CHAPTER 1

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1.1 Plastics in Packaging

Polymers or plastics have a ubiquitous influence on every aspect of our lives due to their extraordinary range of properties. Plastics find use in an enormous and ever expanding range of products from paper clips to spaceships (www.wikipedia.com). Plastics have already displaced many traditional materials, such as wood, stone, horn and bone, leather, paper, metal, glass, and ceramic, in most of their former uses. Some of the major sectors in which polymers are used include packaging, building & construction, transportation, medical & health, electronics, agriculture and sports & leisure.

The global polymer industry is poised to reach sales of an estimated US $560 billion in 2017 with a CAGR of 3.8% over the next four years (www.lucintel.com). The Indian plastics industry is expected to grow between 10 to 12% in this decade with consumption level expected to reach between 8 to 10 MMT (million metric tons) at a CAGR of almost 9% (www.cipet.gov.in). About half of the plastics that are produced worldwide are used in the packaging sector that is comprised of both flexible and rigid packaging. Flexible plastics packaging market comprises mainly of polymer films (both mono and coextruded), laminates and coatings. Global plastic packaging materials and products market is expected to reach US $260 billion by 2015. In particular, the global plastic film and sheets market is expected to reach about 57 MMT by 2017 (www.strategyr.com). The Indian packaging industry is growing at more than 11% per annum and is expected to cross a turnover of US $22 billion by 2015 (www.marketresearch.com). Roughly 50% of the Indian packaging industry’s revenues are plastic based (www.plasticbiz360.com). The Indian packaging industry is seeing a shift from traditional rigid packaging to flexible packaging (see fig. 1.1). One of the
main reasons for this shift is that a smaller quantity of product can be packed in these packages as compared to traditional packaging.

![Figure 1.1 Total flexible packaging market in India in 2010.](image)

An important class of polymers that is converted into flexible packaging (such as films) is polyolefins. The global market for polyolefins was valued at US $152 billion in 2011 and it is expected to reach US $188 billion in 2016 at a CAGR of almost 4.5%. Among the polymers that are converted into flexible packaging products, polyolefins account for almost 53% share (www.cipet.gov.in). The market for polyolefin resins can be broadly categorized into two segments: polypropylenes (PP) and polyethylenes (PE). The PP market totaled US $63 billion in 2011 and should reach nearly US $78.3 billion in 2016, a CAGR of 4.6%. As a segment, the PE market was valued at almost US $90 billion in 2011 and should total nearly US $110 billion in 2016, a CAGR of 4.3% (www.bccresearch.com). Among polyolefin-based packaging, PE is considered as the building block and accounts for the lion’s share of the worldwide plastic films and sheet market (www.strategyr.com).
1.2 Plastic Films

A film is defined as a flat plastic material having thickness less than 250 microns (or 0.25 mm). Typically, a film has a large surface area to volume ratio and is generally considered as a two-dimensional (2-D) object with minimal thickness. In general, polymer or plastic films are used to protect, shield, wrap, hold, and contain things ranging from food products to consumer, agricultural, and industrial goods.

The key attributes that a film must possess are the following:

- superior barrier properties (to gases and liquids),
- high mechanical properties such as tensile strength, impact resistance, tear strength, and puncture resistance,
- high transparency (or low haze), and
- surface properties such as gloss and printability.

There are two main processes to manufacture polymer films: blown film or tubular extrusion and extrusion film casting (EFC) or cast-film extrusion. In blown film extrusion, the polymer melt is extruded through an annular die to form a molten tube that is then expanded by air pressure to form a bubble. The inflated bubble is of much larger diameter than the original diameter of the annular die. This bubble is pinched some distance away from the die and the solidified film is slit and wound on rolls. This process is shown schematically in figure 1.2.

