THE EFFECT OF SURFACE PROPERTIES OF BORON NITRIDE ON POLYMER PROCESSABILITY

by

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Abstract

In commercial polymer processing operation such as extrusion, film blowing and blow molding, product quality and production rate are limited by the appearance of flow instabilities. This flow instability is manifested as distortions on the extrudate surface (melt fracture), usually observed at high production rates. Fluoropolymers have long been used as processing aids for surface melt fracture treatment of polyolefin extrudates. Recent developments have shown that a small amount of Boron Nitride (BN) powder successfully eliminates surface melt fracture and also delays the onset of gross melt fracture. It is also observed that a combination of BN and Fluoropolymer enhances the performance of the extrusion even further. The main objective of the present work is to estimate surface properties of BN mainly surface energy and adsorption capacity to understand its influence in the performance of different grades of BN as processing aids. Based on this study, it can be concluded that surface energy plays a very important role in deciding the possible interaction between the processing aid, polymer melt and the extruding surface. It is observed that lubricious nature of BN along with an optimum balance of surface energy and polarity makes BN (grades: AS 612 and CTF5) successful in both sharkskin as well as gross melt fracture regions.
Table of Contents

ABSTRACT......................................................................................................................... ii
TABLE OF CONTENTS .................................................................................................... iii
LIST OF FIGURES ........................................................................................................... v
LIST OF TABLES ............................................................................................................... vii

1 INTRODUCTION ........................................................................................................... 1

2 LITERATURE REVIEW ................................................................................................. 6
  2.1 Rheological Measurements ...................................................................................... 6
    2.1.1 Capillary Rheometer ......................................................................................... 6
    2.1.2 Rheometer Fitted with Capillary Die ................................................................. 8
    2.1.3 Rheometer Fitted with Crosshead Die ............................................................... 12
    2.1.4 Parallel Plate Rheometer .................................................................................. 13
    2.1.5 Sliding Plate Rheometer ................................................................................... 18
  2.2 Melt Fracture ........................................................................................................... 20
    2.2.1 Mechanisms To Explain Melt Fracture ............................................................. 23
    2.2.2 Die exit effects: Sharkskin / Surface Melt Fracture ......................................... 23
    2.2.3 Die entry effects: Gross Melt Fracture ............................................................. 24
  2.3 Polymer Processing Aids ......................................................................................... 26
  2.4 Surface Energy ........................................................................................................ 29
    2.4.1 Contact Angle Measurement ............................................................................ 31
  2.5 Adsorption .............................................................................................................. 33

3 OBJECTIVES ............................................................................................................... 37

4 MATERIALS ................................................................................................................ 38
  4.1 Polymer .................................................................................................................. 38
  4.2 Boron Nitride ......................................................................................................... 38
  4.3 Blend Preparation .................................................................................................. 40
5 EXTRUSION STUDIES USING BORON NITRIDE ................................. 41
  5.1 Introduction ........................................................................... 41
  5.2 Experimental Details ................................................................. 41
    5.2.1 Capillary Rheometry ......................................................... 41
    5.2.2 Rotational Concentric Rheometry ...................................... 42
  5.3 Results and Discussion .............................................................. 42
    5.3.1 Capillary Rheometry ......................................................... 42
    5.3.2 Rotational Concentric Rheometry ...................................... 46
  5.4 Conclusion .............................................................................. 47

6 SURFACE ENERGY OF BORON NITRIDE ........................................ 48
  6.1 Introduction ........................................................................... 48
  6.2 Experimental Details and Results ............................................ 49
    6.2.1 The Modified Washburn’s Capillary Rise Technique .......... 49
    6.2.2 Results and Discussion – Washburn’s Capillary Rise Method 53
    6.2.3 Measurement of Contact Angle using Sessile Drop Profile ... 54
    6.2.4 Results and Discussion – Direct Measurement of Contact Angle 56
  6.3 Comparison of BN with Fluoropolymers .................................. 61
  6.4 Combination of BN and Fluoropolymer .................................... 66
  6.5 Conclusion .............................................................................. 68

7 ADSORPTION CAPACITY OF BORON NITRIDE ............................ 71
  7.1 Introduction ........................................................................... 71
  7.2 Experimental Details ................................................................. 71
  7.3 Results and Discussion .............................................................. 73
  7.4 Adsorption of Fluoropolymer on BN ....................................... 76
  7.5 Conclusion .............................................................................. 77

8 SUMMARY ................................................................................. 78

REFERENCES .............................................................................. 80
NOMENCLATURE ......................................................................... 83
THE EFFECT OF SURFACE PROPERTIES OF BORON NITRIDE ON POLYMER PROCESSABILITY

List of Figures

Figure 1.1: Typical extrudates of LLDPE at 163 °C .................................................. 3
Figure 1.2: Effect of BN on extrudate appearance at $\dot{\gamma} = 617 \text{ s}^{-1}$, 163 °C .......... 4
Figure 2.1: Schematic of a capillary rheometer ......................................................... 7
Figure 2.2: Wall pressure distribution for capillary flow ............................................ 10
Figure 2.3: Bagley plot for determining the end correction ...................................... 11
Figure 2.4: Crosshead die for wire coating ................................................................. 12
Figure 2.5: Parallel plate rheometer ........................................................................ 14
Figure 2.6: Oscillatory Linear Viscoelastic Characterization ...................................... 15
Figure 2.7: Indicative plot of $G'$ ($\omega$) for linear polymer ...................................... 17
Figure 2.8: Simple Shear Flow .................................................................................. 18
Figure 2.9: Velocity profile in simple shear with and without slip ............................. 19
Figure 2.10: A typical apparent flow curve of a linear polymer ................................. 21
Figure 2.11: Schematic view of surface melt fracture occurring at the die exit ....... 24
Figure 2.12: Picture of PP flow at various shear rate – unstable flow at die entrance ... 25
Figure 2.13: Droplet of a liquid on solid substrate at equilibrium .............................. 30
Figure 2.14: Schematic of original capillary rise method for CA measurement ......... 32
Figure 4.1: Structure of ethylene – butene LLDPE copolymer ................................. 38
Figure 4.2: The structure of boron nitride ................................................................. 39
Figure 5.1: Flow curve of PE - Exact® 3128 using capillary rheometer .................... 43
Figure 5.2: Flow curve of virgin and filled PE - Exact® 3128 ..................................... 44
Figure 5.3: Extrudate samples obtained at 617 s$^{-1}$ and 163 °C ............................... 45
Figure 5.2: Linear viscoelastic data for virgin and filled PE - Exact® 3128 ............... 46
Figure 6.1: Powder packing press ............................................................................ 50
Figure 6.2: Arrangement for liquid penetration rate measurement ............................ 51
Figure 6.3: Close-up image of water droplet on BN surface .................................... 55
Figure 6.4: Arrangement for obtaining sessile drop images .................................... 55
Figure 6.5: Surface energy of BN samples ............................................................... 59
Figure 6.6: Critical shear rate of BN samples ........................................................... 59
THE EFFECT OF SURFACE PROPERTIES OF BORON NITRIDE ON POLYMER PROCESSABILITY

Figure 6.7: CSR vs. 1/SE for BN samples ................................................................. 60
Figure 6.8: Comparison between surface energy of BN and Fluoropolymer ........... 62
Figure 6.9: Schematic diagram showing relative affinity of PTFE and BN ............. 65
Figure 7.1: Filter assembly used for separating BN and adsorbed mLLDPE ......... 73
Figure 7.2: Freundlich Adsorption Isotherm for PE – BN ........................................ 74
Figure 7.3: Freundlich Adsorption Isotherm for Fluoropolymer – BN .................... 76
List of Tables

Table 4.1: Comparison of boron nitride to common fillers ............................................. 39
Table 4.2: The average particle sizes and states of agglomeration properties of BN .... 40
Table 5.1: Performance of different grades of BN .......................................................... 45
Table 6.1: Physical constants for test liquids ................................................................. 52
Table 6.2: Surface energy results using capillary rise method ......................................... 53
Table 6.3: Comparison of CA using direct measurement and capillary rise method .... 56
Table 6.4: Comparison of SE using direct measurement and capillary rise method .... 58
Table 6.5: Surface energy of different materials involved in mLLDPE extrusion ....... 63
Table 6.6: Level of interaction between different surfaces involved in the extrusion ... 64
Table 6.7: Effect of combining BN and Fluoropolymer on melt fracture in LLDPE .... 67
Table 7.1: Freundlich Index and SE for BN ................................................................. 75
1 Introduction

Synthetic polymers have become an indispensable part of our life. Out of all the synthetic polymers, polyethylene is the most frequently encountered polymer in everyday life. This is the polymer that makes grocery bags, milk cans, shampoo bottles, children toys and many such low cost everyday items in addition to specialized products such as underground piping, electrical insulation etc. Present global demand for polyethylene is expected to be in excess of 50 million metric tons annually (World Polyethylene Market Report, 1999).

Commercial production of polyethylene \(-[\text{CH}_2-\text{CH}_2]_n-\) was first carried out in 1939 based on ICI technology. This process used free radical polymerization at very high pressure and temperature of the order of 1400 bar and 200 °C. Polyethylene (PE) produced was strong and virtually unbreakable. This PE had side branches, which made it flexible and translucent. It is known as LDPE (Low Density Polyethylene).

