

Design Considerations For MDO-PE Polyester Replacement Structures

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ABSTRACT

Polyester (PET) print webs find extensive use in flexible packaging. Machine Direction Oriented Polyethylene (MDO-PE) films are an increasingly prevalent recyclable alternative to PET, as companies start to focus more on sustainability. PET functions well as a print web because of its high heat resistance, low haze, and high stiffness. However, these three variables often conflict with each other when designing and producing an MDO-PE print web. Moreover, bubble stability and a low gel count are essential for process stability and must be considered. This presentation will examine the relationship between stiffness, haze, extensibility, heat resistance, bubble stability, and low gel count in an MDO-PE print web.

INTRODUCTION

The use of Machine direction orientation started decades ago but has grown in relevance to the consumer packaging industry over the past five to ten years. This is largely due to its ability to produce Polyethylene structures with the needed characteristics to act as a recyclable replacement to PET print webs.

PET has been the industry standard print web because of its high heat resistance, low haze, and high stiffness. These characteristics allow for the quick sealing of laminations, clear graphics, and self-supported packaging. Conventional blown PE struggles to meet these needs as grades with good heat resistance and stiffness lack the needed clarity. However, unidirectional stretching of polyethylene structures 4-8x results in a material with moderately high heat resistance, low haze, and high stiffness. The main benefit of these structures is that they integrate well into store drop off recycling programs nationwide. Unidirectional stretching occurs in a unit consisting of 4 distinct zones, (preheating, stretching, annealing, and cooling) that contain a varying number of rollers based on the user's needs. Through these zones, the film heats evenly to increase stretchability, undergoes polymer chain orientation through stretching to the desired thickness, heats to remove intermolecular stresses induced during stretching, and then evenly cools before winding into finished rolls. As one would expect, the end characteristics and processability of an MDO structure depend greatly on the base film used. It is also easy to see that process stability during blown film creation is essential consistent product creation. An understanding of the chemical structure of commonly used materials, and of the physical basis for the end characteristics, is the key to meeting both process and material needs successfully.

Physical Properties of Common Polyethylene Resins-

The various grades of Polyethylene resins exhibit large structural differences that lead to unique properties for each group. Four grades and their properties are discussed below. These grades are Low Density Polyethylene (LDPE), Linear Low Density Polyethylene (LLDPE), Metallocene Linear Low Density Polyethylene (mLLDPE), and High Density Polyethylene (HDPE).

LDPE creation occurs through high pressure and temperature polymerization of ethylene gas. The resultant material contains long chain branching (LCB) throughout each molecule [1]. This branching creates distance between polymer parent chains and results in loose packing of the material. The loose packing of material leads to a low haze and low crystallinity material, that often has a low melt index due to the steric hindrance between polymer chains.



Figure 1. The multibranched structure of LDPE.

LLDPE creation occurs through the copolymerization of ethylene monomer with comonomers such as butene, hexene, and octene. The resultant polymer contains a linear backbone with short chain branching (SCB) caused by the comonomers [1]. LLDPE has low to medium haze and experiences some steric hindrance due to its SCB. This has a small effect on bubble stability and stretchability. LLDPE cannot pack tightly due to the branching and therefore has low crystallinity.

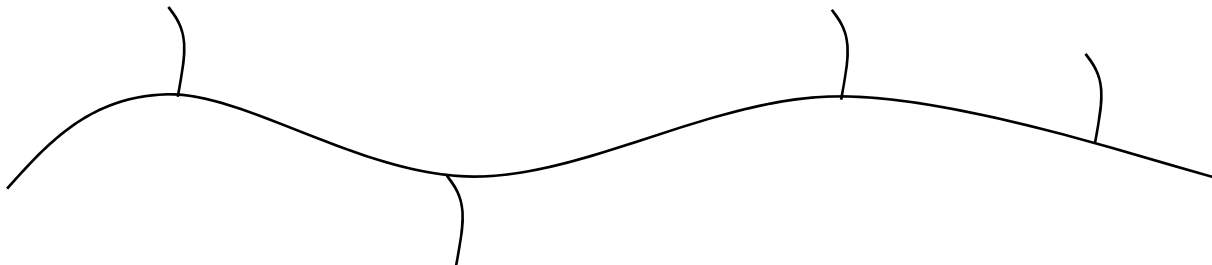


Figure 2. The short chain branched structure of LLDPE.