In the extrusion film casting (EFC) process, a molten web or film of polymer is extruded through a T-shaped slit die, stretched in air for some distance before being solidified on chill-rolls and wound. The EFC process is shown schematically in figure 1.3. In the industry, film widths of 3-5 meters (for EFC), extrusion speeds of the order of 600-800 m/min and throughputs in excess of 1800 kg/hr are not uncommon. In many instances, the best combination of properties are often achieved when polymer films are combined with one another or with other materials such as paper, aluminum
or even glass, through processes such as coating, lamination, coextrusion and metallization shown schematically in figure 1.4.

All of the research mentioned in this dissertation has been focused on the EFC process.

Figure 1.2 Schematic of blown film extrusion process (www.varahii.com).

Figure 1.3 Schematic of extrusion film casting (EFC) process (www.eastman.com).
1.3 Extrusion Film Casting

Extrusion film casting (EFC) is an important polymer processing operation used for producing films (~ 0.025 mm thick) and sheets (~ 0.5 mm thick). The process, shown schematically in figure 1.3 and in more detail in figure 1.5, consists of the following steps: (a) a molten polymer is extruded through a center-fed “T” or a “coat-hanger” die under pressure; (b) the resulting molten film is then stretched in air for a short distance (called as the take-up length, TUL); (c) the film is finally cooled down on a chill roll. After this primary casting process, the film/sheet may be subjected to other processes, such as biaxial stretching, thermoforming, or coating on a substrate. Immediately upon exiting the die an extruded cast film initially swells due to molecular stress relaxation, after which its thickness decreases monotonically because of the stretching forces exerted by the chill roll that operates at a higher velocity as compared to the exit velocity of the molten film at the die. The extent of stretch experienced by the melt in this region is quantified in terms of draw ratio (DR), which is defined as the tangential velocity of the chill roll divided by the linear velocity of the melt at the die exit. There are two main defects that are present during steady-state EFC processing: necking and edge-beading, which are also shown in fig. 1.5.
The EFC process is used for producing monoaxially-oriented (MO film), biaxially-oriented (BO film), laminated, and coextruded films. Monoaxially-oriented or machine direction orientated (MDO) film is produced in an online or offline mode. This process improves the barrier properties and gives the mono and coextruded films enhanced tensile strength and stiffness, better shrink properties, and increased gloss and transparency (www.whcorp.com).

![Diagram of EFC process and associated defects]

**Figure 1.5 Schematic of EFC process and associated defects.**

Biaxially-oriented films are usually produced using a tentering process downstream of the EFC process as shown schematically in figure 1.6. This process is primarily used to produce biaxially-oriented PP (BOPP) and biaxially-oriented PET (BOPET) films. Tentering process imparts high tensile strength, chemical and dimensional stability, transparency, reflectivity, gas and aroma barrier properties, and electrical insulation to the extruded films.
One of the important applications of the EFC process is to produce stretched tapes, also called as raffia. Raffia tapes are produced by slitting the extruded film along machine direction. The slitted tapes are further stretched in a hot oven to enhance their properties. Raffia tapes can be converted into twines, ropes, woven or knitted fabrics.

![Figure 1.6 Schematic of film tentering process.](image)

A major use of woven raffia tapes is in manufacture of woven sacks that have now almost completely replaced jute sacks for cement (unlaminated PP) and fertilizer (PP laminated HDPE) packaging. Woven sacks can hold material from about 50 kg to as much as 4000 kg ([www.ril.com](http://www.ril.com)).

### 1.4 Manufacturing Defects in EFC Process

The EFC process is limited by an unsteady-state instability known as the draw resonance, which happens when the molten film or web is subjected to free surface stretching flow beyond a certain draw ratio. Under constant extrusion and drawing speed, when the DR exceeds a critical value, an oscillatory behavior of film width and thickness is observed. This phenomenon is called as the draw resonance and is shown schematically in figure 1.7 below.
Figure 1.7 Schematic of draw resonance instability in EFC process.

