CHAPTER 2

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In this chapter the salient researches on modeling and experimental investigations on the necking phenomenon in steady state extrusion film casting (EFC) are reviewed. These are also summarized in table 2.1 and table 2.2. Since the main work presented in this dissertation focuses on understanding the linkages between necking during EFC and macromolecular architecture, it is imperative that key aspects of polymer dynamics and in particular the tube theory be reviewed upfront before discussing about the necking phenomenon in EFC. Therefore, this chapter begins with a discussion of some of the key theories of polymer dynamics and the rheological constitutive equations arising from these theories. This is followed by a literature review of necking in EFC.

2.1 Polymer Dynamics

The understanding and prediction of viscoelastic response of polymer solutions and melts from the knowledge of macromolecular structure has been a continuing subject of study in polymer science for over half a century \(^\text{27}\). Polymer dynamics plays a key role in linking macromolecular structure to polymer rheology. The first attempts in this direction were made as early as in 1953 by Prof. P. E. Rouse \(^\text{28}\) and later refined by Prof. B. Zimm \(^\text{29}\). Their models of polymer dynamics can be used to predict the rheology of unentangled polymer solutions.

Most flexible polymers are entangled in the melt state. The rheology in this state is relevant to most polymer melt processing operations. The classical tube model \(^\text{30}\) forms the basis of explaining the dynamics of entangled polymer solutions and melts. The tube model is based on the pioneering ideas proposed by Prof. S. Edwards and Prof. P.G. de Gennes. Since then theories of entangled polymer rheology have advanced to a great extent over the past one and a half decade. They have been recently been used to
make accurate predictions of rapid polymer flows in complex geometries that resemble industrial polymer processing\textsuperscript{16,23,31–35}.

In the next subsections, we review briefly the Rouse model and the tube models. We will then highlight some of the important refinements of the tube model, especially those relevant to the long-chain branched architecture of polymers.

2.1.1 The Rouse Model

The Rouse model\textsuperscript{28} describes the conformational dynamics of an idealized polymer chain in a dilute solution i.e. in an unentangled state. In this model, as shown in the schematic below, the single chain diffusion is represented by the Brownian motion of the beads connected by harmonic springs which make the idealized chain. This model is also known universally as the bead-on-spring model. Rouse model can also be applied to short-time dynamics of chains in polymer melts\textsuperscript{30} where the dynamics is not affected by entanglements. It is assumed in the Rouse model that hydrodynamic interactions between the beads are screened. An important extension to include hydrodynamic interactions mediated by the solvent between different parts of the chain was worked out by Professor Bruno Zimm\textsuperscript{29}.

![Rouse Model](image)

**Figure 2.1 The Rouse Model.**

The Rouse model describes a chain of $N$ beads connected by Hookean springs with a force constant $k$, related to the temperature of the system $T$ and the average bond length $b$ as:
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\[ k = \frac{3k_BT}{b^2} \]  

(2.1)

where \( k_0 \) is the Boltzmann’s constant.

The Brownian force (stochastic in nature) exerted by the solvent molecules on the polymer beads is balanced by the viscous drag force and the elastic restoring force. This happens even in the absence of any external forces on the system. If an extra stress force is exerted on the system, then this force will cause extra drag.

A simple force balance on the ‘nth’ bead of the bead-on-spring chain can be written in the form of the following equation also known as the Langevin equation as

\[ \zeta \frac{\partial \overline{R}_n}{\partial t} = k \frac{\partial^2 \overline{R}_n}{\partial n^2} + \overline{f}_n + k \overline{R}_n \]  

(2.2)

wherein \( \zeta \) is the friction coefficient of the polymer bead; \( \overline{R}_n \) is the position vector of the n\(^{th}\) bead; \( \overline{f}_n \) is the stochastic Brownian force; and \( k \) is the imposed deformation tensor.

The coupled equation (2.2) for all beads of a polymer chain can be solved using Fourier transforms. The microscopic stress in the solution is related to the ensemble averaged dyadic product of the position vector. Once the stress is obtained, expressions for the intrinsic steady-state viscosity, the Rouse relaxation time, and the diffusion coefficient can also be derived and are given below:

\[ [\eta] = \frac{N_A \zeta b^2 N}{M \eta_s 36} ; \quad \lambda_R = \frac{\zeta b^2 N^2}{3\pi^2 k_BT} = \lambda_0 N^2 ; \quad D = \frac{k_BT}{N\zeta} \]  

(2.3)
where \( \lambda_0 = \left( \frac{\zeta b^2}{3\pi^2 k_B T} \right) \) is the relaxation time of a bead in the chain, \( N_A \) is the Avogadro’s number; \( \eta_s \) is the viscosity of the solvent; \( M \) is the molecular weight. The main results here are that the Rouse relaxation time (which is the longest time constant in the system) scales as the square of the molecular weight, while the viscosity is proportional to the molecular weight. The other important result here is the prediction of the diffusion coefficient which is inversely proportional to the molecular length. 36 The Fourier analysis of the Langevin equation shows that the relaxation of a Rouse chain is self-similar. Thus, the relaxation time of a \('p^{th}\)' mode comprising \( N/p \) beads is given by

\[
\lambda_p = \frac{3b^2}{3\pi^2 k_B T} \left( \frac{N}{p} \right)^2 = \lambda_0 \left( \frac{N}{p} \right)^2 \tag{2.4}
\]

Physically, the \('p^{th}\)' mode corresponds to subchains containing \( N/p \) beads and each of the sub-chains relaxes independently by the Rouse dynamics. Thus, at time \( t = \lambda_p \), all subchains equal to or smaller than \( N/p \) will have relaxed after imposition of a step-strain. In other words, \( p \) counts the number of modes that are left unrelaxed at \( t = \lambda_p \). Since the relaxation modulus \((G)\) is proportional to the unrelaxed modes,

\[
G(\lambda_p) \sim \frac{k_B T}{N b^3 p} \tag{2.5}
\]

The constant of proportionality in equation (2.5) is the thermal energy per chain volume \((k_B T/N b^3)\), and corresponds to the modulus of the whole chain at \( t \approx \lambda_R \), where \( \lambda_R \) is the Rouse relaxation time. From equations 2.4 and 2.5, one can write

\[
G(\lambda_p) \sim \frac{k_B T}{b^3} \left( \frac{\lambda_p}{\lambda_0} \right)^{-1/2} \quad \text{or} \quad G(t) \approx \frac{k_B T}{b^3} \left( \frac{t}{\lambda_0} \right)^{-1/2} \tag{2.6}
\]
Whilst in the case of a dilute solution the Rouse model overestimates the decrease of the diffusion coefficient $D$ with the number of beads $N$ as $1/N$, the Zimm model predicts $D \sim N^{-1/2}$ which is consistent with the experimental data for dilute polymer solutions. However, in a polymer melt, the Rouse model correctly predicts long-time diffusion only for chains shorter than the entanglement length. For long chains with noticeable entanglement, the Rouse model holds only up to a crossover time, $\lambda_e$, defined as the time above which entanglement effects are important. For longer times the chain can only move within a tube formed by the surrounding chains. This slow motion is usually approximated by the reptation model.

### 2.1.2 The Reptation Model and the Tube Theory

Reptation is the thermal motion of very long linear, entangled macromolecules in polymer melts or concentrated polymer solutions. Derived from the word *reptile*, reptation suggests the movement of entangled polymer chains as being analogous to snakes slithering past each other in a snake pit as shown in the below schematic. In this scenario, *entanglement* means the topological restriction of molecular motion by other chains.

![Figure 2.2 A snake pit.](image-url)

While the Rouse and Zimm models could predict the rheology of unentangled polymer chains, they failed to predict the rheology of entangled...
polymer chains in melts or concentrated solutions that are present in real-life scenarios such as polymer processing. For example, it is well known that the viscosity and relaxation time of a monodisperse entangled polymer melt scales as 3.4 power of the molecular weight, whereas the center of mass diffusion coefficient scales as -2.0 power of the molecular weight. These scalings are not predicted by the Rouse-Zimm models (see equation 2.3). The dynamics of entangled polymer chains is a complex multi-body problem wherein the chains are interacting with not just nearest neighbors but also with the surrounding medium through the mesh of entanglements. Such multi-body problems are difficult to solve. A conceptual breakthrough was first proposed by Prof. S. Edwards 37, who suggested that the entanglement mesh restricts the chain motion to within a confined nanoscopic region called the tube that generally follows the contours of the chain. Thus the multibody problem simplifies to a binary problem of a chain and its tube. The next breakthrough idea was formulated by Prof. de Gennes 38 who proposed that the large scale motion of the chain in a tube is limited to the curvilinear direction of the chain backbone because of the topological constraint from the tube that inhibits the lateral chain motion over distances larger than the network mesh size. The resulting curvilinear diffusion along the chain backbone is referred to as reptation 39. Figure 2.3 depicts the reptation concept schematically for long linear entangled polymer chains.

In figure 2.3, (A) depicts the polymer chain (shaded in red) surrounded by other polymer chains; (B) depicts the theoretically predicted tube formed of surrounding polymer chains that restricts motion transverse to the polymer chain contour (the black dots represents the topological constraints formed due to the surrounding chains); and (C) depicts the reptation of the entangled linear polymer chain. As the polymer chain reptates (through curvilinear diffusion shown by blue arrows) out of its original tube, a new tube is formed as the old one disappears (represented by the thin segment of the tube).
Figure 2.3 Reptation of a long and linearly entangled polymer chain (http://home.sandiego.edu/~randerson).

Figure 2.4 Steps involved in reptation of entangled polymer chains.