mLLDPE uses metallocene catalysts during production which results in a greater degree of polymer chain uniformity than conventional LLDPE. mLLDPE's typically have a mix of short and long chain branching [1]. The melt index, crystallinity, and stretchability of mLLDPE's can be highly variable and depend greatly on the degree of long chain branching present in the material. The properties of mLLDPE's often fall somewhere between those of LLDPE and LDPE.

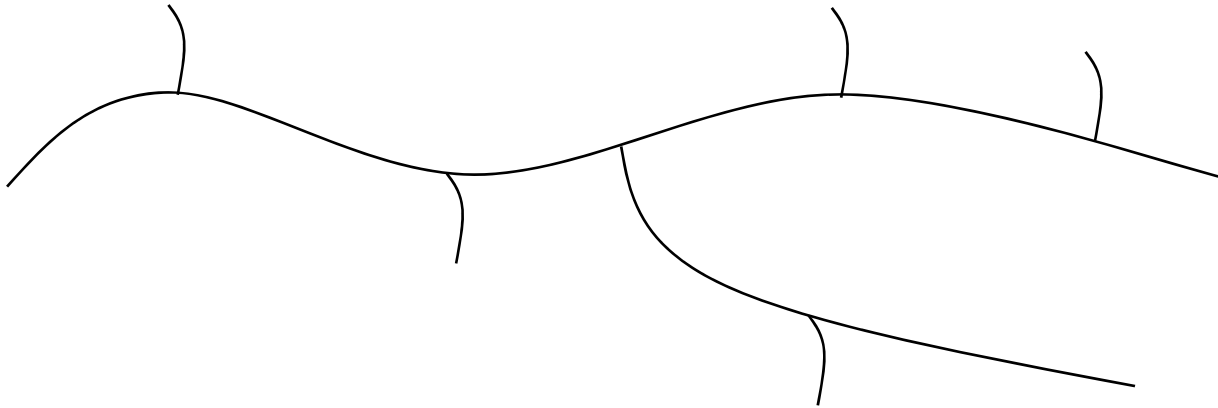


Figure 3. The hybrid short and long chain branched structure of mLLDPE.

HDPE formation occurs at low temperature and pressure using Chromium or Ziegler-Natta catalysts. There is no long chain branching and little to no short chain branching present in the molecules [1]. This leads to a material that stretches well as there is no steric hindrance caused by branching. The lack of significant branching allows HDPE to organize itself into compact crystalline regions throughout the polymer matrix. HDPE has the highest crystallinity of the common polyethylene grades as a result. HDPE has higher haze, heat resistance, and stiffness than lower density materials.



Figure 4. The predominantly linear structure of HDPE.

Physical Basis of Film Characteristics

Desirable print web materials have low haze, high stiffness, and high heat resistance. These properties support the package structure, showcase the graphics, and, at times, showcase the end user's product. Conversely, high bubble stability and low gel count are the main properties desired for the ease of production. An understanding of the physical structures and interactions that cause these phenomena allows the selection of materials that balance these properties and result in a successful product.

Haze is a measurement of the amount of light randomly scattered as it travels through a film. The total haze is the sum of both surface haze and internal haze. Surface haze is the dominant factor and correlates positively with the surface roughness of a film [2]. The surface roughness of material can vary greatly based on molecular weight distribution and chain length [2]. Crystallinity influences the surface roughness due to the presence of spherical crystals (spherulites) at the film's surface [3]. Crystallinity is also the driving force behind internal haze. Materials that are semicrystalline contain pockets of higher and lower density areas throughout the polymer matrix. The

interfaces between these pockets scatter light due to differing refractive indices in each region. Snell's law allows us to calculate the effect of this change.

$$\text{Equation 1: } n_1 \sin \theta_1 = n_2 \sin \theta_2 \text{ [4]}$$

Where n_1 and n_2 are the refractive indices of each material, and θ_1 and θ_2 are the angle of light incident and refracted respectively.