The critical DR above which draw resonance occurs is about 20 for Newtonian fluids such as nyons or polyesters and can be as low as 3 for highly viscoelastic fluids such as polyethylene, polypropylene or polystyrene. The common industrial routes to reducing the draw resonance are (i) reduce the DR, (ii) decrease the die opening, (iii) reduce take-up length (TUL), and (iv) increase melt temperature. This defect has been studied in great detail by various researchers for over six decades but it is, however, not yet amenable to any easy interpretation based on the physics involved as to the fundamental nature of its origin and cause.

Under stable and steady-state extrusion film casting (EFC) operation (as shown in figure 1.5) two major defects occur in the area between the die and the chill-roll. These are necking and edge-beading, which are respectively inhomogeneous reductions in the width and the thickness of the film. Edge-beading corresponds to the film edges being substantially thicker than the central portion of the film, while necking implies a final film width that can be
substantially lower than the width of the die from which the film is extruded. These two inter-related phenomena cause a significant reduction in the usable width of the film and are therefore undesirable.

Polymer film and sheet processors often tend to go for maximum throughput for obtaining maximum profitability. The aim here is to obtain thinner film gauges at highest permissible extrusion speeds. However, the above-mentioned defects limit the EFC process. The necking and the associated edge-beading defects are always inherently present in the EFC process while the draw resonance instability only occurs above critical DR’s. In this PhD research, we have concerned ourselves with the necking defect.

1.5 Polyolefins in EFC

The various types of polyolefins that can be converted into films, laminates or coatings using the EFC process include polyolefins like low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and polypropylene (PP). Other polymers that are also processed into films, laminates or coatings include polyvinyl chloride (PVC), polyethylene terephthalate (PET), polyamide (Nylon), ethylene vinyl alcohol (EVOH) and polyvinylidene chloride (PVDC).

Almost half of the 130 MMT of polyolefins were produced in 2012 (www.chemsystems.com) were converted into flexible packaging products such as films, laminates and coatings by processes such as EFC and others.

Table 1.1 gives the structure, properties and description of polyolefins used in films processing.
Table 1.1 Structure, properties and description of the polyolefins used for film production

<table>
<thead>
<tr>
<th>Polyolefin</th>
<th>Comonomer and micro-structure</th>
<th>Density</th>
<th>Manuf. method</th>
<th>Properties</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-density polyethylene (HDPE)</td>
<td>None; Linear architecture with no branches</td>
<td>0.94-0.96</td>
<td>Zeigler-Natta</td>
<td>High tensile strength, low impact properties</td>
<td>Brittle film with good gas barrier properties</td>
</tr>
<tr>
<td>Low-density polyethylene (LDPE)</td>
<td>None; random short and long chain branching (LCB)</td>
<td>0.91</td>
<td>Radical, with autoclave or tubular reactor</td>
<td>Strain hardening polymer with good impact properties</td>
<td>Both blown and cast films</td>
</tr>
<tr>
<td>Linear low-density polyethylene (LLDPE)</td>
<td>α-olefins (e.g. 1-Butene 1-Hexene 1-Octene) Short chain branching (SCB)</td>
<td>0.91-0.93</td>
<td>Zeigler-Natta</td>
<td>Intermediate strength with elasticity; slightly difficult to melt process</td>
<td>High clarity glossy films by both blown and cast films</td>
</tr>
<tr>
<td>Metallocene-Linear low-density polyethylene (m-LLDPE)</td>
<td>α-olefins (e.g. 1-Butene 1-Hexene 1-Octene) Mainly short chain branching with sparse LCB depending on catalyst used</td>
<td>0.91-0.93</td>
<td>Metalloocene single-site, late transition metal catalyst</td>
<td>Intermediate strength with elasticity; difficult to melt process</td>
<td>High clarity glossy films by both blown and cast films</td>
</tr>
<tr>
<td>Very Low-density polyethylene (VLDPE) with long branches</td>
<td>α-olefins (e.g. 1-Butene 1-Hexene 1-Octene) Mainly short chain branching with some LCB</td>
<td>0.89-0.91</td>
<td>Constrained geometry single site catalyst</td>
<td>Tough, elastic, moderate strength films and easy to process</td>
<td>Both blown and cast films</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>None; Completely linear architecture with no branches</td>
<td>0.90</td>
<td>Zeigler-Natta</td>
<td>Transparent, High tensile properties, temperature resistant</td>
<td>Low melt strength; cannot be processed easily using</td>
</tr>
</tbody>
</table>
This dissertation focuses on the role of the macromolecular architecture of polyethylene (PE) on the EFC performance. Figure 1.7 depicts the macromolecular architecture of linear and branched PE’s.

