single pass through the MDO unit), but only one draw was used. The film was preheated, drawn, and annealed at 100°C.

The final film samples were tested for oxygen transmission rates at various relative humidities. The data was gauge corrected to 1.0 mil of EVOH.

DISCUSSIONS AND RESULTS

MDO Process

There are four basic steps involved with the MDO of film, which are summarized as follows.

Step 1: Preheating

The film is heated to the temperature in which orientation takes place. In this study, that temperature is 100 °C.

Step 2: Drawing or Stretching

In this step, the film is drawn or stretched several 100%. In this experiment, it was drawn between 2 times and slightly over 6 times.

Step 3: Annealing

In this step, the film is held at an elevated temperature for a period of time to anneal or heat set it.

Step 4: Cooling

In the final step of MDO, the film is cooled to the ambient temperature and rewind.

EVOH OTR vs. % RH

As the relative humidity is increased, the oxygen transmission rate (OTR) of the EVOH film drastically increases at a relative humidity greater than 50%, as shown in Figure 1. This corresponds to diminished barrier properties at elevated relative humidities.

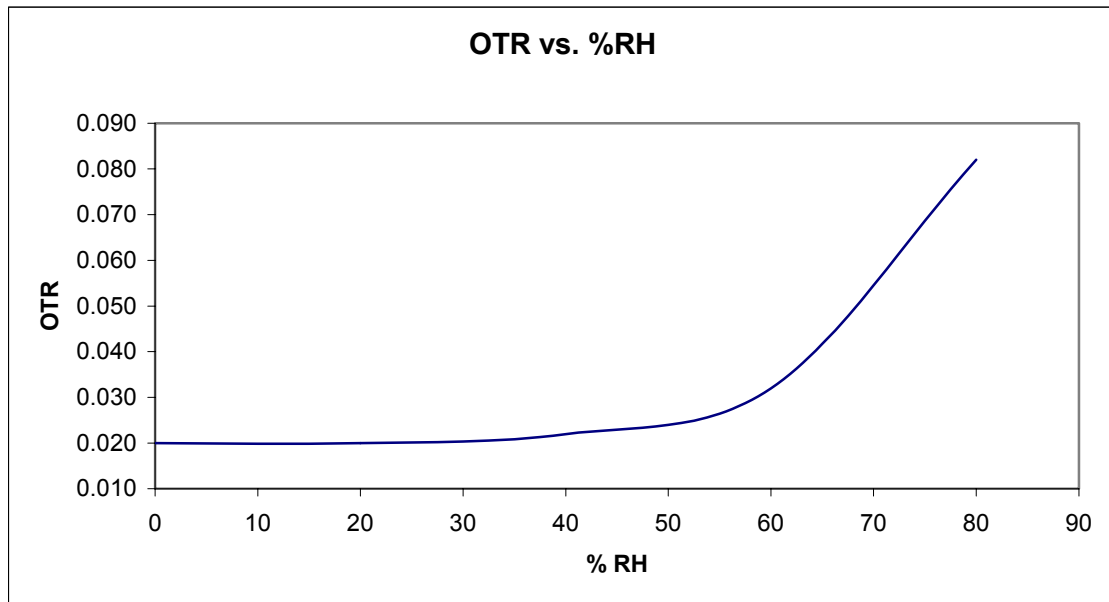


Figure 1: Oxygen Transmission Rate (cc-mil/100in²-day-atm) for 38% Ethylene EVOH²

Unlike SARAN and Bares, EVOH loses oxygen barrier properties as the percent relative humidity increases, as Figure 2 shows.