The chemical and physical interactions between polymer chains that allow them to resist deformation by outside forces are the key sources of bubble stability. The chemical component of these interactions relies on London Dispersion Forces as the driving mechanism. This reliance stems from the lack of permanent dipoles in polyethylene polymer chains which pushes reliance on instantaneous dipoles in adjacent molecules. Longer polymer chains/higher molecular weight materials have a higher number of forces than smaller molecules. These forces are summative, and typically result in increasing bubble stability with increasing molecular size [5]. The physical interactions that drive bubble stability are largely dependent on resistance to deformation caused by polymer chain entanglement. This is most commonly seen in fractional melt index LDPEs, where a high degree of long chain branching results in a high incidence of chain entanglement. This entanglement provides large resistance to deformation and drives material melt flow down [6]. LDPEs are typically the solution to poor bubble stability in thick blown films, but their tendency to tear at high stretch multiples disincentivizes their use in MDO structures. MDO structures typically use materials with chemical interactions that drive bubble stability because of this problem.

High stiffness relies on a material's intermolecular forces and resultant crystallinity. As discussed above, the intermolecular forces are mainly London Dispersion Forces, which increase in strength with an increasing number of interactions. Increased polymer chain length, chain orientation/alignment, and decreased long chain branching serve to increase the number of interactions. The lack of long chain branching is important as branching results in steric hindrance that increases the distance between polymer chains. As the distance between chains increases, the forces between them greatly decrease. Ultimately, the increase in intermolecular forces increases the crystallinity and stiffness of the material.

High heat resistance finds its source in an energetically stable structure. Materials that have both high IMF's and high crystallinity are desirable. Because high heat resistance relies on many of the same factors as high stiffness, searching for materials with long chain length, a lack of long chain branching, and good orientability is key.

Low gel count comes from processing conditions, contamination prevention, and material design. Outside of contamination, gels are both unmelted and crosslinked materials in the polymer melt. Typical causes include high and low molecular weight tails from resin production, and poorly tuned extrusion parameters. Materials with a molecular weight much lower than the average will tend to crosslink at the temperatures required for the average material to melt evenly. On the other end of the spectrum, materials with a molecular weight much higher than the average won't melt at the temperatures required to melt the average material. Extrusion parameters that result in high residence times or excess shear are typical causes of crosslinked gels. Poorly designed heat profiles and inadequate shear in extruders are typically the cause of unmelt gels. The large issue with gels is their difference in yield point compared to the rest of the material. This lack of extensibility leads to tears at gels during stretching, which can cause a host of problems on the downstream side of the process. Minimization of gels requires a homogenous melt/material with a narrow molecular weight distribution and a well-tuned extruder system.

Conclusions

Selecting materials for an all-PE print web requires careful consideration of the physical and chemical properties that drive each desired characteristic. Solving for one factor, such as a low haze film, isn't reasonable because the heat resistance and stiffness stem from opposing material characteristics. The lowest haze film would lack high heat resistance, good stiffness, and good extensibility because it would be mainly LDPE based. Likewise, the stiffest film with the highest heat resistance would have high haze due to the crystallinity and surface roughness of HDPE. Because of this, the most important characteristics according to the stakeholders should be ranked based on their degree of importance. High heat resistance and low haze typically top the converter's list, while good bubble stability and good extensibility top the list for production staff. After identifying the most important factors, one can weigh the tradeoffs of each material and effectively solve for an optimized formulation.