![Molecular structures for linear and branched PE’s](image)

**Figure 1.8** Molecular structures for linear and branched PE’s; (a) linear with no branches, (b) linear with short branches, (c) linear with short branches and sparse long branches and (d) branched structure with both short and long branches.

Between PE’s, the LDPE resin is produced mainly for extrusion coating applications especially for food and beverage packaging. The conventional (Zeigler-Natta LLDPEs) and the metallocene LLDPEs are produced primarily for packaging applications wherein thinner films than those possible with LDPE are required.
1.5.1 Low Density Polyethylene

Low density polyethylene (LDPE) was the first grade of PE produced in 1933 by Imperial Chemical Industries (ICI) using a high-pressure free radical polymerization process. There are two main reactor types that produce LDPE: (i) autoclave reactor and (ii) tubular reactor. The autoclave process tends to produce more branching and a broader molecular weight distribution (MWD). On average, LDPE has about 3-10 long and about 30 short branches per molecule. The presence of LCB affects the melt state properties to a great extent and may also affect the solid-state properties if the degree of LCB is high enough. Higher zero-shear viscosity (ZSV) and greater amount of shear thinning makes LDPE easier to melt process. The peak melting temperature of LDPE is about 110°C. LDPE is used widely for packaging items such as bottles, containers and films, tubing and molded products. Due to its enhanced melt strength on account of the presence of long chain branching; LDPE can be used for both blown and cast film extrusion. Worldwide, LDPE is primarily produced for extrusion coating applications mainly for aseptic packaging. The low crystallinity of LDPE results in films of good clarity and gloss.

1.5.2 Linear Low Density Polyethylene

Linear low density polyethylene (LLDPE) is a copolymer of ethylene and a 1-alkene, typically 1-butene, 1-hexene or 1-octene, though branched alkenes such as 4-methyl-1-pentene have also been used. LLDPE can be produced using conventional multi-site catalysts such as the Ziegler-Natta or with constrained geometry single-site catalyst such as metallocenes. Conventionally produced LLDPE’s tend to be of mainly linear architecture with presence of significant amount of short chain branching (SCB). The metallocene catalyzed LLDPE (m-LLDPE) is also primarily a linear polymer with SCB, but it also contains sparse amounts of long chain branching (LCB). The presence of LCB makes the m-LLDPEs relatively easier to melt process than the linear LLDPEs. The narrow MWD combined with presence of abundant SCB makes LLDPE a lot less shear sensitive than LDPE. The melt
strength of LLDPE is quite inferior to be used for tubular film extrusion and thus EFC is the process of choice to produce films and laminates. High mechanical strength combined with enhanced clarity and gloss make LLDPE resins as preferred choice for packaging films. The properties of LLDPE tend to be in between those of LDPE and HDPE.

1.5.3 High density Polyethylene

High density polyethylene (HDPE) is a PE of a linear architecture and is typically formed by a gas phase or slurry polymerization at relatively low pressures using Ziegler-Natta or chromium based catalysts. HDPE almost always has no LCB though the Philips process does introduce some sparse LCB onto the linear main chain. The presence of the sparse LCB with presence of SCB gives this particular grade of HDPE remarkable impact properties as well as melt strength. Typical products made using HDPE include corrosion-resistant pipes, milk containers, geomembranes, plastics films and bags, plastic lumber and automotive fuel tanks. HDPE films are used for packaging of frozen foods, cheese, powders, etc. HDPE geomembranes are used for important environmental applications such as lining of industrial/farm lakes or ponds, spill containment for chemical industries, solid waste landfill lining, etc. HDPE can be processed by both blown and EFC processes and can also be extrusion coated onto various substrates. HDPE films tend to be translucent due to rapid crystallization of the linear chains.