Figure 2.4 above details the steps involved in reptation of entangled polymer chains. In step (a), there is a formation of an unentangled loop (or kink) at one end of the chain (the tail of the snake) and this leads to the removal of the tail segment of the confining tube. Step (b) involves the propagation of the loop (through wriggling movement of the snake) along the contour of the tube. The final step (c) involves the release of the loop at the other end of the chain (the head of the snake) and formation of a new section of the surrounding tube.

The mechanism of reptation can be explained on the basis of the blob model which is shown in figure 2.5 below. Entangled polymers are
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characterized by an effective internal scale, commonly known as the length of macromolecule between adjacent entanglements $M_e$. In the blob model, the polymer chain is made up of $n$ Kuhn lengths of individual length $b$. The chain is assumed to form blobs between each entanglement, with each blob containing $n_e$ unentangled Kuhn length segments. Therefore if there are $n$ total Kuhn lengths, and $N$ blobs on a particular chain:

$$N = \frac{n}{n_e} \quad (2.7)$$

The mathematics of random walks can show that the average end-to-end distance of a section of a polymer chain, made up of $n_e$ Kuhn lengths is $a = b\sqrt{n_e}$.

The total end-to-end length of the restricted chain $L$ is then:

$$L = Na = \frac{n b \sqrt{n_e}}{n_e} = \frac{nb}{\sqrt{n_e}} \quad (2.8)$$

![Figure 2.5 Blob model of reptation.](image)

This is the average length that a polymer molecule must diffuse to escape from its particular tube, and so the characteristic time for this to
happen can be calculated using diffusive equations. A classical derivation gives the reptation time or the time required by the chain to ‘disengage’ itself from its tube, $\lambda_d$:

$$\lambda_d = \frac{L^2}{D_{\text{chain}}} = \frac{n^2 b^2 \zeta_{\text{chain}}}{n_e k_B T} = \frac{n^3 b^2 \zeta}{n_e k_B T}$$ (2.9)

where $D_{\text{chain}}$ is the curvilinear diffusion coefficient of the chain inside the tube, and corresponds to the diffusion of a Rouse chain, $\zeta_{\text{chain}}$ is the friction coefficient for the curvilinear motion and $\zeta$ is the ‘monomer’ friction coefficient i.e. of a kuhn segment.

Similarly the center of mass diffusion coefficient of the polymer is given by

$$D \sim \frac{R^2}{\lambda_d} = \frac{b^2 N}{\lambda_d} = b^2 n_e \frac{n}{n_e} \frac{n e k_B T}{n^3 b^2 \zeta} = \frac{n e k_B T}{n^2 \zeta}$$ (2.10)

Thus the coefficient of self-diffusion and conformational relaxation times of reptating macromolecules depend on the molecular weight of macromolecule as $M^{-2}$ and $M^3$, respectively $^{42,43}$. This is a reasonable approximation of the actual $^{44}$ observed relationship, $\lambda_d \sim M^{3.4}$.

Linear macromolecules reptate if the molecular weight of macromolecule $M$ is bigger than roughly ten times $M_e$. There is no reptation motion for polymers with $M < M_e$, so that the point $10M_e$ can be said to be a point of dynamic phase transition. For $M < M_e$, the sub chain exhibits Rouse dynamics having a characteristic time scale $\lambda_0 \sim \alpha^2 / D_{\text{Rouse}} = (b^2 n_e^2 \zeta / k_B T) = n_e^2 \alpha_0$; $\lambda_0 = b^2 \zeta / k_B T$ being the monomer (or bead) relaxation time. Note that this gives $\lambda_d = N^3 \lambda_e$. For $t < \lambda_e$, the relaxation modulus is given by the Rouse dynamics so that $G(t) \sim \left[ \left( \frac{k_B T}{b^3} \right) \left( \frac{t}{\lambda_0} \right)^{-\frac{1}{2}} \right]$. 


At $t = \lambda_e$, we have:

$$G(\lambda_e) = \left[ \left( \frac{k_B T}{b^3} \right) \left( \frac{\lambda_e}{\lambda_0} \right)^{\frac{1}{2}} \right]^2 = \left[ \left( \frac{k_B T}{b^3} \right) \left( \frac{1}{n_e} \right) \right] = G_0$$

(2.11)

$G_0$ is defined as the ‘plateau modulus’ and represents the modulus of the entangled network (given as the thermal energy $k_B T$ per entanglement blob volume $n_e b^3$).

Professors Sam Edwards and Masao Doi developed the tube concept into a theory of entangled polymer dynamics and rheology for monodisperse linear chains through a series of papers in the late 1970’s and in a seminal book. An important advantage of the tube theory is that the number of free parameters required to make the predictions is very limited. Along with the Kuhn step length $b$ only one more static parameter is needed namely the tube diameter, $a$ (or equivalently the plateau modulus, $G_0$) and one dynamic parameter – the monomeric friction coefficient $\zeta$ (or equivalently the Rouse time of an entanglement length). Once these parameters are known, quantitative predictions of linear rheology for a polymer with specified chemistry are possible. It is also possible to extend the theory to make predictions of response in highly non-linear deformations and flows that become of supreme importance in complex polymer processing operations.

An expression for the stress in terms of the microscopic structure variables is essential in developing any theory for the rheology of a complex fluid. Doi and Edwards derived a simple and approximate constitutive equation describing the stress-strain relationship for an arbitrary strain. They used the independent alignment approximation (IAA), which assumes that sections of the chain of constant length align independently under imposed deformation. Thus, the stress $\sigma(t)$ is given as:
\( \sigma(t) = 5G_0 \bar{S}(t) \) with \( \bar{S}(t) = \langle \bar{u} \bar{u} \rangle = -\frac{I}{3} = \int_{-\infty}^{t} dt' \frac{\partial \mu_{rep}(t-t')}{\partial t'} Q^{IAA}(E_{t:t'}) \)

(2.12)

Under the imposition of IAA, the Doi-Edwards (DE) universal orientation tensor becomes

\[ Q^{IAA}(E) = \langle \frac{(E \cdot \bar{u}_{eq})(E \cdot \bar{u}_{eq})}{|E \cdot \bar{u}_{eq}|^2} \rangle_o - \frac{I}{3} \quad (2.13) \]

In the above equations, \( E \) is the displacement gradient tensor, \( \bar{S}(t) \) is the orientation tensor averaged throughout the chain contour, \( E_{t:t'} \) is a displacement gradient tensor at the present time \( t \) measured from a past time \( t' \), \( \mu_{rep}(t) \) is the normalized, linear relaxation modulus, and \( G_0 \) is the plateau modulus. (For infinitesimal step shear strain \( \gamma \), the shear component of \( Q^{IAA} \) is given by \( \gamma/5 \) for \( t' < 0 \) and \( t > 0 \). In eq. (2.7) above, the numerical pre-factor “5” is included so as to recover the linear relaxation behavior \( \sigma(t) = \gamma G_0 \mu_{rep}(t) \) for this \( Q^{IAA} \). Additionally, \( \bar{u} \) is a bond vector while \( \bar{u}_{eq} \) is an equilibrium bond vector.

For a small step strain deformation of magnitude \( \gamma_0 \), eqns. (2.12) and (2.13) can be solved for the relaxation modulus to give

\[ G(t) = \frac{\sigma(t)}{\gamma_0} = \frac{\gamma G_0}{\pi^2} \sum_{odd} \frac{1}{p^2} \exp \left( \frac{-p^2 t}{\lambda_d} \right) \quad (2.14) \]

Note that the longest relaxation mode \( \lambda_d \) corresponding to \( p = 1 \) gives the dominant contribution to \( G(t) \). Hence the relaxation modulus can be approximated as \( G(t) \approx G_0 \exp \left( -t/\lambda_d \right) \).
Some of the shortcomings associated with the original DE tube model theory are outlined as: (i) viscosity \( \eta \sim M^3 \) instead of the experimentally observed \( \eta \sim M^{3.4} \), (ii) the distribution of stress relaxation times in the response function is much too sharp, (iii) in strong shear flow the model has all confining tubes aligning in the direction of the flow forcing unstretched chains within them to do the same, so that eventually shear stress would reduce with increasing shear rate indicating a bulk instability that is not observed experimentally. Subsequently, various researchers have attempted to relax some of the assumptions and remove discrepancies between the original DE tube model predictions and actual experimental data \(^{36}\). In the original DE tube model, the primitive chain has a fixed length. By considering \textit{contour length fluctuations} (CLF), it was shown by Doi and Edwards \(^{30}\) that the disengagement time (\( \tau_d \)) shortened with a consequent increase in the center-of-mass diffusion coefficient. Other researchers have also included CLF \(^{50-52}\) in the original tube theory for better predictions. Apart from CLF, the role of \textit{chain stretching} dynamics \(^{53-56}\) under strong flows has also been included in the tube theory which leads to better differentiation between shear and extensional flows \(^{54,55}\). The tube in the DE model is made up of the surrounding chains. For self-consistency, the reptative motions of these chains must be included in the original model for greater predictive capability. These dynamics are called as \textit{constraint release or double reptation} and have been studied in detail by different researchers \(^{57,58}\). In addition to the diffusive \textit{constraint release} described earlier, other researchers \(^{55,59,60}\) have also taken into account the \textit{convective constraint release} (CCR) dynamics that happens due to the relative motion of chains under flow due to an imposed velocity gradient. Finally, the contribution made to the stress by deformation of the tube has been included in the original tube theory through the works of Marrucci and coworkers \(^{61,62}\).

The inclusion of the above mentioned dynamics in the original tube theory have resulted in significantly improved quantitative predictions of the rheology of polymer melts under steady or dynamic as well as slow or fast flows. Based on the DE tube theory, a new class of “molecular” constitutive
equations has been developed. In particular, the ROLie-POLY (ROuse LInear Entangled POLYmers) constitutive equation for entangled linear polymer melts and the eXtended Pom Pom constitutive equation for entangled branched polymer melts are extremely important. In the next sections, these constitutive equations will be discussed in detail.