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Design Considerations for MDO-PE Polyester Replacement Structures

Presented By: Samuel White of ISOFlex Packaging





MDO- A Decades Old Process With Modern Relevance

- Standalone Units – 1960's
- In Line Units – 1990's
- Greatly Changes Properties
 - Haze
 - Extensibility
 - Tensile Strength
 - Modulus





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PET Print Webs Provide a Perfect Trifecta of Properties

- Very Low Haze (3-5%)
- Very High Heat Resistance (~490°F)
- Very High Stiffness (~700,000PSI)



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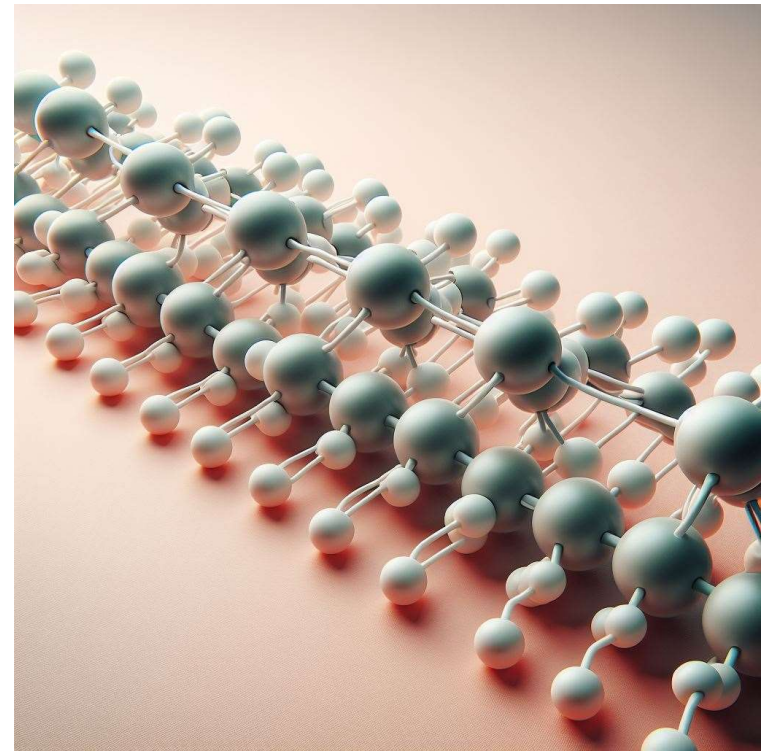
MDO-PE Print Webs Provide a Recyclable Alternative to PET

- Low Haze (5-10%)
- Moderate Heat Resistance (~260-270°F)
- Moderate Stiffness (~190,000PSI)



Where We're Going

- Applied Polymer Science/Chemistry
- Structure and Characteristics of Common Polymers
- Physical Basis for Film Characteristics
- Bring it All Together





Four Types of Polyethylene Make Up Common Grades

- Low Density Polyethylene (LDPE)
- Linear Low Density Polyethylene (LLDPE)
- Metallocene Linear Low Density Polyethylene (mLLDPE)
- High Density Polyethylene (HDPE)





The Multibranched Structure of LDPE Results In a Clear and Flexible Polymer

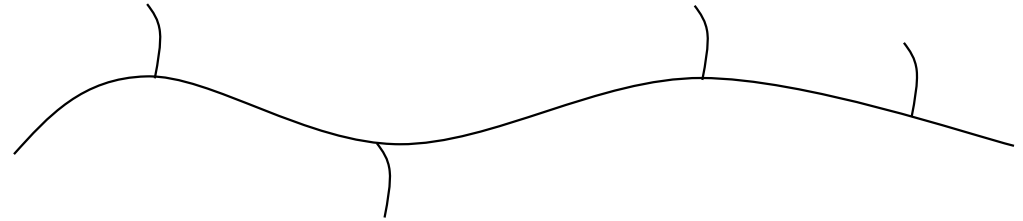
- Steric Hindrance Between Chains
- Low Crystallinity/Intermolecular Force (IMF) strength
- Low Haze
- Good Bubble Stability
- Poor Extensibility