1.6 Role of Macromolecular Architecture on Polymer Processing

An important aspect of research in polymer processing is concerned with linking and understanding relations between melt properties and processibility as shown in figure 1.8. The scientific challenge underlying the exploration of relations shown in figure 1.8 is that of bridging length and time scales over several decades. This has been the underlying theme of research in our group at CSIR-NCL for over a decade. For instance, extrusion
time scales are of the order of seconds or minutes, and the length scales involved in extruding products could be of the order of meters (such as the width of cast films or diameters of extruded pipes) On the other hand, the macromolecular chains have length scales of nanometers with time scales of relaxation of the order of milliseconds. Bridging these length and time scales is the key towards developing an understanding about how macromolecular architecture affects polymer processing.

![Figure 1.9 Linking polymer processing with macromolecular structure via rheology.](image)

It is a known fact today that polymer processing is directly influenced by melt rheology which in turn is influenced to a major extent by the macromolecular architecture of the polymer. Over the past 6-7 decades the theories of polymer dynamics have matured to an extent that allows near-quantitative predictions of the melt rheology from coarse-grained molecular information. Similarly, techniques of computational fluid dynamics (CFD) have become increasingly sophisticated to enable predictions of viscoelastic flow in complex geometries. Thus, it has become possible now to start linking molecular structure of polymers to their melt processing behavior.
One such example wherein macromolecular structure can be linked to polymer processing is of extrudate swell, which is a common phenomenon observed in the polymer extrusion industry. Accurate prediction of the dimensions of an extrudate is important for appropriate design of dies for profile extrusion applications. Prediction of extrudate swell has been challenging due to (i) difficulties associated with accurate representation of the constitutive behavior of polymer melts, and (ii) difficulties associated with the simulation of free surfaces, which requires special techniques in the traditionally used Eulerian framework in CFD simulations. We have studied in detail the extrudate swell phenomenon using an Arbitrary Lagrangian Eulerian (ALE) based finite element formulation that has distinct advantages in simulating free surface deformations (such as in extrudate swell) \textsuperscript{23,26}. Within the CFD framework, the polymer melt rheology was modeled using molecular constitutive equations such as the eXtended Pom Pom or XPP model. The ALE predictions showed favorable comparison with the experimental data on the extrudate swell of commercial grades of linear polyethylene (LLDPE) and branched polyethylene (LDPE).

The EFC process constitutes an interesting example of molecular structure-processing relations. As mentioned before, every viscoelastic polymer when processed in an EFC process undergoes necking which is an inhomogeneous reduction in width of the film. The extent of film necking is different for different polymers. Thus, if an EFC processor wishes to process a polymer into a film that is one meter in width, it is not known apriori how much the die width should be. Using experience and heuristic knowledge, processors are able to work with known and widely used polymers. But if they wish to work with a new and previously unprocessed polymer then a great deal of expensive trial and error will have to be undertaken. In such cases, an in-depth understanding of the relations between molecular structure and polymer processing becomes critical.
1.7 Scope and Organization of this Dissertation

This dissertation focuses on understanding the influence of macromolecular structure on necking defect in steady state EFC process. This dissertation is organized as follows: Chapter 2 provides a comprehensive review of the previous research on necking in EFC in order to place this research in the context of available literature. The materials used in this work and their characterization are described in Chapter 3. Experimental details for the EFC process are described in Chapter 4. The flow model, constitutive equations and the numerical solution procedure are described in Chapter 5. The salient results are discussed in Chapter 6. The conclusions of this research and directions for future research are summarized in Chapter 7. A copy of the synopsis and a list of publications arising out of this research are given at the end of this dissertation.