In 1950s Karl Ziegler and Giulio Natta succeeded in developing a catalyst for the polymerization of ethylene. The Ziegler-Natta catalytic polymerization could be carried out at much lower pressure and temperature and it also improved the linearity of the polymer chain. The absence of side branching resulted in more closely packed structure leading to higher density, greater strength and rigidity and opaque appearance. This type of PE is known as HDPE. With the help of Ziegler-Natta catalyst, branched PE chains could still be developed by copolymerizing ethylene with an alkyl branched comonomer. This type of copolymer is known as LLDPE (Linear Low Density Polyethylene). It has
the advantages of LDPE's flexibility and transparency and at the same time greater strength due to controlled branching and narrow molecular weight distribution.

From 1980s, the single-site metallocene catalysts have started revolutionizing the polymerization of olefins. The single-site catalysts provide very good control during synthesis for specific polymer structure and tacticity. It can produce HDPE with extremely linear structure and very high molecular weight, known as UHMWPE (Ultra High Molecular Weight Polyethylene), which can be even used for bullet proof jackets because of its strength. Similarly, LLDPE made using metallocene catalysts (m-LLDPE) too has narrower molecular weight distribution. Thus m-LLDPE has greater mechanical strength in particular puncture toughness, low melt elasticity, lower die swelling and it permits higher level of pre-stretching for films as compared to Ziegler-Natta LLDPE (Rohse and Bailey, 1997).

Although the development of catalysts has made the synthesis of PE easier and provided it better mechanical properties, the processing of this improved PE has become more challenging for manufacturing of the finished products. Processing techniques normally involve extrusion, film casting, film blowing, blow molding and injection molding. Processing rate in most of these techniques is limited by the appearance of flow instabilities (melt fracture). The problem of melt fracture is significant with the improved versions of PE such as HDPE, LLDPE and more with m-LLDPE. It aggravates as the molecular weight distribution narrows for these polymers (Kazatchkov et al, 1999).
Melt fracture can be broadly categorized into two types, surface melt fracture and gross melt fracture. In extrusion processes, when the processing rate exceeds a certain value (critical shear rate), small amplitude, high frequency periodic distortions appear on the surface of extrudates, this phenomenon is known as surface melt fracture or sharkskin (SMF). At higher throughput rates, these distortions take a more severe form of large irregular distortions referred to as gross melt fracture (GMF). It is now generally accepted by the research community that SMF originates in the land of die exit whereas GMF is initiated at the die entrance (Howells and Benbow, 1962; Cogswell, 1977; Piau et al, 1988, 1990; Kazatchkov et al, 2000; Denn, 2001; Migler et al, 2001). Figure 1.1 illustrates these melt fracture effects on m-LLDPE extrudate.

![Figure 1.1: Typical Extrudates of LLDPE at 163 °C, through 3.0/1.5 mm cross head die (Seth, 2001)](image)

<table>
<thead>
<tr>
<th>( \dot{\gamma} ) (s(^{-1}))</th>
<th>Smooth</th>
<th>Sharkskin</th>
<th>Gross Melt Fracture</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt; 50)</td>
<td>50 - 350</td>
<td>(&gt; 350)</td>
<td></td>
</tr>
</tbody>
</table>

In order to increase the rate of production by overcoming melt fracture, processing additives/aids are used. These are mainly fluoropolymers that are widely used in the processing of polyolefins and other commodity polymers. Fluoropolymers are added to the base polymer at low levels (approximately 0.1%). They essentially act as die
lubricants, modifying the properties of the polymer-wall interface essentially increasing the slip of polymer melt on die wall (Anastasiadis and Hatzikiriakos, 1998; Denn, 2001; Migler et al, 2001; Achilleos et al, 2002). As a result of this lubrication effect along the die wall, SMF is completely eliminated. However, these fluoropolymers are not effective for overcoming gross melt fracture (Yip et al, 2000; Achilleos et al, 2002; Seth et al, 2002).

It has recently been demonstrated that certain grades of Boron Nitride (BN) act as effective processing aids in the extrusion of polyolefins (Kazatchkov et al, 2000; Yip et al, 2000; Achilleos et al, 2002; Seth et al, 2002). BN is a solid lubricant, with a structure resembling that of graphite. BN can successfully be used as a processing aid not only to eliminate SMF but also to postpone GMF to significantly higher shear rates. Figure 1.2 illustrates the effectiveness of BN in overcoming the GMF.

Virgin LLDPE

LLDPE + 0.02% BN

LLDPE + 0.1% BN

Fig. 1.2: Effect of BN on extrudate appearance at $\dot{\gamma} = 617 \text{ s}^{-1}$, 163 °C (Kazatchkov et al, 2001)
It has also been observed that a combination of BN and fluoropolymer enhances the performance of the extrusion even further, where fluoropolymer essentially eliminates the sharkskin and BN delays the appearance of GMF (Rosenbaum, 2000; Achilleos et al, 2002).

Earlier studies on BN have attributed the physical properties namely particle size, shape and degree of agglomerations as deciding factors in the performance of the selected grades of BN for eliminating melt fracture (Yip et al, 2000). Subsequently studies (Seth et al, 2001) on the surface energy of various grades of BN demonstrated an approximate relation between the ratio of dispersive and polar components of surface energy of BN powders and the critical shear rate for the onset of melt fracture.

The main objective of the present work is to use an alternate method for surface energy measurement and use these data of surface energy for different grades of BN to analyze the role of surface energy in the performance of different grades of BN. It is also desired to compare the surface energy of these BN samples with a typical fluoropolymer processing aid such as PTFE for understanding the mechanism of these two processing aids in eliminating extrudate melt fracture. In addition, an attempt is made to test the adsorption capacity of different grades of BN particles for adsorbing m-LLDPE and fluoropolymer. This might prove to be helpful in understanding the possible BN – fluoropolymer interactions, where they are used as a combination in the base LLDPE polymer.
2 Literature Review

This chapter presents the overview of important concepts and terminologies, useful for better understanding the experimental results and analysis presented in the later chapters. The topics covered in this section include Rheological Measurements, Melt Fracture, Polymer Processing Aids, Surface Energy and Adsorption.

2.1 Rheological Measurements

Rheology is the science that deals with the way materials deform when forces are applied to them. Rheological characterization of polymer melts involves several types of experiments: capillary rheometer experiments, in which a molten polymer is forced through a channel of known diameter and length; linear dynamic viscoelastic experiments using a cone-and-plate or a parallel plate configuration; and sliding plate rheometer experiments producing various types of non-linear strain deformations.

2.1.1 Capillary Rheometer

Flow of molten polymer through a tube or a channel under pressure is commonly encountered in polymer processing, for example in an extrusion die or in the runner feeding of an injection mold. A capillary rheometer simulates this type of flow behaviour. In the present research work, capillary rheometer is primarily used to extrude blends of m-LLDPE mixed with different Polymer Processing Aids (PPAs) to study the effect of these PPAs in eliminating / postponing the appearance of melt fracture at a given shear rate. The extrudates obtained were visually examined to see the sharkskin and gross melt fracture taking place at the surface of extrudate.
A typical schematic of capillary rheometer is shown in Figure 2.1, followed by an overview of its underlying principles.

![Schematic of a capillary rheometer](image)

**Fig. 2.1:** Schematic of a capillary rheometer (*Baird and Collias, 1995*).

Capillary rheometers are also used widely to determine the viscosities in the shear rate range of 5 to 5000 s\(^{-1}\) (*Dealy and Wissburn, 1990*). Reproducibility of capillary rheometer experiments is typically ± 5%.

The capillary rheometer consists of a melt reservoir or barrel, for melting the polymer and a plunger or piston that causes the melt to flow through the capillary die of known diameter, \(D\), and length, \(L\). The quantities normally measured are the flow rate, \(Q\), (related to the piston speed) and the driving pressure, \(P_d\), (related to force on the piston...
that is measured by means of a load cell. The measured piston force, $F_d$, is related to $P_d$ as follows:

$$P_d = \frac{F_d}{\pi R_b^2}$$  \hspace{1cm} (2-1)

where $R_b$ is the radius of the barrel or reservoir. Alternatively, $P_d$ can be measured by mounting a pressure transducer directly in the barrel.