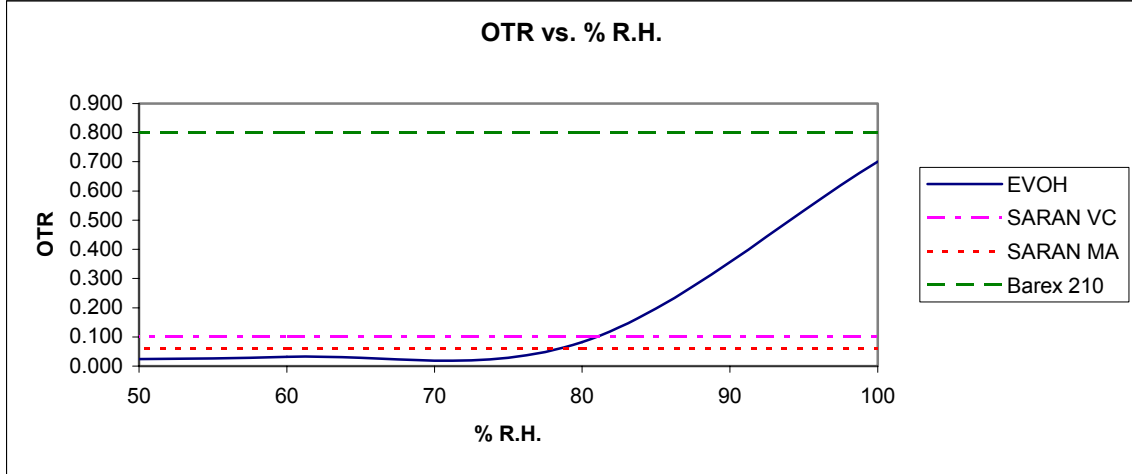


Figure 2: Oxygen Transition Rates (OTR) of Various Barrier Films vs. Percent Relative Humidity ³

OTR vs. Draw Ratio

In this experiment, a common EVOH web, with a standard off-the-shelf EVOH, was uniaxially oriented in the machine direction. The film was oriented at various ratios and then tested for oxygen transmission rate. Following are the results at 0% relative humidity.

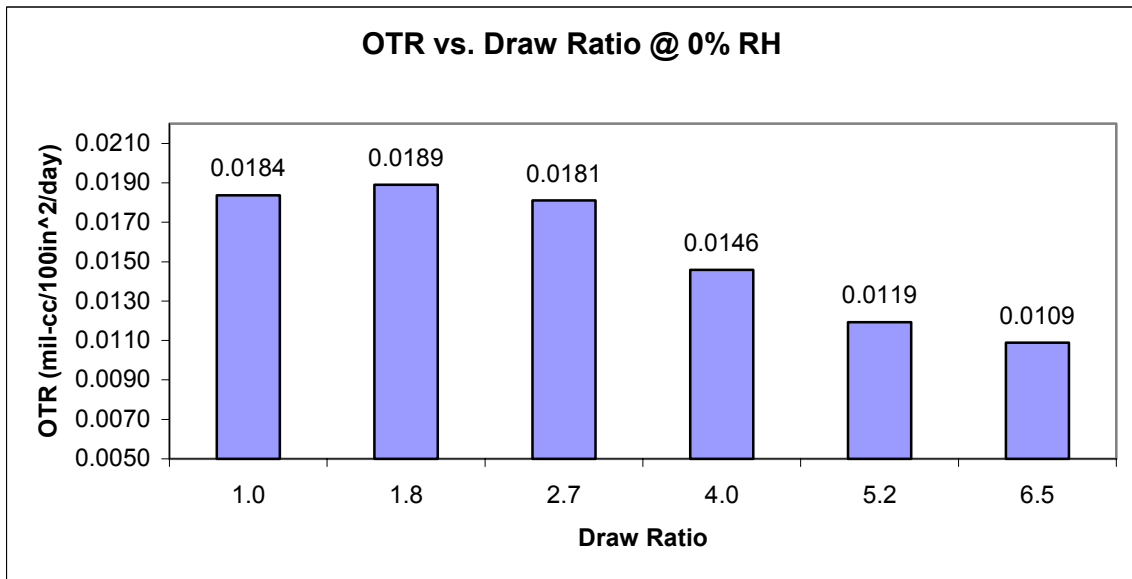


Figure 3: Effect of Increasing Draw Ratio Through MDO on Oxygen Transmission Rate for 38% Ethylene EVOH at 0% Relative Humidity

As shown in Figure 3, the oxygen barrier of the EVOH is nearly doubled after a draw ratio of 6.5:1 with respect to the unoriented blown film.

The same improved barrier is seen at 50% relative humidity as shown in Figure 4.