2.2 The ROLIE-POLY Constitutive Equation

The ROLIE-POLY (RP) constitutive equation has been developed by Likhtman and Graham \(^{63}\) particularly for fast flows of entangled polymer melts. This particular constitutive equation is based on the original DE tube theory and includes the processes of reptation, convective constraint release (CCR) and chain stretch. The RP constitutive equation has its origin in the full theory \(^{64}\) developed for fast flows of entangled polymer melts. The theory has been derived from a stochastic microscopic equation of motion of the polymer chain inside the tube and of the tube itself. The stochastic equation is given below as:

\[
R(s, t + \Delta t) = R(s + \Delta \xi, t) + \Delta t \left( \nabla v \cdot R + \frac{3}{2} \frac{\nu}{|R'|} R'' + g(s, t) + \frac{1}{2\pi^2\lambda_c} \frac{(R''.R'')(R'R'')}{R'^2} \right)
\]

(2.15)

In the above equation, \(R(s, t)\) is a stochastic variable that describes the vector position of the tube segment. The variable \(s\) labels monomers along the tube and runs from \(s = 0\) to \(N\), where \(N\) is the number of entanglements (\(N = n/n_e\), \(n\) is the number of monomers per chain, \(n_e\) the number of monomers per entanglement segment and \(t\) is the time. The first term on the RHS describes reptation, the second represents deformation by the flow (\(\nabla v\) is the velocity gradient tensor), the third and fourth describe constraint release (CR), and the last term models retraction along the tube contour due to the stretch relaxation. There are two terms in this stochastic equation that generate noise and assumptions are made concerning only their second
moments. \( \Delta \xi \) is the random noise due to reptation, \( \langle \Delta \xi(t)\Delta \xi(t') \rangle = 2D_c \delta(t - t') \), \( g(s, t) \) is the random noise due to CCR, \( \langle g(s, t)g(s', t') \rangle = Iva^2 \delta(s - s') \delta(t - t')/|R'| \), where \( I = \delta_{\alpha \beta} \) is isotropic tensor (\( \alpha \) and \( \beta \) are Cartesian coordinates) and \( v \) is the frequency of constraint release, which must be determined self-consistently from the motion of the chain ends. The timescales are as following: \( \lambda_c \) is the Rouse relaxation time of one entanglement segment, and \( D_c = 1/(3N\pi^2 \lambda_c) \) is the curvilinear diffusion constant. The mechanisms available for stress relaxation are depicted in the figure below.

**Figure 2.6** Mechanisms available for stress relaxation for linear entangled polymer chain: (a) reptation, (b) constraint release, and (c) retraction.

Using the stochastic equation (2.15) and after making several decoupling assumptions, the authors derived the main RP constitutive equation containing stretching terms (RP-S) as:

\[
\nabla \frac{\tau_i}{\lambda_{r,i}} = -\frac{1}{\lambda_{d,i}} \left( \tau_i - I \right) - \frac{2}{\lambda_{r,i}} \left( 1 - \frac{3}{tr\tau_i} \right) \left( \tau_i + \beta \left( \frac{tr\tau_i}{3} \right) \delta \left( \tau_i - I \right) \right)
\]

(2.16)

\[
\frac{d\tau_i}{dt} = \nabla_{\tau_i} - \nabla_{x, \tau_i} - \tau_i \nabla V^T
\]

(2.17)
In the above equations, $\nabla_{\tau_i}$ is the upper convected derivative of the stress tensor; the subscript $i$ indicates the $i^{th}$ relaxation mode, $\lambda_{d,i}$ and $\lambda_{r,i}$ are the reptation and Rouse relaxation times, respectively; $\beta$ is the CCR coefficient $^{59}$ and $\delta$ is a fitting parameter. The stretch $\Lambda$ is given by $\sqrt{(tr\tau_i/3)}$ and the net deviatoric stress is given by $\tau = \sum_i \tau_i$. In the above equation, the reptation term (with $\lambda_{d,i}$) implies relaxation towards equilibrium. The CCR term also implies a relaxation towards equilibrium, but with a rate dependent on the amount of stretch $(tr\tau_i)$, and retraction is relaxation to zero stress, also with rate dependent on $\tau_i$.

It is possible to derive the non-stretching version of the RP equation by taking the limit $\lambda_{r,i} \to 0$ which yields the RP-NS equation given below as:

$$\nabla_{\tau_i} = -\frac{1}{\lambda_{d,i}}(\tau_i - I) - \frac{2}{3} tr(\nabla \tau_i)(\tau_i - I) + \beta \left(\tau_i - I\right)$$  \hspace{1cm} (2.18)

The multi-mode version of RP-S constitutive equation is capable of fitting both steady and transient rheological data of linear polymers satisfactorily. In shear, the RP-S equation has three regimes (similar to full theory $^{64}$) as a function of the shear rate: linear regime $\dot{\gamma} < \lambda_{d,i}$, CCR regime $\lambda_{d,i} < \dot{\gamma} < \lambda_{r,i}$ and CCR+stretch regime $\dot{\gamma} > \lambda_{r,i}$. The largest quantitative disagreement is at high rates, where the RP-S equation produces faster stress growth compared to the full theory. This discrepancy can be reduced by introducing finite extensibility for the polymer chain. The concept of finite extensibility becomes particularly important for polymer melts and for extensional flows. The RP-S model is indeed capable of being used in complex flow modeling involving linear entangled polymer melts.

A number of researchers $^{32,33,65-67}$ have used the multi-mode RP constitutive equation to describe or model industrially complex flows of linear entangled polymers. Valette and coworkers $^{32}$ carried out transient 2-D
FEM simulations for entry and exit slit flow of a LLDPE melt. The rheology of the LLDPE melt was modeled with a 6-mode non-stretching version of the RP constitutive equation. Using a multi-pass rheometer (MPR), pressure-driven processing experiments were carried out under different flow conditions and stress birefringence and time-dependent pressure data was obtained. The transient flow of the polymer within the MPR was simulated using a 2-D FEM code. The authors found that exact comparison of the flow birefringence patterns was possible but difficult and a detailed comparison of pressure behavior was more useful. Compressibility of the polymer melt was included within the simulation and was found to have a mild but quantitative effect that improved the predictions. The LLDPE pressure build up and steady flow were in good accord with the experiment and both the short and long time pressure relaxation were well matched. The simulation was also able to provide insights into the pressure behavior within both barrels of the MPR.

Graham et al. 65 used a 5-mode RP-S constitutive equation to model the rheology of a series of monodisperse linear entangled polystyrenes (PS) flowing rapidly through an abrupt 4:1 contraction. Clear signatures of melt deformation and subsequent relaxation were observed through small-angle neutron scattering (SANS) measurements. The flow of the PS melt was simulated using a Lagrangian viscoelastic FEM code (FlowSolve) that contained either the full theoretical model 64 or the simplified equation 63. Experimental stress birefringence data could be successfully compared with the numerical predictions that validated the constitutive model and also the numerical technique. Finally, the SANS data comparison with the numerical predictions showed that the model was able to capture the results of this direct probe of the effect of flow at a molecular level. The model was able to quantitatively predict the variation of chain relaxation over length scales ranging from several molecules down to the tube diameter, as measured experimentally by simultaneous SANS and stress birefringence data. This systematic comparison constituted a strong confirmation of current theoretical ideas about the microscopic dynamics of entangled polymers.
under strong flow, at least for the range of deformation rates studied
\[ \frac{1}{\lambda_d} < \dot{\varepsilon} < \frac{1}{\lambda_r}. \]

A 2-mode RP-S constitutive equation was also used to study a flow instability \(^{68}\) that occurs in a contraction-expansion geometry for linear entangled monodisperse polystyrenes. The viscoelastic instability is observed at the slit outlet and propagates back upstream over time. Flow birefringence experiments using the given PS materials were performed using a multi-pass rheometer (MPR) and stress profiles during both stable and unstable flow were recorded. The numerical simulations focused on the linear stability properties of the polymer flow that was considered to be two-dimensional (2-D) and the stability to 3-D perturbations was studied. It was found that the chain stretching dynamics played a critical role in the instability mechanism and also highlighted the effectiveness of the presence of a low molecular weight tail in the MWD that enhanced processability of the polymer. There have been other significant studies \(^3,33,66,67,69\) in which the RP constitutive equation has been used for modeling complex flows of entangled linear polymer melts.

### 2.3 The Pom Pom Constitutive Equation

Long chain branched polymer melts show unique rheological properties. In particular, they exhibit significant amount of strain hardening in extensional flows, while at the same time showing considerable shear-thinning \(^{70}\). Thus, modeling the rheological behavior of entangled long chain branched polymer melts is a challenging task. Commercial long-chain branched polymers are very polydisperse and the branching structures present are topologically and geometrically irregular. The Pom-Pom constitutive equation is based on a simplified structure of long chain branched polymers, and is described here briefly.

Taking a cue from the tube theory, de Gennes recognized that a tube-like confining field would endow a dangling arm (such as a long-chain branch
on a main polymer chain or an arm in a star-shaped polymer) with an exponentially slow relaxation time. In this scenario, the immovable branch point would suppress the reptation mechanism and only exponentially-rare occurring retractions of the dangling arm would disengage it from its original tube\(^7^1\) as shown below in figure 2.7. In the case of star polymers, the free end of the branch allows it to retract quickly so that large stresses do not readily build-up. Thus, the non-linear rheology of simple star-shaped polymers follows closely that of linear polymer melts\(^7^2\).