### 2.1.2 Rheometer Fitted with Capillary Die

To calculate the viscosity, it is necessary to know the wall shear stress and the wall shear rate, and it is therefore necessary to have reliable techniques for evaluating these basic rheological quantities on the basis of experimental data. For steady-state, fully-developed flow of an incompressible Newtonian fluid, the wall shear stress, $\sigma_w$, can be calculated as:

$$\sigma_w = \frac{\Delta P D}{4L}$$  \hspace{1cm} (2-2)

Where $\Delta P$ is the total pressure drop along the capillary. The magnitude of the wall shear rate, $\dot{\gamma}_w$, for a Newtonian fluid can be calculated as:

$$\dot{\gamma}_w = \frac{32Q}{\pi D^3}$$  \hspace{1cm} (2-3)

For the case of a non-Newtonian fluid, this quantity is called the apparent wall shear rate, $\dot{\gamma}_A$, that is the rate that a Newtonian fluid would have at the same volumetric flow rate $Q$:

$$\dot{\gamma}_A = \frac{32Q}{\pi D^3}$$  \hspace{1cm} (2-4)
Capillary flow of a Newtonian fluid is a controllable flow which means that the flow kinematics does not depend on the nature of the fluid. Capillary flow of molten polymers, however, is only a partially controllable flow. This means that the velocity distribution in this flow is governed not only by the boundary conditions but also depends on the nature of the fluid. To account for this, at least two corrections should be applied to the experimental data. First, the velocity profile in the flow of a polymeric fluid is nonparabolic, and one must correct the wall shear rate, $\dot{\gamma}_w$, defined by Equation (2-3). This correction, generally known as the Rabinowitch correction, can be calculated as (Dealy and Wissbrun, 1990):

$$b = \frac{d(\log \dot{\gamma}_A)}{d(\log \sigma_w)}$$

(2-5)

It is noted that the correction factor $b$ is a local quantity depending on $\dot{\gamma}_A$. It can be shown that the true wall shear rate then can be obtained by use of the following equation (Dealy and Wissbrun, 1990):

$$\dot{\gamma}_w = \left( \frac{3 + b}{4} \right) \dot{\gamma}_A$$

(2-6)

A power-law fluid is defined as

$$\sigma = K\dot{\gamma}^n$$

(2-7)

where $\sigma$ is the shear stress, $\dot{\gamma}$ is the shear rate, $K$ is the consistency index, and $n$ is the power law exponent. It can be shown that the wall shear rate for a power law fluid can be expressed as:

$$\dot{\gamma}_w = \left( \frac{3 + 1/n}{4} \right) \dot{\gamma}_A$$

(2-8)
Thus, it can be seen from Equations (2-6) and (2-8) that the Rabinowitch correction is equal to $1/n$ for a power law fluid and 1 for a Newtonian fluid. It mainly represents deviation from Newtonian behavior. Second, the pressure drop must be corrected for the additional pressure required for the melt to pass through the contraction between the barrel and the capillary. The wall pressure distribution actually observed for capillary flow of molten polymers is sketched in Figure 2.2.

![Wall pressure distribution for capillary flow](image)

**Fig. 2.2:** Wall pressure distribution for capillary flow *(Dealy, 1982)*

It can be seen that the pressure drop, $P_d$ is clearly not the pressure drop that one would observe for fully developed flow in a capillary of a length $L$. There is a significant pressure drop near the entrance of the die, $\Delta P_{ent}$. There may also be residual pressure at the die exit, called the exit pressure, $\Delta P_{ex}$, but it is quite small compared to $\Delta P_{ent}$. The total pressure correction for exit and entrance regions is called the end pressure, $\Delta P_{end}$, that is,
\[ \Delta P_{\text{end}} = \Delta P_{\text{ex}} + \Delta P_{\text{ent}} \]  \hspace{1cm} (2-9)

The true wall shear stress is then obtained as:

\[ \sigma_w = \frac{(\Delta P - \Delta P_{\text{end}})}{4(L/D)} \]  \hspace{1cm} (2-10)

The pressure correction, \( \Delta P_{\text{end}} \), or the Bagley end correction can be determined by use of a scheme proposed by Bagley (1957). He suggested to measure the driving pressure, \( P_d \), at various values of the flow rate, \( Q \), using a variety of capillaries having different lengths. For each value of the apparent wall shear rate, he then plotted driving pressure versus \( L/D \) and drew a straight line through the points as shown in Figure 2.3. Extrapolating the lines to the \( P_d=0 \) axis, he then obtained an end correction, \( e \).

![Fig. 2.3: Bagley plot for determining the end correction.](image)

Thus, the true wall shear stress can then be calculated as follows:

\[ \sigma_W = \frac{P_d}{4(L/D + e)} \]  \hspace{1cm} (2-11)
An alternative way to determine the end correction is to use orifice capillaries with $L/D=0$. This will directly measure $\Delta P_{\text{end}}$ and thus equation (2-10) can be used directly to infer the wall shear stress.

2.1.3 Rheometer Fitted with Crosshead Die

In addition to capillary dies, a crosshead die can also be used to assess the processability of the various m-LLDPE, mixed with PPAs. The crosshead die used in this work is a Nokia Maillefer 4/6 that includes dies and tips of various diameters ("tip" is the wire guide) with equal entry cone angles of $60^\circ$ and die land length of 7.62 mm. The schematic of the crosshead is shown in Figure 2.4.

![Crosshead die for wire coating](Buckmaster et al., 1997)

The molten polymer enters the port 11 of the die 2. Then the polymer is guided through to orifice 8 by the wire guide 16. The interior and the exterior surface of the wire tubular shape are formed by the passage 24 and 4 respectively. The wire guide provides a channel as a mandrel to produce the tubular shape extrudate (10). Polymer reaches orifice 8 and draws down to a thinner cross-section, making a thin coating 26 on the wire. Wire was not used in our study. Therefore, a hollow shape extrudate was obtained during the
experiment. The apparent shear rate was calculated by using the formula applied for slit
dies having a large aspect ratio (Bird et al, 1987):

\[ \dot{\gamma}_A = \frac{6Q}{0.25(D-d)^20.5\pi(D+d)} \]  \hspace{1cm} (2-12a)

Where \( Q \) is the volumetric flow rate, \( d \) and \( D \) are the tip and die diameters. The apparent
wall shear stress was estimated as the average of the shear stress at the inner and outer
walls by using the following formula which is based on the assumption of a power-law
fluid (Bird et al, 1987). The general formula for the shear stress distribution is:

\[ \tau_r = \frac{\Delta PD}{4L} \left( \frac{2r}{D} - \frac{r^2}{D} \frac{D}{2r} \right) \]  \hspace{1cm} (2-12b)

Where \( \tau_r \) is the shear stress at radius \( r \), \( \Delta P \) is the pressure drop, \( L \) is the length of the die
land, and \( \beta \) is the parameter depending on the geometry and the power law index.

### 2.1.4 Parallel Plate Rheometer

Parallel plate rheometer shown in Figure 2.5 is one of the most versatile rheometers
available for rheological analysis. In this rheometer, two plates are mounted on a
common axis of symmetry, and the sample is inserted in the space between them. The
upper plate is rotated at a specified angular velocity \( \alpha(t) \) and as a result the sample is
subjected to shear. The motion of the upper plate is programmed, and the resulting
torque, \( M_r \), is measured (so called constant strain rheometers). Another mode of operation
is fixing the torque and measuring the displacement (constant-stress rheometers).
Most polymeric materials are said to be rheologically viscoelastic, i.e. a combination of viscous (representing liquid – loss of energy) and elastic (representing solid – storage of energy) components. If sufficiently large strain is applied, it is possible to break the structure or elastic component of the material, resulting in purely viscous flow. This is the simplest type of test possible on this rheometer, leading to determination of bulk viscosity of the sample or its characterization in terms of one of the several non-Newtonian flow models.

![Parallel plate rheometer](image)

**Fig. 2.5:** Parallel plate rheometer

The real power of this instrument lies in its ability to apply very small amount of deformations in dynamic or oscillatory fashion, without breaking the elastic structure of the sample. This is known as linear viscoelastic characterization of the material and provides very useful information about the morphology of the material.

In addition, the rheometer can also carry out Creep Analysis (slow deformation of material, measured under constant stress) and Stress Relaxation (stress response of the material under constant strain). Creep Analysis is useful for predicting effects such as
sedimentation, sagging and leveling. The Stress Relaxation is mainly used as a quality control tool.

Since the Oscillatory Linear Viscoelastic Characterization is the most important and useful test, a brief overview of it is presented here. In this test, a very small shear strain is applied to the sample sinusoidally – this is similar to vibrating the sample within its linear elastic range, and the stress response of the sample is observed. Since viscoelastic sample is composed of viscous and elastic component, the elastic or solid component is expected to follow Hook’s law, where stress is directly proportional to strain – leading to stress responses ‘in phase’ with the applied sinusoidal strain. The viscous or liquid component on the other hand, tends to follow Newton’s law, where stress is directly proportional to shear rate and not strain – leading to stress responses completely ‘out of phase’ to the applied strain. This is explained schematically in Figure 2.6.