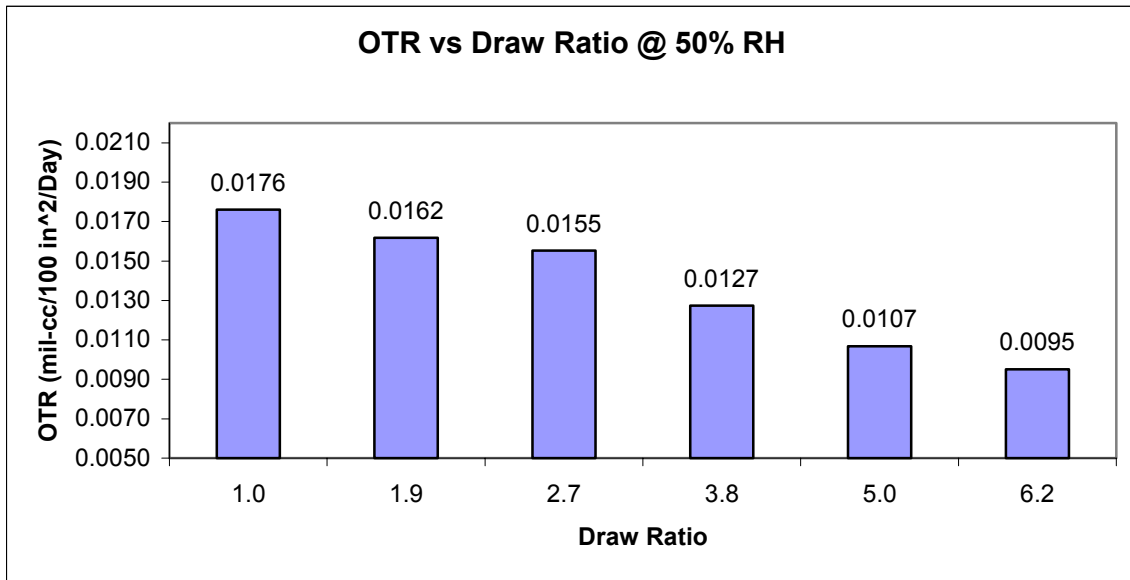


Figure 4: The effect of MDO Draw Ratio on OTR Properties of EVOH at 50% Relative Humidity

MDO OTR vs. RH

As shown in Figure 5, the improvement in oxygen barrier as a result of the MDO of the coextruded EVOH film increases with respect to increasing relative humidity. In other words, the detrimental effect of increasing relative humidity on the oxygen barrier of EVOH coextruded films is dramatically reduced as a result of the MDO process.

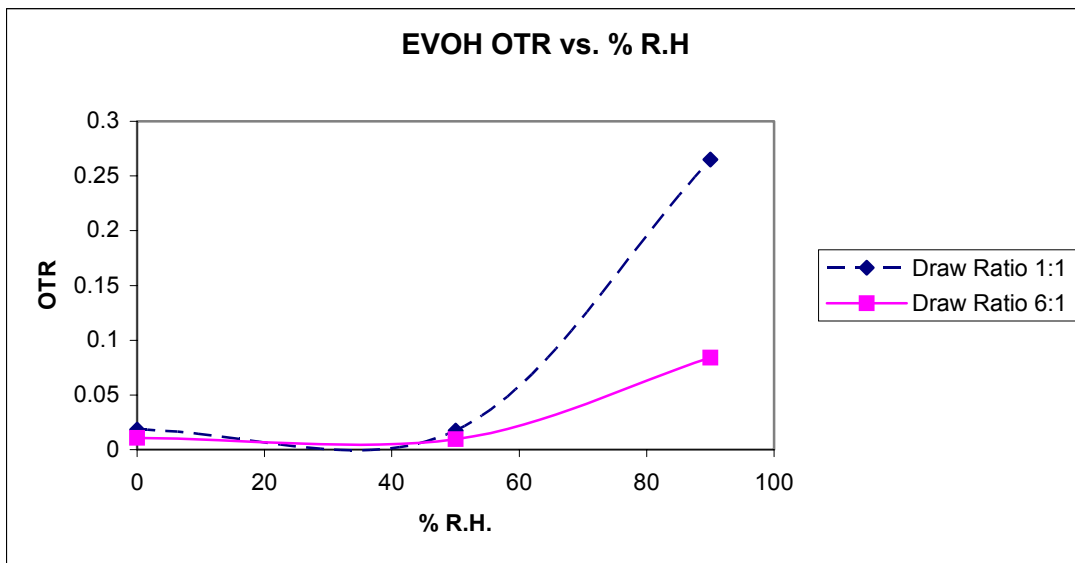


Figure 5: The Oxygen Barrier (cc-mil/100in²-day-atm) of EVOH Coextruded Film at a 6:1 Draw Ratio Relative to an Unoriented EVOH Coextruded Film at Various Relative Humidities

MDO provides the benefit of reducing the detrimental effect of increasing relative humidity on EVOH OTR, making the barrier performance of an MDO EVOH structure comparable to other barrier polymers.