![Figure 2.7 Tube model predictions for a 3-arm star polymer.](image)

McLeish and Larson extended the theory of star polymers for the case of branched polymer melts through the development of the Pom-Pom model\(^7^3\), which represents a simplified topology of branched molecules. The pom-pom molecule has its origins in the H-polymer structure first demonstrated by Roovers\(^7^4\) and then by McLeish\(^7^5\). As depicted in the figure below, the macromolecules are represented by a simple branched architecture consisting of two pom-poms of \(q\) arms each, linked by a backbone that is confined in a tube. The variables are the molecular weight of the backbone \(M_b\), molecular weight of the arms \(M_a\) and the number of arms on each branch point \(q\). Two additional quantities can be defined: \(s_a\) and \(s_b\), which are the measures of the entangled path lengths of the arm and backbone, respectively. If \(M_e\) is the entanglement molecular weight, \(s_a = \frac{M_a}{M_e}\) and
The key feature of this constitutive model is the presence of separated relaxation mechanisms for the macromolecular orientation and stretch.

![Diagram showing the structure of a pom-pom polymer with a backbone and 2q dangling arms, with q=3, under various degrees of stretch \( \varepsilon \).]

In the above depiction, the stretch of the backbone is denoted by the \( \varepsilon \) and the path length of the arm withdrawn into the backbone tube is denoted by \( s_c \), both of which are functions of time. In a long-chain branched polymer, there can be multiple branch points on the same chain. Because of these multiple branch points, there are molecular strands that lie between two branch points and hence have no free ends. The tube models for branched polymers propose that such molecular strands produce the strain hardening properties of long-chain branched melts (such as LDPE) in extensional flows. Upon imposition of a deformation (such as a step-strain) on a pom-pom molecule, the drag that the melt exerts on the arms (as a result of friction) causes the backbone to stretch. The backbone reptation process is inhibited due to the pinning of the backbone at the branch points. The free ends of the arms are able to move and they work their way out of their tubes.
by a diffusion process called as arm retraction (similar to star polymers). Once the arms relax, the backbone can then relax by diffusion of branch points and reptation.

The mechanism of branch-point withdrawal is important in explaining the dynamics of branched polymers. In a branched polymer, the curvilinear stretch experienced by any segment is naturally limited through a mechanism provided by the tube theory. If the tube has to be maintained in equilibrium, then it implies that a net Brownian force of \( kT/a \) has to be imposed on every free chain end so that the curvilinear path of the chain segment is maintained within its tube. Thus, for \( q = 3 \) pom-pom polymer depicted in figure 2.8, the backbone may be stretched by the three free ends until it sustains a curvilinear tension of \( 3kT/a \) which amounts to maximum allowed stretch of three. Thus, the molecular stretch is bounded. If the maximum stretch starts to exceed the maximum value, then the tension in the backbone is sufficient to retract the free chain ends into the tube (see figure 2.8(c)) originally occupied only by the backbone. An apt way to explain the effect is that: it is less costly to lose entropy in the free ends by withdrawing them all inside the same tube than to lose it by continuing to stretch the backbone leading to restrictions on its own configuration space. Backbone stretch and withdrawal play complementary roles wherein \( s_c = 0 \) whenever \( \epsilon < q \), but \( s_c \) assumes its own dynamics in flows where \( \epsilon = q \), its maximum value. Therefore the role of \( s_c \) is important since it sets the configurational changes of the chain which in turn leads to changes in the effective relaxation times of the backbone stretch and orientation.

For branched polymers, at early times after a deformation, the backbone segments do not relax at all beyond an infinitesimal motion confined to within the tube. Therefore, all relaxation is confined to arms, which relax as if they were present in a melt of star polymers except in this case, the arms are attached to a backbone leading to a spectrum of relaxation times for the arms given below as:
\[ \lambda_a(x) = \lambda_0 e^{\exp\left[ \frac{15}{4} s_a \frac{(1 - x)^2}{2} - (1 - \phi_b) \frac{(1 - x)^3}{3} \right]} \]  

where \( \lambda_0 \) is the monomer relaxation time \( \left( = \frac{b^2\zeta}{k_B T} \right) \); \( \lambda_a(x) \) is the relaxation time of a tube segment a fraction \( x \) from the branch point to the free end, and \( \phi_b = \frac{s_b}{(s_b + 2qs_a)} \) is the fraction of effectively fixed backbone.

One major difference between reptation of linear and branched polymers is that for the latter, at long times, all of the effective friction to curvilinear motion is located at the branch points rather than distributed along the chain as is the case for the former. McLeish and Larson used the Einstein argument and a requirement that the drag on a branch point increases linearly with the number of arms \( q \) to obtain an expression for the branch point friction constant as:

\[ \zeta_b = \frac{kT}{D_c} = 2kT \frac{\lambda_a(0)}{a^2} - q \]  

where \( D_c \) is the diffusion coefficient and the rest symbols have been explained earlier. The characteristic time for orientational relaxation of the backbone is given by the following expression:

\[ \lambda_b = \frac{4}{\pi^2} s_b^2 \phi_b \lambda_a(0) q \]  

For a wide range of flow rates, the bulk of the contribution to the stress arises from the backbone segments only; the arms merely contribute to an effective background Newtonian viscosity. Thus, McLeish and Larson noted that only the variables concerning the backbone alone (orientation and stretch) are important. Therefore, the orientation contribution to the stress
tensor, which becomes valid at timescales longer than those involved in arm relaxations, is given by:

\[
\tau = \frac{15}{4} G_0 \phi_b^2 \langle uu \rangle
\]  

(2.22)

Here, the angular brackets denote an average over the orientation distribution. As the backbones stretch, the thermodynamic tension that they carry grows proportionately with stretch. Furthermore, the number of tube segments occupied by the backbone, which contribute to stress, also increases proportionately with stretch. Therefore, the stress contribution from backbone is quadratic in the stretch \( \varepsilon(t) \). Strong flows lead to partially withdrawn configurations (as seen in figure 2.8(c)) wherein some arm material near a branch point also gets oriented and this material then also must contribute to the stress since it shares the same orientation distribution. The final expression of stress in terms of the dynamical variables becomes:

\[
\tau = \frac{15}{4} G_0 \phi_b \left( \phi_b \varepsilon^2(t) + \frac{2qs_c(t)}{s_b + 2qs_a} \right) S(t)
\]  

where, \( S(t) = \langle uu \rangle \) is the orientation tensor which captures the distribution of unit vectors describing the orientation of tube segments in a deforming polymer melt. For conditions wherein \( s_c > 0 \), the backbone relaxation time is given by

\[
\lambda_b(t) = \frac{4}{\pi^2} s_b^2 \phi_b \varepsilon(t) q
\]  

(2.24)

where \( x_c = \frac{s_c}{s_a} \).

A differential expression for the \( S \) can be written below as:
A deformation rate tensor \( \dot{D} \) can be defined such that \( \frac{\partial E(t, t')}{\partial t} = D \cdot E(t, t') \). Additionally, \( E(t, t').u \) is the local deformation tensor for a segment created with orientation \( u \) at time \( t' \). The segment having an orientation of \( E(t, t').u \) at time \( t \) will also increase in length by \( |E(t, t').u| \).

The backbone stretch is controlled by the local force balance of dissipative drag and elastic recovery. Under flow, the extension of the tube around the backbone tends to drag the backbone segment with it. The extension is opposed by the Gaussian elasticity of the backbone whose effective spring constant is \( kT/s_b a^2 \). If the curvilinear distance between the two branch points along the tube is \( L(t) \), then the stretch is given by \( \varepsilon = L/s_b a \) where the equilibrium separation is \( s_b a \). Using equation (2.20) for branch point friction coefficient \( z_b \) and performing the force balance that equates the frictional drag force to the elastic restoring force, an expression for evolution of backbone stretch can be written as:

\[
\frac{\partial}{\partial t} \varepsilon = \varepsilon \left( \frac{D \cdot S}{S} \right) - \frac{1}{\lambda_s} (\varepsilon - 1); \quad \text{strictly for } \varepsilon < q \tag{2.26}
\]

where the stretch relaxation time is given by

\[
\lambda_s = s_b \lambda_a(0) q \tag{2.27}
\]

For instances when \( \varepsilon = q \), the dynamical evolution of the molecular chain stretch \( \varepsilon \) stops in favor of the parameter \( s_c \) which describes the branch-point withdrawal. Whenever \( s_c \) returns to zero, the evolution of \( \varepsilon \) recommences. The evolution of \( s_c \) also involves a force balance involving frictional drag force coming from parts of the arms that are not withdrawn.
inside the confining backbone tube and an elastic restoring force (or tension in the arms $qkT/a$). Similar to the parameter $\zeta_b$, an expression for frictional drag coefficient for the blob of arms is found below as:

$$\zeta_{blob} = 2kT \frac{\lambda_a(x_c)}{a^2}q$$  \hspace{1cm} (2.28)

The evolution equation for $s_c$ is derived by balancing the drag and elastic tension and cancelling all dimensional factors of the backbone tube diameter as:

$$\frac{\partial s_c}{\partial t} = \left(q \frac{s_b}{2} + s_c \right) \left(D : \frac{\nabla}{\nabla} \right) - \frac{1}{2\lambda_a(s_c)}; \hspace{0.5cm} \text{when } \varepsilon = q$$  \hspace{1cm} (2.29)

In summary the Pom-Pom set of equations are given below once again:

Expression for stress (eq. 2.23):

$$\tau = \frac{15}{4} G_0 \phi_b \left( \phi_b \lambda^2(t) + \frac{2qs_c(t)}{s_b + 2qs_a} \right) S(t); \hspace{0.5cm} \phi_b = \frac{s_b}{s_b + 2qs_a}$$