![Figure 2.6: Oscillatory Linear Viscoelastic Characterization](image)
In practice, most materials are a combination of viscous and elastic components and so the measured phase angle ($\delta$) will be somewhere between $0^\circ$ and $90^\circ$. Since in this test, stress and strain are constantly changing, the viscoelastic properties are described in terms of Elastic (storage) Modulus ($G'$) and Viscous (Loss) Modulus ($G''$) defined below. Applied sinusoidal strain can be represented as:

$$\gamma(t) = \gamma_0 \sin(\omega t)$$

Where $\gamma_0$ is the strain amplitude and $\omega$ is the frequency. The stress response can be shown as:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta)$$

Where $\sigma_0$ is the stress amplitude and $\delta$ is a phase angle shift in the response. Using a trigonometric identity, one can rewrite Equation (2-14) in the following form:

$$\sigma(t) = \gamma_0 \left[ \frac{\sigma_0}{\gamma_0} \cos(\delta) \sin(\omega t) + \frac{\sigma_0}{\gamma_0} \sin(\delta) \cos(\omega t) \right]$$

Now, 

$$G' = \left[ \frac{\sigma_0}{\gamma_0} \cos(\delta) \right] \quad \text{and} \quad G'' = \left[ \frac{\sigma_0}{\gamma_0} \sin(\delta) \right]$$

There are other two parameters, frequently used to present the test results. These are complex modulus ($G^*$) and complex viscosity ($\eta^*$), defined below.

$$G^* = G' + iG''$$

$$\eta^* = \eta' - i\eta''$$

Where,

$$\eta' = \frac{G'}{\omega} \quad \text{and} \quad \eta'' = \frac{G''}{\omega}$$
As mentioned earlier, the oscillatory tests are very sensitive to the molecular structure of the polymer sample. Figure 2.7 (Dealy and Wissbrun, 1990) shows the indicative plot of storage modulus for three samples of a linear polymer. It may be observed that at high frequencies, glassy behaviour is exhibited. At smaller frequencies, molecular rearrangement becomes possible and there is a transition zone. For the low molecular weight materials (A) such transition zone does not exist and we move to the terminal zone directly. For the higher MW sample (B), we have a plateau zone. The plateau zone is not clear for polydisperse material (C).

![Indicative plot of G'(ω) for three samples of a linear polymer.](image)

Fig. 2.7: Indicative plot of $G'(ω)$ for three samples of a linear polymer. (A) is monodisperse with low MW, (B) is monodisperse with high MW, and (C) is polydisperse with high MW.

Figure 5.4 (chapter 5 of this thesis) shows the results of such linear viscoelastic oscillatory test for LLDPE sample. It may be observed that at small frequencies (terminal
zone) $G'$ tends to become proportional to $\omega^2$ (slope of $\sim 2$) whereas $G''$ is proportional to $\omega$ (slope of $\sim 1$). It may also be noted that at low frequency, $G'' > G'$, implying a rubbery or liquid like behaviour. At higher frequency, a crossover takes place indicating a rigid, glassy or solid like behaviour.

Several empirical relationships between molecular structure and linear viscoelastic properties have been proposed for linear polymers. No such relationships have been proposed for branched polymers because of the difficulty of separating the effects of the degree and the type of branching from that of molecular weight distribution (Dealy and Wissbrun, 1990).

2.1.5 Sliding Plate Rheometer

The laboratory procedure that most closely approximates simple shear is to place a thin layer of fluid between two flat plates, clamp one of the plates in place, and move the second plate at a constant velocity, $u$, as shown in Figure 2.8.

![Fig. 2.8: Simple shear flow](image)
The main advantages of sliding plate geometry are that there are no effects of pressure on measurements, and that the edge effects can be eliminated by measuring the shear stress locally using a flush-mounted shear stress transducer. It can be also very useful to study orientation effects for example, in glass fiber reinforced plastics.

Under no-slip conditions (Figure 2.9 a),

Shear strain, \( \gamma(t) = \frac{\Delta x}{h} \) \hspace{1cm} (2-18)

Shear rate, \( \dot{\gamma}(t) = \frac{u}{h} \) \hspace{1cm} (2-19)

Shear stress, \( \sigma = \frac{F}{A} \) \hspace{1cm} (2-20)

If one assumes that the no-slip boundary assumption is valid, then the actual shear rate, \( \dot{\gamma} \), is equal to the nominal shear rate, \( \dot{\gamma}_n \). When slip is present, the actual shear rate is less than the nominal shear rate and these two cases are shown schematically in Figure 2.9.

![Fig. 2.9: Velocity profiles in simple shear a) without slip and b) with slip](image)
In fact $\dot{\gamma}$ and $\dot{\gamma}_n$ under slip condition are related through the following expression

$$\dot{\gamma}_n = \dot{\gamma} + 2u_s / h \quad (2-21)$$

where $u_s$ is the slip velocity.

### 2.2 Melt Fracture

Melt fracture is a term, used collectively for appearance of instability, which occurs beyond a critical shear rate in a capillary, slit or annular dies during extrusion of polymers. The term melt fracture was introduced by Tordella (1956) because of the audible tearing noises which accompanied the distortion of the extrudate. Melt fracture is a major problem in the extrusion of polyolefins and many other commercial polymeric materials. In addition to shear rate or processing speed, it depends on various operational and geometric factors which mainly include the polymer structure and its molecular characteristics, die geometry and the process temperature.

There are various types of flow instabilities observed in the flow of polymeric liquids through capillary, slit and annular dies. These are also reflected in the apparent flow curve, determined by means of a capillary rheometer. This is essentially a log-log plot of the wall shear stress, $\sigma_w$, vs. apparent shear rate, $\dot{\gamma}_A$. A typical apparent flow curve for a linear polymer such as HDPE and LLDPE is shown in Figure 2.10.
One can easily identify the five different flow regions. Initially there is a *stable* region where the extrudate appears smooth and glossy (region 1). In this region, the behavior of the melt resembles that of a non-Newtonian fluid and the viscosity can be represented by a power-law expression, equation (2-7). In this region, the no-slip boundary condition can be assumed to be valid. Beyond some critical wall shear stress, $\sigma_{c1}$, which is typically of the order of 0.1-0.2 MPa, the first visual manifestation of an extrusion instability appears as a high-frequency, small-amplitude distortion of the extrudate known as *sharkskin* or *surface melt fracture* (region 2). As the name implies, sharkskin is a roughness that usually modulates the extrudate diameter by no more than 1% and consists of semiregular cracks or grooves that run mainly perpendicular to the flow *(Benbow and Lamb, 1963;*
Piau, 1990). The onset of sharkskin appears to coincide with a change in the slope of the apparent flow curve.

At a second critical value $\tau_{c2}$ and within a certain range of apparent shear rates, the flow ceases to be stable (region 3). It is the region of oscillating, cyclic or stick-slip melt fracture where the extrudate has the appearance of alternating smooth and distorted portions. In this region, the pressure drop oscillates between two extreme values. The periodic variations of the pressure and apparent shear rate define a hysteresis loop that connects the two branches of the apparent flow curve. Despite the scatter in the reported values of the second critical shear stress, it is generally accepted that gross melt fracture is a basic characteristic of the particular polymer systems. The greater the molecular weight and the narrower its distribution, the greater the amplitude of the hysteresis loop.

At higher throughputs there is sometimes a transition to a second stable flow regime in which the extrudate again becomes smooth. This is a superextrusion region (region 4). Finally, at still higher shear rates, there is a transition to a wavy chaotic distortion (gross melt fracture), which gradually becomes more severe with increase in apparent shear rate $\dot{\gamma}_A$ (region 5). This typical behavior has been observed in the capillary extrusion of many linear polymers such as high density and linear low-density polyethylene (Kalika and Denn, 1987), polytetrafluoroethylene (Tordella, 1969), polybutadiene (Vinogradov et al, 1972b), and others.
2.2.1 Mechanisms to Explain Melt Fracture

As a result of the large number of research work and the use of sophisticated flow visualization techniques, there is a general agreement among the researchers about the causes of two types of melt fracture – Sharkskin Melt Fracture (SMF) and Gross Melt Fracture (GMF).

2.2.2 Die Exit Effects: Sharkskin / Surface Melt Fracture

There is universal agreement that sharkskin is initiated at the die exit. The first theory about surface melt fracture (sharkskin) was proposed by Howells and Benbow (1962) and later by Cogswell (1977). They hypothesized that the polymer fractures due to high stretching rates and high stresses as a result of the abrupt change (shear to free surface flow) in the boundary condition at the exit of the die. The melt leaving the die in the neighborhood of the wall experiences a large, rapid, tensile deformation as the velocity field adjusts from the no-slip boundary condition to the free-surface condition. Polymer chains are stretched during the tensile deformation, which causes the highly entangled polymer to respond like a rubber. The large stresses on the free surface cause the cracks to open up giving them the appearance of sharkskin. There are several other views available on the origin of sharkskin. However, this original proposition of fracture at the die exit as the cause of sharkskin has been substantiated by the microscopic flow visualization observations made by Migler et al (2001). Figure 2.11 presents a schematic view of the surface melt fracture taking place at the die exit.
If we analyze the dynamics of polymer melt movement near the die exit, as shown in the above figure, we realize that inside the die, there is a typical boundary layer velocity distribution having zero or a small sliding velocity close to the wall and maximum at the centre. Outside the die, the velocity distribution is uniform throughout the cross-section as there is no resistance to flow. Therefore, as the melt is extruded, it experiences a sudden jump in velocity near the die exit leading to large extensional stresses on the polymer surface which result in the surface distortion or sharkskin. In short, the absence of lubrication at the die exit is considered as the main cause of sharkskin.

2.2.3 Die Entry Effects: Gross Melt Fracture

Most authors agree in claiming that above a certain extrusion rate, the flow upstream of the die contraction becomes unstable. These instabilities occur in the form of sudden pulsations or cavitation which were confirmed by visualization (Piau et al, 1990;
Kazatchkov et al, 2000; Migler et al, 2002) and birefringence measurements (Tordella, 1969). They have shown that such instabilities started along the upstream flow axis owing to the high elongation stresses that develop in this area. These instabilities trigger the phenomenon of gross melt fracture, which is often seen in the form of a regular helix oscillating at the same frequency as that of the pulsations of the upstream elongational flow (Piau et al, 1990). Figure 2.12 shows the flow visualization of virgin PP at various shear rate in the die entrance region, carried out by Kazatchkov et al (2000).