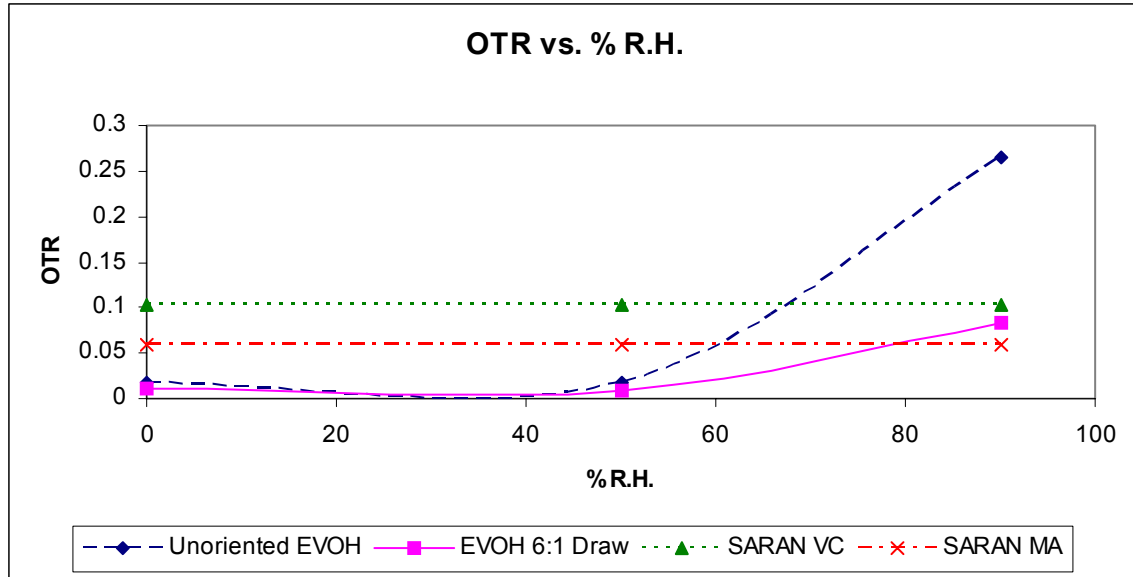


Figure 6: OTR vs. % RH for Various High Barrier Grade Polymers

OTR at 90% RH

Looking more closely at the 90% RH values in Figure 6, we can see that MDO EVOH films can be a competitive material choice.