The Short Chain Branching of LLDPE Results in a Strong But Flexible Polymer

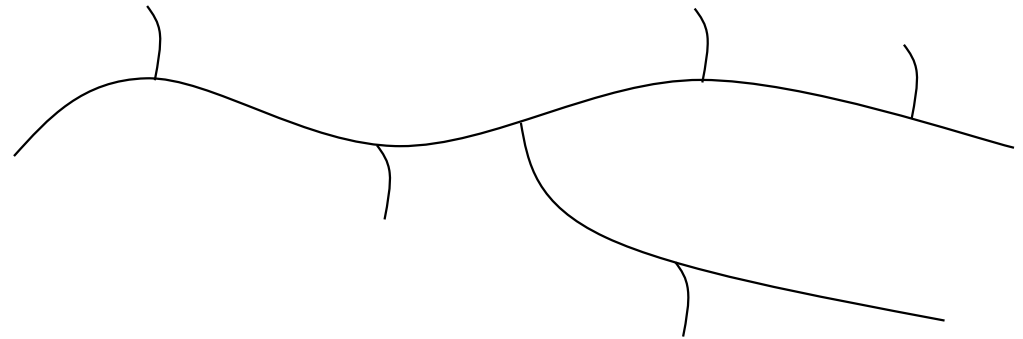
- Branching stems from comonomers
 - Butene, Hexene, Octene
- Increased IMFs Compared to LDPE
- Minor steric hindrance
- Moderate Haze





High Uniformity Among Chains and a Hybrid Branched Structure give mLLDPE Properties between LLDPE and LDPE

- SCB from comonomers
- Properties vary with LCB content





The Largely Unbranched Structure of HDPE Results in a Rigid and Strong Polymer

- Highest IMFs out of common PE's
- Crystallinity increases with IMFs
- Good Extensibility
- Nominal Steric Hindrance

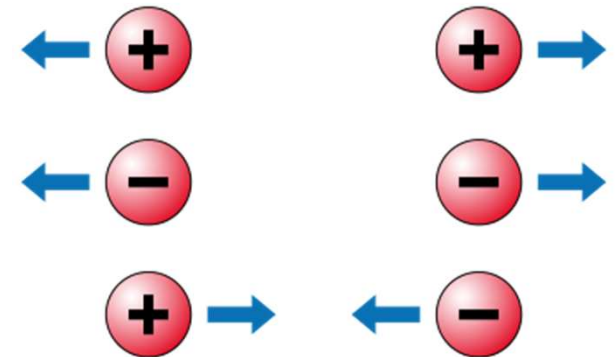




London Dispersion Forces are the Dominate Intermolecular Forces of PE

- Rely on instantaneous dipoles
- Scale with molecular weight and distance
- Result of Coulombs Law

- $F = k * \frac{|q_1 * q_2|}{r^2}$





Stiffness and Heat Resistance Rely on Strong Intermolecular Forces

- Crystallinity \propto IMFs
- Increasing IMFs = Increasing Force/Heat to Deform



Bubble Stability Reflects the Polymer Melt's Resistance to Deformation

- Low Melt Flow Rate (MFR) Desirable
- Chemical or Mechanical
 - Strong IMFs Vs. Chain Entanglement
- Mechanical Reduces Extensibility



Haze is a Measure of Light Scattered as it Moves Through a Film

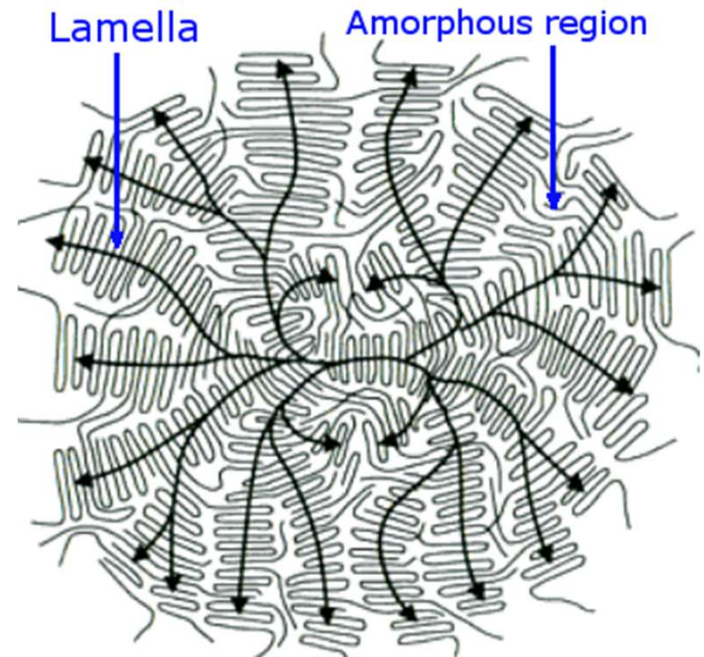
- Total Haze = Surface Haze + Internal Haze
- Surface Haze = Dominant Factor