Fig. 2.12: a) Pictures of the flow of polypropylene at various apparent shear rates of 32 s\(^{-1}\), 320 s\(^{-1}\) and 650 s\(^{-1}\) at 200°C (Kazatchkov et al, 2000).

b) A schematic diagram illustrating the unstable flow development in the die entrance region.

It can be observed from the above figure that as the melt flow rate increases, flow streamlines are no longer smooth. By observing the above visualization in a movie format, it can be readily seen that at higher rates, the flow is discontinuous with breaks in the motion, causing the zigzag streamlines. A schematic in Figure 2.12 b explains this flow pattern at higher rate. The flow in the die entry region appears to be broken into several layers, and each layer moves with its own velocity. At regular time intervals, different in each layer, the motion stops for a brief period. The frequency of flow and
stops are higher in the layers close to the centre of the stream. This instability observed in the form of discontinuous streamlines is believed to be caused by the absence of lubrication in the bulk of the polymer melt resulting in the form of severe distortions or gross melt fracture.

2.3 Polymer Processing Aids

As discussed before, melt fracture poses an undesirable constraint on the rate of production. It is necessary to eliminate melt fracture or postpone it to higher rates in order to increase the rate of production. Processing aids used for melt fracture elimination include additives and surface coatings, which mainly target at slip promotion at the die exit, thereby eliminating surface melt fracture. This in turn also reduces the extrusion pressure. Typical polymer Processing Aids are fluoropolymers, stearates and certain waxes which have been used traditionally for surface melt fracture elimination. These are used in small quantities of the order of about 1000 ppm. They have a tendency to migrate towards wall and make a fine coating on the die wall during extrusion. The extruding polymer then slips along the smooth coating on the die, thus eliminating the surface melt fracture (Rudin et al, 1985; Migler et al, 2001).

Priester and Stika (1992) suggested that the factors that may affect the performance of the processing aid include the level of additive, dispersion quality and the interaction with other ingredients (antioxidants and stabilizers) in the resin. They have also mentioned that a large number of small particles of the additive can result into a better dispersion quality than a small number of large particles. Stewart (1992) reported that a
masterbatching step was required in order to provide a good quality of dispersion of additives into the resin.

In general, fluoropolymer based processing aids reduce the pressure required to extrude the resin at a particular flow rate and eliminate or postpone melt fracture to higher extrusion rates. Note that these additives can eliminate only sharkskin and the so-called stick-slip (oscillating or cyclic) melt fracture. They do not appear to have an effect on the extrudate appearance in the gross melt fracture region (Rosenbaoum et al, 1998).

Recently, it has been reported that certain Boron Nitride (BN) based compositions may act as effective processing aids in the extrusion of a number of fluoropolymers and polyolefins (Buckmaster et al, 1997; Rosenbaoum et al, 1998; Yip et al, 1999; Lee and Lee, 2000). It has been reported that BN can successfully be used as a processing aid to eliminate not only sharkskin melt fracture but also substantially postpone gross melt fracture to significantly higher shear rates well within the gross melt fracture region. It is noted that conventional fluoropolymers can only eliminate sharkskin; they do not appear to have an effect on the gross melt fracture phenomena.

Yip et al (1999) reported that BN is an effective processing aid when it possess the following characteristics (i) average particle size of up to about 10µm, (ii) no agglomerations (iii) absence of boron oxides in its structure and (iv) good dispersion into the resin under process. Also, BN must be used at its optimal concentration depending on
the type of polymer and the extrusion temperature. It is observed that the presence of BN
does not alter the flow curve during extrusion however, it has significant effect on

It had also been reported that the BN additive had little additional effect on the extrudate
appearance in the capillary geometry (both capillary and orifice dies with different
entrance angle) compared to the effect seen in the case of fluoroelastomer. The greatest
influence of the additive occurred in crosshead dies and tips where the additive particles
seemed to enhance melt slippage and relieve internal stresses. (Rosenbaum et al, 1998;
Yip et al, 2000). Lee and Kim (2000) reported that the critical apparent shear rate for
onset of melt fracture and the shape of extrudate are highly dependent on processing
temperature, L/D and content of the BN. They found that the addition of 0.5 wt % of BN
in LLDPE eliminate or delay sharkskin, stick-slip melt fracture and gross melt fracture to
much higher rates, even though there is no difference in the linear viscoelastic and
mechanical properties between virgin and LLDPE containing BN.

Combining a BN powder with fluoropolymer has an enhanced effect on melt fracture
elimination. Fluoropolymers mainly act as a slip promoter, eliminating sharkskin and
reducing the extrusion pressure whereas BN primarily influences the melt flow in die
entrance region, delaying the gross melt fracture. The fact that these two additives act by
different mechanisms for suppressing the instabilities, explains why their combination
results in a synergistic effect for melt fracture elimination (Rosenbaum, 2000; Achilleos
et al, 2002).
2.4 Surface Energy

Surface energy is defined as the energy required to form a unit area of surface and it also represents the interfacial tension of the solid in equilibrium with its vapor. It influences all physical interactions between different material surfaces. It is especially important in applications involving lubricants and release agents, adhesives, cleansing agents, paints and coatings.

Surface energy of a solid surface is most easily estimated from the contact angle of a liquid droplet placed on the given solid surface. This is because surface energy of solid and surface tension of liquid decide the contact angle and hence the wettability of liquid for a given surface. The contact angle is the angle formed by the solid/liquid interface and the liquid/vapor interface measured from the side of the liquid as shown in Figure 2.13. Liquids wet surfaces when the contact angle is less than 90 degrees. In fact, the contact angle for most liquid penetrants is very close to zero degrees.

To cite a practical example, the contact angle formed by a drop of ink on the paper determines the printing quality of ink. For good quality of paper, contact angle should be between 90° and 110°. If contact angle is less than 90° then ink will spread on paper and if it is greater than 110° then breaks will occur while printing.

Interfacial force equilibrium of a liquid drop on a solid substrate, known as Young’s equation relates the interfacial forces shown in Figure 2.13 by the following equation.

\[ \gamma_{sv} = \gamma_{lv} \cos \theta + \gamma_{sl} \]  

(2-22)
In the above equation, suffix \( s \) stands for solid and \( l \) for the test liquid. The total surface energy or surface tension is divided into dispersive and polar components. Thus,

\[
\gamma = \gamma^D + \gamma^P
\]  

(2-23)

Where \( \gamma^D \) is the surface energy resulting from London dispersion forces. \( \gamma^P \) is the surface energy resulting from dipole-dipole, induced dipole and hydrogen bonding interactions. Each of these surface energy components can be estimated by selecting two different test liquids – polar and non polar ones for contact angle measurement.

The solid – liquid interfacial tension, \( \gamma_{sl} \) can be expressed by the Good and Girifalco’s Geometric Mean approach, equation (2-24) which assumes that only intermolecular force interactions are important in determining surface tension components between a liquid and a solid.

\[
\gamma_{sl} = \gamma_s + \gamma_l - \left[ 2\sqrt{\gamma_s^D \gamma_l^D} + 2\sqrt{\gamma_s^P \gamma_l^P} \right]
\]  

(2-24)
Combining equations (2-22) and (2-24), a single equation is obtained with two unknowns in the form of \( \gamma_s^D \) and \( \gamma_s^P \) (Girifalco and Good, 1957; Owens and Wendt, 1969).

\[
(1 + \cos \theta) = \frac{2}{\gamma_1} \left[ \sqrt{\gamma_s^D \gamma_1^D} + \sqrt{\gamma_s^P \gamma_1^P} \right] 
\]  
(2-25)

Once the contact angle \( \theta \), is estimated, equation (2-25) can be used with two different test liquid with known surface tension to solve for the two unknowns: \( \gamma_s^D \) and \( \gamma_s^P \).

2.4.1 Contact Angle Measurement

The methods used for contact angle measurement can be categorized into direct and indirect methods. The direct methods involve direct observation of the liquid droplet placed on the solid surface. The image of the droplet can be photographed and magnified or can be directly viewed under a microscope fitted with angle calibrated eye piece (known as goniometry).

The indirect method of contact angle measurement estimates contact angle using the wettability of test liquid for a solid surface. It either measures the force / tension exerted on solid plate brought in contact with test liquid (known as tensiometry or Wilhmely plate method) or measures the penetration rate of test liquid through a vertical bed of solid particles (known as Washburn’s capillary rise method).

Goniometry and tensiometry are normally preferred for plane solid surfaces whereas capillary rise method is prevalent for solid particles and powders. Both methods have their own advantages and disadvantages. Advanced goniometry is expected to be highly
accurate with an accuracy level within +/- 1° on flat solid surfaces and it is very easy to carry out the test. On the negative side, there is a possibility of human error in measuring the tangent and hence contact angle when the angle is measured manually. In addition, for porous surfaces, the major challenge in goniometry is to measure the contact angle before the liquid drop gets absorbed on the surface. This difficulty can be overcome by using high speed video images of the droplet and then analyzing the very first image of the droplet on the solid surface.