Evolution of backbone orientation (eq. 2.25):

$$\frac{\partial}{\partial t} S = D \frac{\nabla}{\nabla} S + \frac{1}{2} S : D \frac{\nabla}{\nabla} - 2 \left( S : D \right) S - \frac{1}{\lambda_b} \left( S - \frac{1}{3} I \right)$$

Evolution of backbone stretch (eq. 2.26):

$$\frac{\partial}{\partial t} \varepsilon = \varepsilon \left( D : \frac{\nabla}{\nabla} S \right) - \frac{1}{\lambda_s} (\varepsilon - 1); \hspace{1cm} \text{strictly for } \varepsilon < q$$

Evolution of arm withdrawal measure (eq. 2.29):
Timescales involved in pom-pom dynamics:

Backbone orientation (eq. 2.24): this timescales changes

$$\frac{\partial s_c}{\partial t} = \left( q \frac{s_b}{2} + s_c \right) \left( \frac{D}{2} \right) - \frac{1}{2\lambda_a(s_c)}; \quad \text{when } \varepsilon = q$$

Arm spectrum (eq. 2.19): this timescales changes

$$\lambda_a(x) = \lambda_0 e^{x \left[ \frac{15}{4} \frac{s_a}{s_b} \frac{(1-x)^2}{2} - (1 - \phi_b) \frac{(1-x)^3}{3} \right]}$$

Backbone stretch (eq. 2.27): this timescale is fixed

$$\lambda_s = s_b \lambda_a(0) q$$

2.4 The eXtended Pom-Pom Model

The original pom-pom model has been investigated thoroughly by several researchers. The pom-pom model has three serious problems: (a) prediction of a zero second normal stress difference; (b) unphysical discontinuity in the gradient of extensional viscosity when \( \lambda = q \); and (c) a maximum in shear stress. These problems were addressed by Verbeteen and coworkers in an extended version of the original pom-pom model which they called as the eXtended Pom-Pom (XPP) equation. A modification to the stretch equation that allows for branch point displacement takes care of the problem of unphysical discontinuity in the gradient of extensional viscosity. By ignoring the arm retraction mechanism, the constraint of the stretch not being larger than the number of arms, has been removed. Also, by adding a Giesekus-like term in the orientation equation, a non-zero second normal stress difference is obtained. Lastly, the orientation equation is bounded for high strain rates.
Chapter 2  Comprehensive Literature Review

The original Pom-Pom equations given in the previous section were re-casted by Verbeteen et al. 81 single-equation multi-mode eXtended Pom-Pom (XPP) constitutive model is given below as:

\[
\nabla \tau_i + \lambda_i^{-1} \cdot \tau_i = 2G_i D
\]

\[
\lambda_i^{-1} = \frac{1}{\lambda_{b,i}} \left( \frac{\alpha_i}{G_i} \tau_i^i + F(\tau_i)I + G_i [F(\tau_i) - 1] \right)^{-1}
\]

\[
\frac{1}{\lambda_{b,i}} \frac{F(\tau_i)}{G_i} = \frac{2}{\lambda_{s,i}} e^{\nu_i (\Lambda_i - 1)} \left( 1 - \frac{1}{\Lambda_i} \right) + \frac{1}{\lambda_{b,i} \Lambda_i^2} \left( 1 - \frac{\alpha_i I_{\tau_i \tau_i}}{3G_i^2} \right); \Lambda_i < q_i; \nu_i = \frac{2}{q_i}
\]

\[
\Lambda_i = \sqrt{1 + \frac{I_{\tau_i \tau_i}}{3G_i}}
\]

In the above equations, \( \nabla \tau_i \) is the upper convected derivative of the stress tensor, the subscript \( i \) indicates the \( i \)th relaxation mode, and for this mode \( G_i \) is the relaxation modulus, \( \lambda_{b,i} \) is the orientation relaxation time of the backbone (taken as the mode relaxation time in the relaxation spectrum obtained from linear rheology), \( \lambda_{s,i} \) is the backbone stretch relaxation time, \( \Lambda_i \) is the backbone tube stretch, and \( q_i \) is the number of arms attached to the backbone of the \( i \)th mode pom-pom. Also, \( I_{\tau_i \tau_i} = tr(\tau_i \tau_i) \) and \( I_{\tau_i \tau_i} = tr(\tau_i \tau_i) \). The net deviatoric stress is given by \( \tau = \sum_i \tau_i \). The scalar parameter \( \alpha \) controls the anisotropic drag and is particularly important; the model predicts a non-zero second normal stress difference provided \( \alpha \neq 0 \). The backbone tube stretch \( \Lambda_i \) is directly coupled to the polymer contribution in the XPP constitutive equation. Finally, the parameter \( \nu_i \) (usually found by data fitting) provides a measure of the influence of the surrounding polymer chains on the backbone.
tube stretch and is incorporated into the model to remove the discontinuity from the gradient of the extensional viscosity.

The original XPP model suffers from defects such as excessive shear thinning at high Weissenberg number flows and other unphysical (or spurious) rheological effects. To help alleviate these problems Clemeur et al. developed the double convected pom-pom (DCPP) model and later improved this model by developing the MDCPP model which contained an additional exponential term. Due to the effectiveness of the pom-pom model and its variants, quite a number of researchers have used these models in investigating increasingly complex flows particularly for branched polymer melts. We cite below two recent examples where the XPP model has been successfully used to simulate melt processing flows of branched polymers.

In an earlier work we have used the Arbitrary Lagrangian Eulerian (ALE) finite element simulation technique with the XPP constitutive equation to predict the extrudate swell of long chain branched polymer melts. The ALE simulations were performed and then compared with experimental data on the extrudate swell of commercial grades of linear polyethylene (LLDPE) and branched polyethylene (LDPE). Rheological behavior of the polymers was characterized in shear and uniaxial extensional deformations, and the data was modeled using either the Phan-Thien Tanner (PTT) model or the eXtended Pom-Pom (XPP) model. Additionally, flow birefringence and pressure drop measurements were done using a 10:1 contraction–expansion (CE) slit geometry in a MultiPass Rheometer (MPR). Simulated pressure drop and contours of the principal stress difference were compared with experimental data and were found to match well. This provided an independent test for the accuracy of the ALE code and the constitutive equations for simulating a processing-like flow. The polymers were extruded from long (L/D=30) and short (L/D=10) capillaries dies at 190°C. ALE simulations were performed for the same extrusion conditions and the simulated extrudate swell showed good agreement with the experimental
data. Subsequently, a similar exercise was carried out\textsuperscript{24} for predicting steady and transient planar extrudate swell using the XPP model in an ALE type FEM simulation.

Very recently, the XPP constitutive equation has been used by Figueiredo et al.\textsuperscript{35} for solving 3-D viscoelastic incompressible free surface flows such as extrudate swell and jet buckling. They assessed the role of XPP parameters on the extrudate swell ratio and the occurrence of the oscillation effect in the jet buckling problem. They found that the extrudate swell ratio results were in qualitative agreement with Tanner’s model\textsuperscript{88,89} (of extrudate swell) wherein the increase in swell ratio occurred when the stress ratio of the viscoelastic fluid increased. Additionally, the Reynolds number ($Re$) of the fluid played an important role in determining the onset of the jet buckling phenomena with the onset caused by lowering of $Re$.

With this background in polymer rheology and dynamics, the focus in the next section is on the relevant literature on the necking phenomena in the extrusion film casting (EFC) process.

### 2.5 Literature on Necking in Extrusion Film Casting

Over the past four to five decades several researchers have attempted to study various aspects of the extrusion film casting (EFC) process in great detail due to its industrial importance. In particular, much attention has been paid to modeling the steady state EFC process as well as investigating its stability\textsuperscript{1,90–103}. Considerable amount of work has also been done on the modeling of EFC under non-isothermal conditions by Lamberti and coworkers\textsuperscript{104–111}. The flow models provide experimentally verifiable predictions of the effects of process parameters such as take-up length (TUL), draw ratio (DR) and extrusion temperature on the development of width, thickness, velocity and stress profiles during EFC of Newtonian and non-Newtonian fluids. In all modeling efforts of EFC so far the non-Newtonian fluids have been described using a variety of phenomenological constitutive
models. A large number of experimental studies have been done to interrogate the effects of process parameters such as the take-up length, draw ratio and temperature profile on the film width, thickness and velocity profile of the film during EFC. In this section we summarize the salient researches on numerical modeling and experimental investigations on the necking phenomenon in extrusion film casting. These are also summarized in Table 2.1 and Table 2.2. The schematic of the EFC process and the flow kinematics is depicted in figure 2.10.