Surface Haze is Heavily Correlated with Surface Roughness

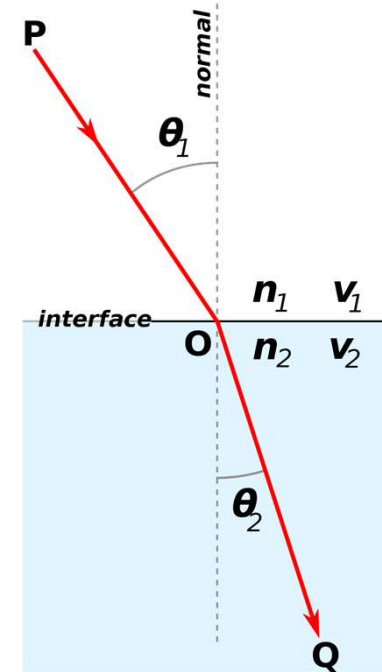
- Random Diffraction and Reflection
- Crystalline Spherulites Increase Roughness





Internal Haze is Driven by Differences in Crystallinity Throughout the Material

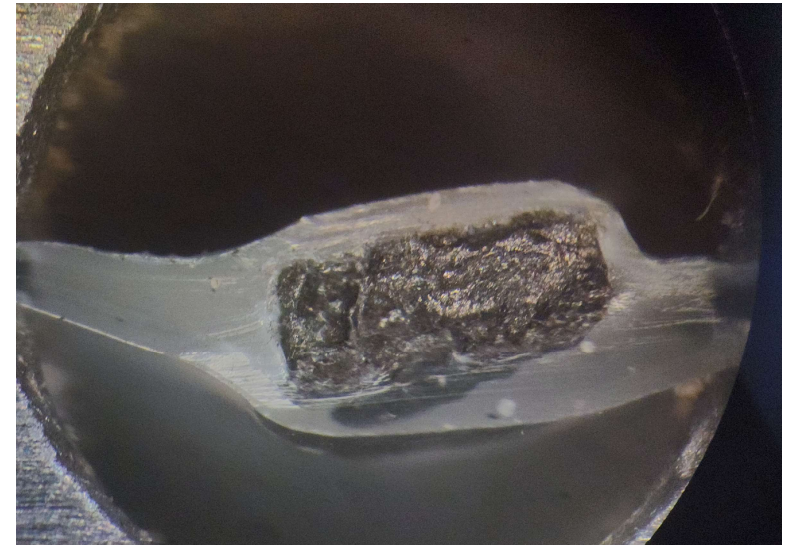
- Pockets of Crystalline/Amorphous Material
- Density Differentials Created
- Snell's Law Provides the Calculation
 - $n_1 \sin \theta_1 = n_2 \sin \theta_2$





Gels Result from Improperly Melted Or Contaminated Material

- Good Manufacturing Processes Prevent Contamination
- Excess Heat Causes Cross Linking and Carbon
- Insufficient Heating Leads to Unmelts





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A Low Gel Count Film Requires Careful Resin Selection and Precise Extruder Tuning

- Narrow Molecular Weight Distribution
- Evenly Heated Extruder Barrel
- Appropriate shear for material



Stakeholder Input is Key to Designing a Successful MDO Structure

- Converter and Production Staff are Central Stakeholders
- Converter
 - Low Haze
 - High Heat Resistance
 - High Stiffness
- Production
 - Good Bubble Stability
 - Good Extensibility
 - Low Gel Count



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