Although Washburn’s capillary rise method is normally preferred for porous surfaces and powders, there are several issues related to its accuracy and reproducibility. In the original method, the solid powder is packed in a capillary and brought in contact with the test liquid and the rising rate is measured. See Figure 2.14.

Penetration rate of the liquid through the bed of packed solid is then given by Washburn’s equation (2-26).

\[
\frac{dh^2}{dt} = \frac{K \gamma_l \cos \theta}{2 \mu}
\]

Fig. 2.14: Schematic of original capillary rise method for contact angle measurement
Where $\gamma_v$ and $\mu$ are the surface tension and viscosity of liquid, respectively, $\theta$ is the liquid contact angle on the solid surface, $r$ is the capillary radius, $K$ is tortuosity constant, a property of packed solid bed, which depends on its porosity and its distribution in the bed.

For accurate measurement of the rate of liquid rise through the solid bed, equation (2-26) is modified to measure the rate of liquid weight rise through the capillary, which can be measured using a sensitive weigh scale.

$$\frac{d(\Delta w)^2}{dt} = \frac{K' \rho^2 \gamma_v \cos \theta}{2\mu}$$  \hspace{1cm} (2-27)

The major disadvantage of the capillary rise method is the precise measurement of tortuosity constant, $K'$. Measurement of $K'$ is carried out by using a liquid that is considered to wet the given solid perfectly, so that the contact angle, $\theta$ in the Washburn's equation can be assumed equal to 0. Secondly, since $K'$ represents porosity and its distribution inside the packed bed, for reproducible results it is necessary to obtain the reproducible packing of the solid bed in terms of its porosity. This is a challenging task because it is observed that the packing is likely to get unevenly disturbed once the packing pressure is removed. It also develops fine hair cracks or capillaries as the liquid wets the bed, subsequently changing the rate of liquid rise for the remaining liquid.

### 2.5 Adsorption

The adsorption exploits the ability of certain solids to preferentially concentrate specific substances from a solution onto their surfaces. In this manner, components of either gas
or liquid solutions may be separated from each other. The solid surface is termed as adsorbent and the component preferentially separated by the adsorbent is known as adsorbate.

There are two types of adsorption phenomenon identified – physical adsorption and chemisorption. Chemisorption is the result of chemical interaction and formation of chemical bond between the solid and the adsorbed substance. It is particularly important in catalytic processes and not pertinent to the present topic.

Physical adsorption, a readily reversible process, is a result of intermolecular forces of attraction between molecules of the adsorbent and adsorbate. The adsorbed substance does not penetrate within the crystal lattice of the adsorbent and does not get dissolved in it but stays on the surface. It could however, get inside the capillaries of a porous adsorbent. Typical characteristics of adsorbents are high effective surface area and higher surface free energy. Prominent example of adsorption process is decolorization and drying of petroleum products using clay, alumina or charcoal.

Two important physiochemical aspects of the adsorption process are the equilibria of the adsorption and the kinetics. The equilibrium studies give the capacity of the adsorbent to selectively adsorb the adsorbate. The equilibrium relations between adsorbent and adsorbate are normally described by the adsorption isotherm, representing the relationship between the quantity adsorbed and that remaining in the solutions. There are
two types of adsorption isotherms: Langmuir adsorption isotherms and Freundlich adsorption isotherms.

Langmuir adsorption isotherm represents a theoretical adsorption isotherm in the ideal case. It is often used for adsorption of a solute from a liquid solution. The Langmuir adsorption isotherm can be expressed as:

\[
Q_e = \frac{X_m K_L C_e}{1 + K_L C_e}
\]  

(2-28)

Where,
- \( Q_e \) = Adsorption density at equilibrium solute concentration, \( C_e \) (mg of adsorbate per g of adsorbent)
- \( C_e \) = Concentration of adsorbate in solution at equilibrium (mg/l)
- \( X_m \) = Maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbate)
- \( K_L \) = Langmuir constant related to energy of adsorption (l of adsorbent per mg of adsorbate)

The above equation can be rearranged to the following linear form.

\[
\frac{C_e}{Q_e} = \frac{1}{X_m K_L} + \frac{C_e}{X_m}
\]  

(2-29)

The Langmuir constants \( X_m \) and \( K_L \) can be evaluated from the slope and intercept of a straight line, obtained by plotting \( C_e/Q_e \) against \( C_e \).

Freundlich presented an empirical adsorption isotherm for non-ideal systems. The Freundlich isotherm can be expressed as:
\[ Q_e = K_F C_e^n \]  \hspace{1cm} (2-30)

Where,

\( Q_e \) = Adsorption density at equilibrium (mg of adsorbate per g of adsorbent)

\( C_e \) = Concentration of adsorbate in solution at equilibrium (mg/l)

\( K_F \) and \( n \) are the empirical constants dependent on several environmental factors.

The equation can be conveniently linearized by taking logarithmic on both sides as:

\[ \ln Q_e = \ln K_F + n \ln C_e \]  \hspace{1cm} (2-31)

A plot of \( \ln Q_e \) vs. \( \ln C_e \) yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and intercept.
3 Objectives

The main objective of the present work is a comprehensive study of the effect of surface energy of BN on processability of m-LLDPE. The specific answers sought are as follows.

- Why different grades of BN have dissimilar influence on the appearance of melt fracture during m-LLDPE extrusion? Does surface energy play a role in determining the performance of these BN grades?
- Can the performance of BN and Fluoropolymers be compared and explained on the basis of their surface energies?

In addition, an attempt is made to test the adsorption capacity of different grades of Boron Nitride (BN) particles for adsorbing m-LLDPE and fluoropolymers. This might be helpful in explaining the possible interaction between BN and fluoropolymers when they are used in a combination, for eliminating melt fracture from LLDPE.
4 Materials

This chapter describes the important characteristics of the polymer and the processing aids used to carry out the experimental research work.

4.1 Polymer

The resin studied in this work in order to investigate the effect of various BN powders on their processability during extrusion is metallocene catalyzed Polyethylene: Exact® 3128, provided by Exxon Mobil.

Exact® 3128 is ethylene – butene LLDPE copolymer with ρ = 0.9 and MI = 1.2. Its melting point is about 92 °C, determined by DSC. The chemical structure of poly(ethylene-co-1-butene) is shown below.

\[ \text{Fig. 4.1: Structure of ethylene – butene LLDPE copolymer} \]

4.2 Boron Nitride

Boron nitride is a white solid lubricant. It has a high thermal conductivity, low dielectric loss modulus, low thermal expansion and high lubricity over a wide temperature range. BN has one of the highest thermal conductivity of any commercial electrical insulator in
the polymer system. Boron nitride powder has been shown to be an excellent additive for coatings and release agents, as well as for oils, potting compounds, friction plates, etc.

In addition, the powder is white, clean, and safe-to-use directly as a high-temperature lubricant and release agent. The product typically enhances lubricity, chemical resistance, and thermal conductivity. Table 4.1 shows the comparison of boron nitride powder to other common fillers.

**Table 4.1: Comparison of boron nitride to common fillers**

<table>
<thead>
<tr>
<th></th>
<th>BN</th>
<th>AL₂O₃</th>
<th>ALN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity (W/m/K)</td>
<td>~300</td>
<td>40</td>
<td>50-170</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>4</td>
<td>9</td>
<td>9</td>
</tr>
</tbody>
</table>

**Fig. 4.2: The structure of boron nitride**

Figure 4.2 shows a typical structure for BN. Each boron atom is connected to four nitrogen atoms, and each nitrogen atom is connected to four boron atoms. The structure
of BN is similar to that of graphite. The average particle size and state of agglomeration of each type of boron nitride used in our study are summarized in Table 4.2.

Table 4.2: The average particle sizes and states of agglomeration properties of BN

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Particle size from SEM, approx. (µm)</th>
<th>Agglomerated</th>
<th>Agglomerated Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTF5</td>
<td>10</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>CTUF</td>
<td>3</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>AS 427</td>
<td>4</td>
<td>Yes</td>
<td>&gt;180</td>
</tr>
<tr>
<td>AS 428</td>
<td>1.5</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>AS 429</td>
<td>3</td>
<td>Yes</td>
<td>&gt;300</td>
</tr>
<tr>
<td>AS 430</td>
<td>20</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>AS 612</td>
<td>4</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>AS 614</td>
<td>12</td>
<td>No</td>
<td></td>
</tr>
</tbody>
</table>

4.3 Blend Preparation

It is noted that a uniform dispersion is a necessary condition for obtaining a good performance of processing aids (Yip, 1999; Rosenbaum et al, 2000). The following technique was used for blend preparation. The BN powders were mixed with appropriate amounts of the virgin resin. Then, a master batch of 10 wt % BN with ground PE was prepared by using a preparation mixer. A desired final concentration of a particular blend was obtained by mixing virgin ground PE with the master batch by means of a ¾” extruder equipped with a cooling system and a 2” pelletizer. This procedure results into a uniform dispersion of BN into the polymer. Some of the blends were prepared by means of a twin screw extruder. Both methods resulted into similar degree of dispersion.
5 Extrusion Studies using Boron Nitride

5.1 Introduction

Capillary Rheometer described in Chapter 2 is used for testing the polymer melt extrusion. It is also very useful equipment in studying the performance of different polymer processing aids in eliminating melt fracture. In addition, parallel plate rheometer has also been used to test the effect of processing aids on melt rheology during linear viscoelastic deformations. This chapter provides an overview of the experimental procedure employed to establish the performance of different grades of BN in controlling melt fracture.