2.5.1 Numerical Modeling of the Necking Phenomenon in EFC

A. Isothermal Modeling

The first effort on flow modeling of EFC process was made by Yeow. He assumed one-dimensional (1-D) planar extensional isothermal free surface flow of a Newtonian fluid and also investigated the stability of the flow to small perturbances. The solution for the stationary state predicted an exponential increase in the velocity and normal stress $\sigma_{xx}$ (see Fig. 2.10) as a function of the axial length $x$ (Fig. 2.10) between the die exit and chill roll. The film thickness decreases exponentially so that the force along the machine direction is constant. The assumption of one-dimensional flow kinematics does not allow for prediction of necking of the film.
The next important advance in understanding the EFC process, especially the neck-in and edge beading effects, came from Dobroth and Erwin. They suggested that the necking and edge beading phenomena have the same origin and that the higher edge thickness was responsible for the necking phenomenon; higher the edge thickness the larger would be the extent of necking. They considered three causes: extrudate swell, surface tension and edge stresses, as being responsible for edge-beading. A simple argument was proposed for the edge stress model based on the assumption that while the central part of the film undergoes planar extension, the edges experience uniaxial extension. As a result the bead ratio ($B$), defined as the ratio of edge to center thickness, varies with the draw ratio ($DR$) as $B \sim \sqrt{DR}$. They also proposed that surface tension and extrudate-swell affect the edge beading and necking phenomena only for low viscosity and elastic fluids, respectively.
Anturkar and Co. \(^92\) investigated the stability of isothermal EFC of a viscoelastic fluid. The flow kinematics was assumed to be the same as that proposed by Yeow \(^90\). The constitutive model used was a single mode upper convected Maxwell (UCM) model with a Carreau viscosity function. They developed analytical solutions for two asymptotic cases: a Newtonian fluid (relaxation time \(\rightarrow 0\)) and an elastic fluid (large relaxation time). The solution for a Newtonian fluid matched with that of Yeow \(^90\), while for an elastic fluid the solution was given by

\[
De(DR - 1) = 1
\]  

(2.34)

when the tensile force at the die exit was assumed to be equal to the tensile force in the film. Here, \(De = \lambda v_0 / L\) is the Deborah number defined as the ratio of the material relaxation time \(\lambda\) and the characteristic process time \(L/v_0\), \(L\) being the take-up length and \(v_0\) the velocity at the die exit. Also in the elastic limit the velocity in the stretch direction was predicted to increase linearly with axial distance. Necking profile could not be predicted because of the assumption of one dimensional flow kinematics. Iyengar and Co. \(^97,114\) carried forward the work of Anturkar and Co. \(^92\) using a modified Giesekus constitutive model and calculated the velocity and stress profiles in steady isothermal EFC process as well as analyzed the stability of the process.

The first comprehensive attempt to predict necking phenomena during EFC was made by Sergent \(^91\) for isothermal conditions. This was followed by the works of Cotto et al. \(^93\) (Newtonian fluid), Duffo et al. \(^95\) (Newtonian fluid) and Barq et al. \(^96,98\) for non-isothermal flows (UCM fluid). The model assumed two-dimensional (2-D) flow kinematics. Gravity and inertia were included in the analysis. The film thickness was assumed to be constant across the film width. Thus, edge beading was not considered. Numerical solutions to the set of governing equations were obtained for film width, thickness, film curvature, temperature distribution, velocity and stresses.
d’Halewyn et al. 94 and Silagy et al. 1 developed a membrane model for an isothermal EFC process of a Newtonian fluid with two dimensional flow kinematics neglecting inertia and gravity. Finite element simulations were used to solve the governing equations and predictions for both neck-in and edge beading were obtained. Numerical solutions for a viscoelastic fluid were obtained by Barq et al 98, Sakaki et al. 115 and Debbaut et al. 116. The elegant approach of Silagy et al. 1 has been widely used, and is also the basis of modeling done in this work. It is therefore described in more detail below and in Chapter 5.

Silagy and coworkers 1 developed a membrane model for isothermal EFC using flow kinematics first suggested by Narayanaswamy 117 for the float glass process. In this model, while all three velocity components are considered (see Fig. 2.9), the kinematic approximations result in all components becoming functions of only the axial length $x$. Thus the flow is assumed to be primarily extensional in nature. Necking phenomenon was predicted assuming constant thickness across the film width. Analytical solutions for thickness, film width, velocity and stresses were obtained for Newtonian fluid, while numerical solutions were obtained for a viscoelastic fluid using the UCM model. The model predicted a linearly varying film width profile for a Newtonian fluid. Deviations from the linear profile were predicted for viscoelastic fluids, in agreement with experiments. The final film width increased with draw ratio for high Deborah numbers. The velocity increased exponentially along the stretch direction for a Newtonian fluid and nearly linearly for a viscoelastic fluid. Analytical solutions under simplified assumptions for Newtonian fluid explain the linear width profiles and exponential velocity profiles as given in equation (2.35).

$$L \sim 1 - \frac{A}{\sqrt{2}} x; u \sim \exp \left( \frac{x - 1}{4E} \right)$$  \hspace{1cm} (2.35)

Similarly, analytical solutions for highly elastic fluids are as below:
\( L \sim \frac{1}{Ax + 1}; u \sim Ax + 1 \)  \hspace{1cm} (2.36)

Wherein, \( L \) and \( u \) are respectively the necking length and centerline velocity, \( x \), \( E \), and \( A \) are respectively the axial distance (from die exit to chill roll), dimensionless force and aspect ratio (AR).

Ito et al. \(^{101,102}\) developed a model for neck-in based on the ideas proposed by Dobroth and Erwin \(^2\). They assumed isothermal conditions and neglected gravity, inertia, surface tension, and extrudate swell. They also assumed one dimensional flow kinematics (the axial velocity component) and normal stresses \( \sigma_{xx} \) and \( \sigma_{yy} \) (see Fig. 2.9) as being functions of only the axial distance \( x \). By using a force balance along a uniaxially deforming edge they related the necking profile to the planar stresses developed at the center of the film along the stretch direction. It was further assumed that the stretching force was balanced primarily by the planar stresses in the central region; contribution from the edge tension was neglected. Analytical solutions for a Newtonian fluid were derived, while numerical solutions were obtained for a viscoelastic fluid modeled by a single mode UCM equation. The model predicted a decrease in necking with increasing draw ratio.

Bourrigaud et al. \(^{118}\) also used the flow kinematics of Silagy et al. \(^1\) together with the UCM constitutive model and investigated the possibility of non-existence of solution to the governing equations. They found that the locus of points given by Eq. (2.34) divides the \( De-DR \) plot into attainable and unattainable regions; the latter happens because of divergence of the stretching force. Shiromoto et al. \(^{103}\) proposed a variant of the Ito et al. model \(^{102}\) that relates the necking profile to the ratio of stresses along the center (planar) and edges (uniaxial).

**B. Non-Isothermal Modeling**

The first comprehensive work towards developing a non-isothermal framework for modeling the EFC process was undertaken by Cotto and
coworkers. They assumed a Newtonian fluid behavior for a polypropylene (PP) resin and proposed a 1-D flow kinematics. A two-dimensional (2-D) energy equation coupled with an Arrhenius-like viscosity-temperature dependence and accounting for polymer crystallization constituted the thermo-mechanical model. They also performed a detailed study on the heat transfer coefficients (HTC’s) and the characteristic dimensions to predict these accurately. Their thermo-mechanical model correctly predicted the decrease in film width (or necking) and temperature. Their model also predicted the evolution of axial velocity with stretching distance. For a short stretching distance or TUL, the model also correctly predicted that the isothermal assumption would hold true. In a related paper Duffo and coworkers investigated the temperature gradients in the thickness direction of the extruded PP film and the crystallinity of the polymer on the chill roll by employing constant heat transfer coefficients. They concluded that their model could describe the effects of stretching in air and cooling on roll on the final microstructure of the film. Another paper from Prof. Haudin’s research group built on their previous thermomechanical model. The model assumed 2-D flow kinematics. Gravity and inertia were included in the analysis. The film thickness was assumed constant across width. Thus, edge beading was not considered. Numerical solutions to the set of governing equations were obtained for film width, thickness, film curvature, temperature distribution, velocity and stresses. The predictions were in reasonable agreement with experimental observations except for the film width showed a linear variation in contrast to experimental observations.

Beaulne and Mitsoulis performed both isothermal and non-isothermal 1-D numerical simulations of the EFC process assuming uniaxial extensional flow. Viscoelasticity was incorporated using a K-BKZ constitutive equation containing a spectrum of relaxation times while the non-isothermal conditions were described using the Morland-Lee hypothesis that incorporates an appropriate shift factor and pseudo-time into the constitutive equation. Non-isothermal simulations for PP melt closely matched previous experimental data from Kase especially for the
thickness and temperature of the film. The necking predictions from non-isothermal simulations for a PET melt resembled most the results for a Newtonian model whereas the predictions for a low density polyethylene (LDPE) melt resembled a combination of the results from the Newtonian and the upper-convected Maxwell (UCM) models.

A more simplified 1-D non-isothermal model was proposed by Acierno and coworkers \(^{112}\) by neglecting the polymer crystallization kinetics. They studied EFC of two PET materials of different intrinsic viscosities (IV’s). DR was varied between 10 and 20, while the take-up length was varied from 50 to 150 mm. The rheological behavior of these polymers was considered to be Newtonian for the processing strain rates. They also used an IR thermography system (sensitivity of up to 0.1°C) to measure the machine and transverse directions (MD & TD, respectively) surface temperatures. 1-D non-isothermal flow modeling based on the kinematics developed by Barq and coworkers \(^{96}\) was used to predict the temperature, width, and thickness of the film as a function of the distance from die. The authors concluded that temperature profiles in both the MD and TD are important in determining final film width. The model always underestimated the final film width, the cause of which was attributed to the kinematic limitations of the model.

The Silagy et al. model \(^{1}\) was further used by Lamberti and coworkers \(^{104,107}\) to include non-isothermal conditions and crystallization. In their first paper \(^{104}\), the authors studied EFC of a commercial isotactic polypropylene (i-PP) for draw ratios ranging from 28 to 70. The i-PP melt was modeled as a viscous (non-Newtonian) fluid while the crystallization kinetics was modeled using the Nakamura form of the Avrami equation. The authors noted that the final film width increased or decreased upon increasing DR when the DR increase was effected respectively by a decrease in the velocity at the die exit or an increase in the take-up velocity. The film necking also decreased when the flow rate was decreased under a constant DR. In subsequent papers mentioned above, the authors investigated flow-induced crystallization during EFC of PP resins using several experimental methods such as IR
pyrometer (temperature distribution), online FT-IR (crystallinity and orientation measurement) and image analysis (width and velocity). They also studied the effect of cooled air quenching on film (one or both sides). Additionally, they also performed a detailed analysis to predict the heat transfer coefficient accurately and its effect on cooling of the polymer film and on crystallization kinetics.