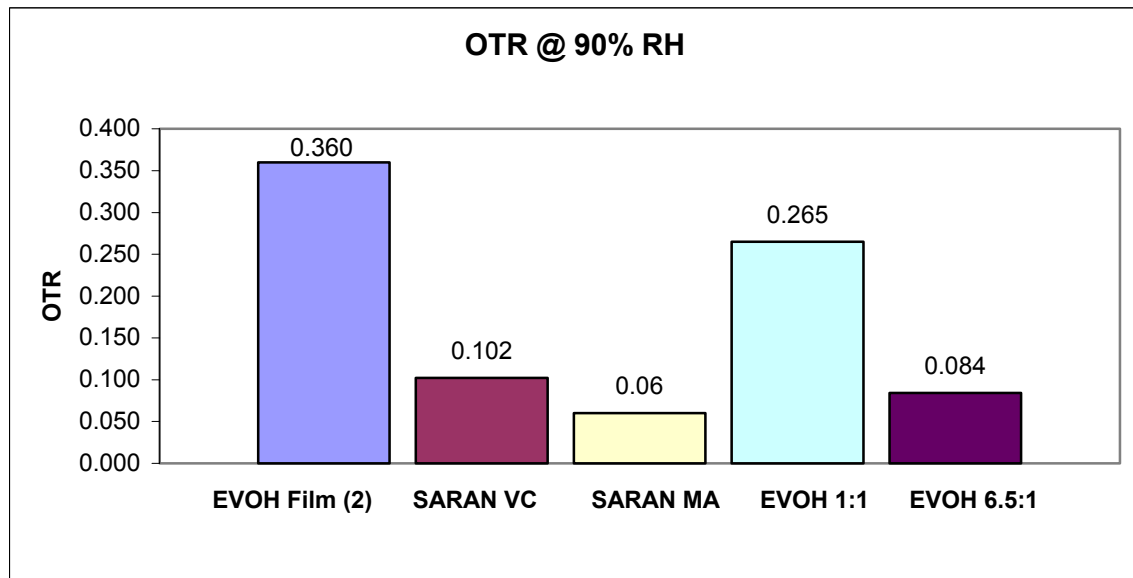


Figure 7: Oxygen Transmission Rates for Various Materials at 90% RH²

Optics vs. Draw Ratio

The optics of the EVOH film under study drastically improved as the MDO draw ratio increased and plateaued at a draw ratio of 5:1, as shown in Figure 8.

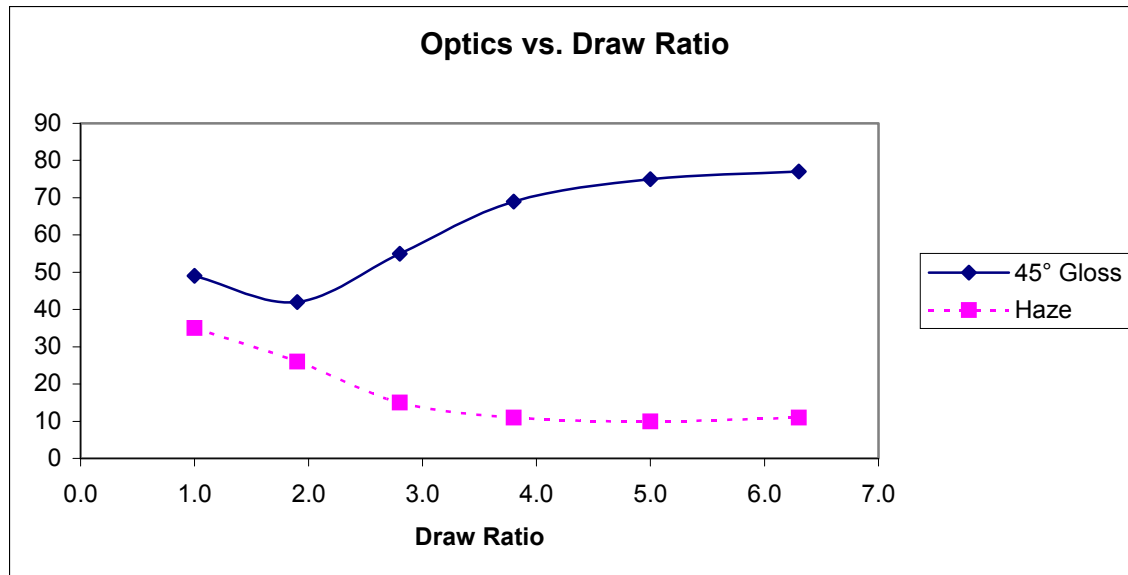


Figure 8: Optics (45° Gloss and Haze) for the EVOH Core Film vs. Draw Ratio

CONCLUSIONS

When a common coextruded film with an EVOH core and LLDPE skins is machine direction oriented, the oxygen transmission rate is significantly reduced. This provides an opportunity for down gauging, or reducing the EVOH layer thickness.

Possibly even more important is the dramatic reduction of the effect of moisture on the oxygen barrier of EVOH at higher draw ratios. This could make an EVOH barrier film that has been machine direction oriented a viable alternative to other materials used in high-moisture applications.

Finally, the optics (gloss and haze) of such a film can be improved by two to three times as a result of MDO.

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REFEREANCES

¹ Robert B. Armstrong, *Effects of Polymer Structure on Gas Barrier of Ethylene Vinyl Alcohol (EVOH) and Considerations for Package Development*, TAPPI 2002 PLACE Conference.

² *Moisture Absorption and Drying of EVAL Resins*, Technical Bulletin No. 100, p.2, EVAL RESINS, BY EVAL Company of America.

³ *Gas Barrier Properties of Resins*, Technical Bulletin No. 110, p.9, EVAL RESINS, BY EVAL Company of America.