5.2 Experimental Details

5.2.1 Capillary Rheometry

An Instron Capillary Rheometer, is used to extrude the blend of m-LLDPE and different grades of BN through a crosshead die – Nokia Maillefer 4/6, at 163 °C. Details of the Capillary Rheometer and Crosshead die are shown in Figure 2.1 and 2.4 respectively.

Compounding of BN in m-LLDPE is separately carried out in an extruder in two steps. In the first step, a master batch of 10% (w/w) BN with ground PE was prepared. A desired final concentration of 0.1% (w/w) BN was obtained by mixing the pure ground PE with the master batch in either a single screw or twin screw extruder. The blend was chopped using a 2” Palletizer.
These pallets of compounded BN in m-LLDPE are extruded through the capillary rheometer at different processing rates or plunger speed. The processing rate is measured in terms of shear rate as explained in the section 2.1.3, equation 2-12b. Performance of the PPA is measured in terms of critical shear rate (CSR), which is the maximum possible shear rate at which the polymer blend can be extruded without any melt fracture appearance.

5.2.2 Rotational Concentric Rheometry

A Rheometrics System IV parallel plate rheometer was used to study the possible effect of BN on the LLDPE melt Rheology. Linear oscillatory shear experiments were carried out as explained in section 2.1.4.

5.3 Results and Discussion

5.3.1 Capillary Rheometry

An exhaustive study of different BN grades, blended with m-LLDPE has been carried out by Kazatchkov et al (2000) and Seth et al (2001) using the above experimental technique. Figure 5.1 shows the flow curve of m-LLDPE Exact® 3128 obtained in capillary rheometer at 163 °C by using the crosshead die. The onset of surface melt fracture for virgin polymer is between 40 – 60 s⁻¹. The surface melt fracture is followed by gross melt fracture between 350 – 500 s⁻¹. There is no stick-slip region unlike capillary die, as explained in section 2.2.
Figure 5.1: Flow curve of PE - Exact® 3128 using capillary rheometer at 163 °C using crosshead die (Kazatchkov et al, 2000).

Figure 5.2 shows the flow curve of virgin and filled m-LLDPE Exact® 3128 with BN (CTF5) at different concentrations, obtained in capillary rheometer at 163 °C by using the crosshead die. It can be seen that by using 0.1% BN (CTF5), smooth extrudate can be obtained up to the CSR of 926 s\(^{-1}\). However, addition of BN did not have any effect on extrusion pressure or apparent shear stress.
Fig. 5.2: Flow curve of virgin and filled PE - Exact® 3128 with BN (CTF5) using capillary rheometer at 163 °C using crosshead die (Kazatchkov et al, 2000).

Figure 5.3 shows the extrudate samples obtained at 617 s⁻¹. It shows the severe gross melt fracture that is observed while extruding virgin mLLDPE, whereas smooth PE extrudates are obtained in the presence of 0.02% and 0.1% BN (CTF5).

Similar experiments have been carried out for the blend of mLLDPE and different grades of BN (0.1%) in order to estimate the performance of these BN samples in terms of critical shear rate, i.e. the maximum shear rate to which the polymer can be extruded without any melt fracture. Results of these experiments indicating the performance of different BN grades have been compiled in a decreasing order of CSR in Table 5.1.
Fig. 5.3: Extrudate samples of obtained at $617 \text{s}^{-1}$ and $163^\circ\text{C}$. 1) Virgin mLLDPE, 2) 0.02% BN, 3) 0.1% BN, 4) 0.5% of BN (CTF5) (Kazatchkov et al, 2000).

Table 5.1: Performance of different grades of BN

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Critical Shear Rate for extruding m-LLDPE at 163$^\circ$ C ($\text{s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 431</td>
<td>1080</td>
</tr>
<tr>
<td>AS 612</td>
<td>1049</td>
</tr>
<tr>
<td>CTF5</td>
<td>926</td>
</tr>
<tr>
<td>AS 614</td>
<td>617</td>
</tr>
<tr>
<td>AS 429</td>
<td>360</td>
</tr>
<tr>
<td>AS 428</td>
<td>300</td>
</tr>
<tr>
<td>AS 430</td>
<td>155</td>
</tr>
<tr>
<td>CTUF</td>
<td>155</td>
</tr>
<tr>
<td>AS 427</td>
<td>70</td>
</tr>
</tbody>
</table>

From the above experiments it is clear that not all BNs are effective PPAs, and that different grades of BN behave differently in eliminating melt fracture.
5.3.2 Rotational Concentric Rheometry

Linear viscoelastic oscillatory tests of virgin and filled m-LLDPE Exact® 3128 with different BN throw some light on the role of BN on melt rheology. Figure 5.4 shows a result of one such test carried out for m-LLDPE Exact® 3128 mixed with different concentrations of BN (CTF5).

![Figure 5.4: Linear viscoelastic data for m-LLDPE Exact® 3128 with and without BN (CTF5) (Kazatchkov et al, 2000).](image)

It is interesting to note that despite of BN’s ability to eliminate the melt fracture, it has little influence on the linear viscoelastic polymer melt rheology. The same observations have been made for all the other grades of BN except AS 431. 0.1% AS 431 in mLLDPE
has been found to have marginally lower storage and loss moduli (by as much as 12%) as compared to virgin mLLDPE. It also has a slightly lower extrusion pressure in capillary rheometry extrusion compared to other grades of BN (Kazatchkov et al, 2000; Yip, 2001). This reduction in pressure was reported to be a result of wall slip at the interface (Yip, 2001).

5.4 Conclusion

Different grades of BN have widely varying critical shear rates in the capillary rheometer extrusion. Therefore, it is clear that not all BNs are effective PPAs and they behave differently in eliminating melt fracture.

With the help of parallel plate rheometer, linear viscoelastic polymer melt rheology of different BN samples have been tested and it is found that all the samples of BN (except AS 431) have no effect on the rheology of mLLDPE.

In coming chapters we will analyze the surface properties of these BN grades in order to study their role in the performance (CSR) of BN as processing aid.
6 Surface Energy of Boron Nitride

6.1 Introduction

As discussed in the previous chapter, certain grades of BN are more successful in eliminating melt fracture as compared to others. The capacity of BN to eliminate melt fracture has been effectively characterized in terms of critical shear rate – the maximum possible shear rate at which polymer can be extruded without any melt fracture.

In a recent study Yip et al (2000) examined the effects of physical properties of BN, namely particle size, shape and degree of agglomeration on the ability of specific grades of BN in eliminating melt fracture. Seth et al (2001) measured surface energy (SE) of the various grades of BN and demonstrated an approximate relation between the ratio of dispersive and polar components of surface energy of BN powders to Critical Shear Rate.

The main objective of this work is to reanalyze the surface energy of the various grades of BN and make a comprehensive study of the effect of surface energy of BN on the processability of m-LLDPE. The specific objectives are as follows:

- Why different grades of BN have dissimilar influence on the appearance of melt fracture during m-LLDPE extrusion? Does surface energy play a role in determining the performance of these BN grades?
- Could the performance of BN and fluoropolymers be compared and explained on the basis of their surface energies?
6.2 Experimental Details and Results

As pointed out in the section 2.4, surface energy of a solid surface is most easily estimated from the contact angle of a liquid at the solid–liquid interface. This is because surface energy of solid and surface tension of liquid decide the contact angle at the interface and hence the wettability of liquid for the given surface.

Once the contact angle values are available for two different test liquids, they can be used in conjunction with a model for surface energy measurement. In the present case the Young & Good – Girifalco model (Geometric Mean approach) has been used to obtain the dispersive and polar components of the surface energy (Girifalco and Good, 1957; Owens and Wendt, 1969).

6.2.1 The Modified Washburn’s Capillary Rise Technique

Seth et al (2001) used a modified Washburn’s capillary rise method for obtaining SE data. The method was earlier developed and used by Liu and Laskowski (1996) for talc powders. In this method, a packed bed of BN powder in a glass tube was used with different liquids to obtain their penetration rate through the packed powder bed. A powder packing press, shown in Figure 6.1 was fabricated and used to compact the BN powder accurately to a pressure of 1.8 MPa, the pressure at which Seth et al (2001) found fair repeatability in the liquid penetration rate measurements. The glass tube used for compacting the BN powder was open from both the ends, having inside diameter of 14 mm and length of 95 mm. The piston of the powder packing press fits exactly inside the glass tube with a clearance of about 1 mm. A filter paper is glued at one end of the tube.
to hold the powder but at the same time, allows the liquid to penetrate through the bed of powder. Approximately 1 gram of BN powder is filled in to the glass tube and is packed using the powder packing press by using a pressure of 1.8 MPa.