Non-isothermal numerical simulations of the EFC process were also carried out by Sollogoub and coworkers\textsuperscript{121} by considering an Arrhenius-like temperature dependence of a viscoelastic UCM-like fluid. They developed a 2-D model using finite element method applying the membrane hypothesis and investigated the effect of non-isothermal conditions and other process parameters like DR and aspect ratio (AR) on the viscoelasticity (as quantified by the Deborah number) and the final film geometry. They showed that both viscoelasticity and heat transfer coefficient have a similar effect on the film profile.

Recently Shiromoto and coworkers\textsuperscript{103} performed EFC experiments on three LDPE’s of which one was a made by vessel (or autoclave) technique and the remaining two were made by the tubular technique. They also performed non-isothermal viscoelastic simulations using a multi-mode Phan-Thien-Tanner (PTT) constitutive equation wherein the viscosity-temperature dependence was as per the Arrhenius law. Additionally, a theoretical necking model based on force balance and deformation type at the center and at the edge of the film was proposed. The LDPE made by vessel technique had wider molecular weight distribution (MWD). All materials were fully characterized by shear and extensional rheology. The authors varied the take-up length, the take-up velocity and the extrusion rate but kept the DR constant at 40 for all their experiments. They observed that the film necking of the vessel-made LDPE was lower as compared to the tubular-made LDPE. Necking was found to increase with take-up length. A reduction of take-up velocity (leading to reduction of strain rate) led to increase in film necking. The numerical predictions were in good agreement with experimental data for a wide range
of take-up velocities and air-gap lengths. The theoretical necking model suggested that the necking length correlated with the ratio of planar to uniaxial elongational viscosity and that the model could predict the film shape for LDPE resin.

Though considerable amount of work has been done in modeling the effect of temperature in the EFC process little or no efforts have been made in modeling the role of macromolecular chain architecture on film necking.

Table 2.1 Review of theoretical models for steady state stable EFC process.

<table>
<thead>
<tr>
<th>Reference no.</th>
<th>Flow kinematics</th>
<th>Constitutive model</th>
<th>Other phenomenon</th>
<th>Salient predictions for necking</th>
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<tbody>
<tr>
<td>Yeow 90</td>
<td>$v_z = v_x(x)$, $v_y = z g(x)$</td>
<td>Newtonian</td>
<td>Isothermal</td>
<td>Necking cannot be predicted</td>
</tr>
<tr>
<td>Dobroth &amp; Erwin 2</td>
<td>Planar extensional flow in central region, uniaxial extensional flow at edges</td>
<td>Isothermal</td>
<td></td>
<td>Necking is related indirectly to edge beading, $B \sim \sqrt{D R}$</td>
</tr>
<tr>
<td>Co and coworkers 92,97,114</td>
<td>$v_x = v_x(x)$, $v_y = 0$, averaging done over $z$</td>
<td>UCM, Giesekus</td>
<td>Isothermal</td>
<td>Necking cannot be predicted</td>
</tr>
<tr>
<td>Sergent 91, Barq 96</td>
<td>$v_x = v_x(x)$, $v_y = 0$, $v_z = v_z(x,z)$</td>
<td>Newtonian</td>
<td>Non-isothermal</td>
<td>Necking cannot be predicted</td>
</tr>
<tr>
<td>Cotto et al. 93</td>
<td>$v_x = v_x(x)$, $v_y = v_y(x,y)$, $v_z = v_z(x,z)$</td>
<td>Newtonian</td>
<td>Non-isothermal</td>
<td>Linear Necking profile with $x$</td>
</tr>
<tr>
<td>Barq et al. 98</td>
<td>$v_x = v_x(x)$, $v_y = 0$, $v_z = v_z(x,z)$</td>
<td>UCM</td>
<td>Isothermal</td>
<td>Necking cannot be predicted</td>
</tr>
<tr>
<td>Silagy et al. 1</td>
<td>$v_x = v_x(x)$, $v_y = y f(x)$, $v_z = z g(x)$</td>
<td>Newtonian and UCM</td>
<td>Isothermal</td>
<td>Linear Necking for Newtonian; non-linear for viscoelastic; Necking length decreases with increasing $De$</td>
</tr>
<tr>
<td>d’Halewyn et al. 94, Silagy et al. 100</td>
<td>1D: $v_x = v_x(x)$, $v_z = z g(x)$ 2D: $v_x = v_x(x,y)$, $v_y = v_y(x,y)$, $v_z = z f(x,y)$</td>
<td>Newtonian</td>
<td>Isothermal</td>
<td>Linear Necking for 1D model; non-linear neck-in for 2D model</td>
</tr>
</tbody>
</table>
2.5.2 Experimental Investigations of Necking Phenomenon in EFC

One of the early experimental researches on EFC was performed by Dobroth & Erwin \(^2\) to explain the causes of edge-beading phenomena in extruded cast films. Polyethylene films were extrusion casted and characterized for their thickness at the center portion and at the edges. It was observed that the experimental values of the bead ratio (B) varied with the draw ratio as \(B \sim \sqrt{DR}\), which was in agreement with their model. By experimenting with polymers of different viscosities they found that surface tension was not an important parameter controlling the edge beading.

Acierno et al. \(^{112}\) studied extrusion film casting of two PET materials of different IV’s. DR was varied between 10 and 20, while the take-up length was varied from 50 to 150 mm. The rheological behavior of these polymers was considered to be Newtonian for the processing strain rates. They also used an IR thermography system (sensitivity of up to 0.1°C) to measure the machine and transverse directions (MD & TD, respectively) surface temperatures. The authors concluded that temperature profiles in both the MD and TD are important in determining final film width for take-up lengths greater than 1/10 times the die width.
Satoh et al. \textsuperscript{113} conducted experiments of extrusion film casting on a viscoelastic polymer (namely LDPE) with an objective to validate numerical viscoelastic simulations of the process. EFC experiments were done on lab-scale and commercial-scale extruders over a wide range of draw ratios for a LDPE melt which was modeled as a Larsson fluid with multiple relaxation times. Final film width was found to either increase or remain nearly independent of draw ratio. Finite element simulations were done using a membrane model with two-dimensional flow to predict the film width and thickness profiles. While there was good agreement between the experimental and simulated values for film width and thickness at lab-scale, there was poor agreement between the same at commercial level. The authors attributed the poor agreement to the change of the level of polymer viscoelasticity mainly due to polymer cross-linking and amount of long chain branching (LCB) increasing during the film lamination process.

Canning et al. \textsuperscript{122} studied the cast-film extrusion of a commercial LDPE. They measured the surface velocity and streamlines using particle-tracking velocimetry (PTV). Film width was determined using video imaging, molten film tension measurements were made using a non-contacting air-nozzle system (developed in-house) and edge-beading was studied using microscopy analysis of the film cross sections. The measured molten film tensions increased as a function of the draw ratio. Final film width decreased with increasing draw ratio. The experimentally determined non-dimensionalized velocity profile became more concave as the draw ratio (DR) increased.

A series of papers from the research group of Lamberti \textsuperscript{104–111} have studied the cast film extrusion process in great detail. In their first paper \textsuperscript{104}, the authors studied the cast-film extrusion of a commercial isotactic polypropylene (PP) for draw ratios ranging from 28 to 70. The authors noted that the final film width increased or decreased upon increasing DR when the DR increase was effected respectively by a decrease in the velocity at the die exit or an increase in the take-up velocity. The film neck-in also decreased.
when the flow rate was decreased under a constant DR. In subsequent papers, the authors investigated flow-induced crystallization during EFC of PP resins using several experimental methods such as IR pyrometer (temperature distribution), online FT-IR (crystallinity and orientation measurement) and image analysis (width and velocity). They also studied the effect of cooled air quenching on film (one or both sides).

Ito et al.\textsuperscript{101} performed isothermal EFC experiments on a metallocene-catalyzed LLDPE (m-LLDPE) for draw ratios in the range of 4 to 14. In this study, the authors tracked the motion of 5 mm aluminum particles placed on the free surface of the film during casting. From the measured 2-D velocities of the particles they also calculated the width and thickness profiles. Their data showed clear evidence of edge-beading; the film thickness at the edges was high and scaled approximately as the inverse square root of the draw ratio ($t_{\text{film-edges}} \sim DR^{-0.5}$). The central region of the film width showed constant thickness, which scaled inversely with draw ratio ($t_{\text{film-center}} \sim DR^{-1}$). These experimental findings were in qualitative agreement with the Dobroth and Erwin model\textsuperscript{2}. From the PTV measurements, the authors observed that the velocity at the film's edge was initially slower than that at the film center, but eventually it caught up later. In their second paper\textsuperscript{102}, isothermal EFC experiments were performed on polyethylene resins (LDPE, HDPE and LLDPE) of different molecular architectures (linear and branched) to validate the experimentally observed film neck-in behavior with theory. The draw ratios utilized in this case ranged from about 2 to 24. Film necking lengths were obtained at different take-up lengths and draw ratios (DR's) and were compared with analytic model predictions. Experimentally, it was observed that for all the PE's, the film widths decreased with increasing take-up lengths (at a constant DR). Between the PE's studied, LDPE displayed the least film necking compared to the HDPE and LLDPE melts at comparable DR and take-up length.

Bourrigaud et al.\textsuperscript{118} performed EFC experiments on six LDPEs at different temperatures (260 to 320\textdegree C), DR's (~ 80 to 200), take-up lengths
and Deborah numbers. The authors found that when the process parameters at which film rupture occurred for all six polymers were plotted on a DR-De diagram a mastercurve was obtained, which delineated regions of stable and unstable conditions. The mastercurve had the same shape as that suggested by Eq. (2.34). The authors indicated that the mastercurve could have several practical implications in determining the process stability for a given melt.

Aniunoh and Harrison 123,124 investigated the EFC of commercial PPs at various draw ratios, take-up lengths and extrusion speeds. Along with a detailed rheological study, they utilized Laser Doppler Velocimetry (LDV) and IR thermal imaging to obtain axial and transverse velocity profiles and temperature distribution in the film. Film necking was quantified with digital image capturing and film thickness was measured offline. Film necking increased with increase in the die temperature and draw ratio. From thermal measurements, the authors established that the film cooled more rapidly in machine direction as the DR increased. Additionally, the central portion of the film cooled down more rapidly than film edges on account of edge beading. From LDV studies, the authors concluded that the centerline strain rate increased as a function of the DR. Strain rates at low DR, initially increased with increasing distance from die, went through a maximum and then started to decrease due to increase in melt viscosity upon cooling. At higher DR’s, where the increase in tension in film overcame the thermal effects, the strain rates were found to increase with increasing distance from die. The authors also measured the transverse direction velocity profiles.

In recent years there has been a growing interest in understanding the role of macromolecular architecture on necking and edge-beading in EFC. Seay and Baird 125 investigated EFC of three m-LLDPE’s along with a conventional Zeigler-Natta catalyzed LLDPE and a tubular LDPE. While the conventional LLDPE did not contain any long chain branching (LCB), the m-LLDPEs contained sparse amounts of LCB and the tubular LDPE contained significant amounts of LCB. The polymers were characterized using GPC-LALLS, 13C-NMR, shear and extensional rheology. The experimental data sets
for the various polyethylenes were fit to the multi-mode Pom-Pom constitutive model and the branching parameter $q_i$ for each mode was used as the indicator for characterizing the rheologically relevant branching distribution in the polymers. Experimental data for the m-LLDPEs showed that film necking decreased with increasing LCB at low draw ratios. However at high draw ratios there was no difference between the sparse LCB containing LLDPE’s and the linear LLDPE. The high LCB containing LDPE though displayed a much reduced amount of necking at all draw ratios as compared to all LLDPE’s. The effect of LCB on reducing necking was more pronounced than the effect of broadening the MWD. The authors also noted that a distribution of branches along shorter relaxation time modes is important in reducing necking at higher draw ratios.

McGrady et al. $^{126}$ investigated EFC of a series of sparsely branched metallocene catalyzed high density polyethylenes (m-HDPE’s). They observed that m-HDPE’s containing lower LCB had final film widths that were identical to that of linear HDPE’s. In contrast, m-HDPE’s containing higher LCB retained larger final film widths as compared to the linear and low LCB containing m-HDPE’s. Fitting the uniaxial extensional data for these polymers to multi-mode Pom-Pom model and obtaining the values of the branching parameter $q_i$ therefrom suggested that if branching was distributed across a larger range of backbone lengths, it served to increase resistance to film necking.

Shiromoto et al. $^{103}$ performed EFC experiments on three LDPE’s of which one was an autoclave grade and the remaining two were tubular grades. The autoclave LDPE had the widest molecular weight distribution (MWD). All materials were characterized by shear and extensional rheology. The authors varied the take-up length and also the take-up velocity and the extrusion rate such that the DR was kept constant for all their experiments. Necking was found to increase with take-up length. For constant DR of 40, a reduction of take-up velocity accompanied by a corresponding reduction in extrusion output (by lowering of screw rpm) led to increase in film necking.
The authors observed that the film necking of the autoclave LDPE was lower than the tubular LDPE.

It is evident that while some understanding about the effects of macromolecular structural attributes on the necking behavior in EFC is emerging from recent experimental research, the theoretical understanding of these issues is far from complete. As described in the previous section on Polymer Dynamics, it is now well established that constitutive equations based on the tube model framework can capture the essential effects of macromolecular architecture on melt rheology. Use of such constitutive equations in the modeling of EFC can therefore be expected to provide better understanding about how molecular structural details affect the extent of necking.

The work presented in this dissertation is the first step in linking macromolecular architecture to steady state EFC. Specifically, the effects of long chain branching (LCB) and molecular weight distribution (or polydispersity, MWD or PDI) on the extent of necking in the EFC process are studied in detail. In particular, the necking of four well characterized commercial polyethylene (PE) resins is studied. The PE resins include: two having linear chain architecture but relatively narrow (LLDPE) and broad (HDPE) molecular weight distributions and the other two having sparse (m-LLDPE) and considerable (LDPE) numbers of long-chain branches on the chains. The rheology of the two linear resins is modeled using the multimode Rolie-Poly-Stretch constitutive equation, while that of the branched resins is modeled using the multimode eXtended Pom Pom (XPP) equation. The EFC process is analyzed using the one-dimensional flow model of Silagy et al. in conjunction with the two chosen constitutive equations. It is demonstrated that predictions of the film necking behavior are in qualitative agreement with the experimental data and provide useful insights into the roles of long chain branching and molecular weight distribution on necking.
Table 2.2 Review of experimental research in EFC process.

<table>
<thead>
<tr>
<th>Reference no.</th>
<th>Materials</th>
<th>Die Geom. (mm²) and Temp (°C)</th>
<th>DR Range</th>
<th>Data Obtld.</th>
<th>Salient Observ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dobroth &amp; Erwin²</td>
<td>LDPE</td>
<td>153 x adjustable thick (not given) mm² 177°C</td>
<td>1-20</td>
<td>Thickness profile</td>
<td>Effect of edge-stress, surface tension and extrudate swell on edge beading phenomena</td>
</tr>
<tr>
<td>Acierno et al.¹¹²</td>
<td>PET</td>
<td>200 x 0.3 mm² 290°C</td>
<td>10 &amp; 20</td>
<td>Temp. profile</td>
<td>Temp. profiles in machine dirn. (MD) and transverse dirn. (TD) important in determining film width</td>
</tr>
<tr>
<td>Satoh et al.¹¹³</td>
<td>LDPE</td>
<td>250 x 0.95 mm² (lab-EFC) 190°C 600 x 0.8 mm² (production line-lamination) 310°C</td>
<td>16-65 (EFC) 72 (for lamination)</td>
<td>Velocity, film thickness and necking profiles</td>
<td>Very high processing temp. led to increase in LCB for LDPE; leading to lesser necking compared to that for LDPE processed at lower temp.</td>
</tr>
<tr>
<td>Canning et al.¹²²</td>
<td>LDPE</td>
<td>254 x adjustable thick (not given) mm² 260°C</td>
<td>2.68, 4.84 and 7.27</td>
<td>Film necking, film thickness, velocity and molten film tension</td>
<td>Velocity profile as a funcn. of take-up length became more concave as DR was increased.</td>
</tr>
<tr>
<td>Lamberti and coworkers¹⁰⁴-¹¹¹</td>
<td>iPP</td>
<td>200 x 0.5 mm² 200-300°C</td>
<td>28-70</td>
<td>DSC, FTIR, temp. and velocity profile</td>
<td>Film necking was observed to decrease with increase in DR when effected by decrease in die exit velocity</td>
</tr>
<tr>
<td>Ito et al.¹⁰¹</td>
<td>m*-LLDPE</td>
<td>650 x 0.8 mm²</td>
<td>4-14</td>
<td>Velocity and</td>
<td>First experimental</td>
</tr>
<tr>
<td>Study</td>
<td>Material(s)</td>
<td>Temperature</td>
<td>Thickness Profile</td>
<td>Confirmation of Dobroth-Erwin theory where $t_{film\text{-}center} \sim DR^{-1}$ and $t_{film\text{-}edges} \sim DR^{-0.5}$</td>
<td>Film Necking behavior was coupled to the TD velocity component</td>
</tr>
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<td>---------------------------------------------------------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Ito et al. 102</td>
<td>LDPE, LLDPE, HDPE</td>
<td>190°C</td>
<td>2-24</td>
<td>Film necking increased with increasing take-up length at constant DR; branched LDPE displayed lower film necking as compared to linear PE materials</td>
<td></td>
</tr>
<tr>
<td>Bourrigaud et al.</td>
<td>LDPE</td>
<td>Die details not given 260-320°C</td>
<td>80-200</td>
<td>DR-De map constructed to predict performance in coating or extrusion film casting process</td>
<td></td>
</tr>
<tr>
<td>Aniunoh and Harrison 123,124</td>
<td>PP, m*-PP</td>
<td>101 x 0.01 mm² 180, 200, 220°C</td>
<td>6-15</td>
<td>Thermal effects played a dominant role at low DR in determining film width and edge-beading; Film necking behavior was coupled to the TD velocity component</td>
<td></td>
</tr>
</tbody>
</table>
| Seay and Baird 125, McGrady et al. 126 | m*-LLDPE, ZN*-LLDPE, LDPE, HDPE | 100 x 0.57 mm² 150°C and 190°C | 5, 10, 15, 20 | LCB or sparse LCB (affecting viscoelasticity of PE) affected film necking as per deductions made using Pom-Pomasurer
Shiromoto et al. 103  |  Autoclave-LDPE, Tubular-LDPE  |  600 x 0.8 mm²  |  320°C  |  40 (constant)  |  Film necking  |  Broadening of MWD in autoclave-LDPE led to lower film necking as compared to that for tubular-LDPE

*: metallocene catalyzed; ^: Zeigler-Natta catalyzed

This concludes the chapter on comprehensive literature review relevant to the present research on EFC. In the next chapter the polymer materials used in this research and the techniques to characterize these materials are discussed.