![Diagram of Powder Packing Press](image)

**Fig. 6.1: Powder packing press**

Once the powder is packed into the glass tube at the desired pressure for about 10 minutes, the pressure is released and the packed glass column is carefully placed at the bottom of a sensitive weight scale for observing the penetration rate of the test liquid through the packed tube. The arrangement for measuring the liquid penetration rate through the packed glass tube is shown below in Figure 6.2.
The liquid bath is slowly moved up and brought in contact with the powder packed glass tube. The liquid penetration as a function of time is recorded by a computer interfaced with the sensitive electronic weight scale (Make: AND, model: GR 200).

The liquids used for the penetration rate measurements are methanol, water and α-bromonapthalene. These liquids do not dissolve the BN powder, and have relatively moderate viscosity and volatile.

Methanol is used initially as an ideal wetting liquid so that \( \cos \theta \) is assumed equal to 1 in equation (2-27), allowing the determination of tortuosity constant \( K' \) for the powder bed at the given packing pressure.
Knowing $K'$, $\cos \theta$ for other testing liquids can be estimated from their penetration rate by using equation 2-27. $\alpha$ - Bromonaphthalene, a nonpolar liquid, allows for the calculation of the dispersive component of the surface energy, whereas water, a polar liquid, allows for the determination of the polar component of surface energy at the solid/liquid interface. Surface energies, density and viscosity of all three liquids at 20 °C are given in Table 6.1.

**Table 6.1: Physical Constants for Test Liquids at 20 °C**

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\gamma$ (mJ/m²)</th>
<th>$\gamma^D$ (mJ/m²)</th>
<th>$\gamma^P$ (mJ/m²)</th>
<th>$\rho$ (kg/m³)</th>
<th>$\eta$ (mPa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>22.55</td>
<td>22.55</td>
<td>0</td>
<td>791</td>
<td>0.59</td>
</tr>
<tr>
<td>Water</td>
<td>72.6</td>
<td>21.6</td>
<td>51</td>
<td>1000</td>
<td>1.002</td>
</tr>
<tr>
<td>$\alpha$-Bromonaphthalene</td>
<td>44.6</td>
<td>44.6</td>
<td>0</td>
<td>1483</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Contact angle values obtained above were utilized to obtain surface energy components of the BN powder by using the Young and Good – Girifalco equation (Geometric mean approach) as shown earlier in equation 2-25:

\[
(1 + \cos \theta) = \frac{2}{\gamma_i}\left[\sqrt{\gamma^D_i \gamma^D_i} + \sqrt{\gamma^P_i \gamma^P_i}\right]
\]  

(2-25)
6.2.2 Results and Discussion – The Modified Washburn’s Capillary Rise Method

Based on his surface energy experiments Seth (2001) observed that BN powders having a high ratio of dispersive to polar component of SE were found as better PA with higher critical shear rate. Results obtained by Seth (2001) are summarized below in Table 6.2

Table 6.2: Surface energy results using capillary rise method (Seth et al, 2001)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\gamma^D$ (mJ/m²)</th>
<th>$\gamma^P$ (mJ/m²)</th>
<th>$\gamma$ (mJ/m²)</th>
<th>$\gamma^D/\gamma^P$</th>
<th>CSR for extruding mLLDPE @ 163°C (S⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS612</td>
<td>44.36</td>
<td>10.58</td>
<td>54.94</td>
<td>4.19</td>
<td>1049</td>
</tr>
<tr>
<td>CTF5</td>
<td>36.89</td>
<td>13.20</td>
<td>50.09</td>
<td>2.79</td>
<td>926</td>
</tr>
<tr>
<td>AS614</td>
<td>24.03</td>
<td>9.03</td>
<td>33.06</td>
<td>2.66</td>
<td>617</td>
</tr>
<tr>
<td>AS 429</td>
<td>23.08</td>
<td>16.34</td>
<td>39.43</td>
<td>1.41</td>
<td>360</td>
</tr>
<tr>
<td>AS 428</td>
<td>15.40</td>
<td>17.62</td>
<td>33.03</td>
<td>0.87</td>
<td>300</td>
</tr>
<tr>
<td>AS 430</td>
<td>20.35</td>
<td>30.10</td>
<td>50.45</td>
<td>0.68</td>
<td>155</td>
</tr>
<tr>
<td>CTUF</td>
<td>28.01</td>
<td>33.78</td>
<td>61.79</td>
<td>0.83</td>
<td>155</td>
</tr>
<tr>
<td>AS 427</td>
<td>16.98</td>
<td>32.95</td>
<td>49.93</td>
<td>0.52</td>
<td>70</td>
</tr>
</tbody>
</table>

It was however difficult to reproduce these results. Results obtained by following the above procedure, lacked consistency and showed large deviations for some grades of BN. A possible explanation for this inconsistent behaviour may be explained with the help of tortuosity constant – $K'$ of Washburn equation. $K'$ represents the degree of porosity and its distribution obtained in the process of packing the mass of powder. It is believed that after the packing pressure is lifted, the fine dust particles become relatively free for movement, and even a slightest disturbance could change the degree of porosity inside
the powder bed thereby changing the $K'$ value. It was also observed that some grades of BN powder beds developed minor cracks on absorption of liquid, which could lead to channeling thereby altering the penetration rate for the remaining liquid.

6.2.3 Measurement of Contact Angle using Sessile Drop Profile

The alternate way of measuring contact angle was to obtain contact angles directly from the magnified images of the liquid droplet, placed on the BN powder surface.

A smooth surface of BN was prepared by compacting the powder inside a hollow metallic ring of 1 inch nominal bore diameter. A pressure of 1.8 MPa was applied in compacting the powder. A drop of the test liquid (Water and α-Bromonaphthalene) was carefully formed on the BN surface using a fixed syringe. The major challenge with this arrangement was the rapid absorption of liquid droplet through the solid surface, leading to changing drop profile and hence the changing contact angle with time. In order to overcome this problem, the images were captured on a 3.3 MP CCD camera in the digital video format. The video was analyzed frame by frame to obtain the very first image of a stable droplet on the solid surface. This process helped in obtaining the images at ‘zero time’ so that the effect of liquid absorption on contact angles can be minimized. These ‘zero time’ images were magnified and used to measure the contact angle of the test liquid with the solid surface. Figure 6.3 shows a typical image of the water droplet placed on the BN surface.
Fig. 6.3: Close-up image of water droplet on BN surface

Figure 6.4 shows the experimental arrangement for obtaining sessile drop images for direct contact angle measurement.

Consistent values of contact angles were obtained for all the BN samples tried, with variation in contact angle limited between ± 5-7 %.
6.2.4 Results and Discussion – Direct Measurement of Contact Angle

Table 6.3 shows the contact angle values obtained by direct measurement using sessile drop profile. The contact angle values obtained by Seth (2001) using the capillary rise method are also listed below for comparison.

Table 6.3: Comparison of Contact Angles on BN surface using Direct Measurement and Capillary Rise Method

<table>
<thead>
<tr>
<th>BN Grade</th>
<th>Contacting Liquid</th>
<th>Contact Angle (°) by Direct Measurement</th>
<th>Contact Angle(°) by Capillary-Rise</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 431</td>
<td>1 Bromonaphthalene</td>
<td>34</td>
<td>Not Available</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>AS 612</td>
<td>1 Bromonaphthalene</td>
<td>40</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>70</td>
<td>55</td>
</tr>
<tr>
<td>CTF5</td>
<td>1 Bromonaphthalene</td>
<td>38</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>65</td>
<td>61</td>
</tr>
<tr>
<td>AS 614</td>
<td>1 Bromonaphthalene</td>
<td>34</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>57</td>
<td>70</td>
</tr>
<tr>
<td>AS 429</td>
<td>1 Bromonaphthalene</td>
<td>35</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>33</td>
<td>71</td>
</tr>
<tr>
<td>AS 428</td>
<td>1 Bromonaphthalene</td>
<td>35</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>44</td>
<td>77</td>
</tr>
<tr>
<td>AS 430</td>
<td>1 Bromonaphthalene</td>
<td>34</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>40</td>
<td>73</td>
</tr>
<tr>
<td>CTUF</td>
<td>1 Bromonaphthalene</td>
<td>35</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>38</td>
<td>67</td>
</tr>
<tr>
<td>AS 427</td>
<td>1 Bromonaphthalene</td>
<td>35</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>55</td>
<td>76</td>
</tr>
</tbody>
</table>
It can be seen that, for most of the cases, values obtained from capillary rise method are on the higher side than the corresponding contact angle values obtained by direct measurement. Another interesting observation is about the variation of contact angle values among different grades of BN by the two methods: with direct measurement, contact angle values are similar for α Bromonaphthalene with variations seen in water contact angle values whereas it is opposite with the capillary rise method.

Based on the above listed values of contact angles, surface energy of all the BN samples can be calculated using Young and Good – Girifalco equation (2-25). The surface energy values are compared below in Table 6.4. It can be seen that barring a couple of cases of CTF5 and CTUF, the agreement between the two methods is not very good.

Figures 6.5 and 6.6 depict the surface energy of different BN samples obtained using direct contact angle measurement, and their critical shear rate (CSR) for eliminating melt fracture in m-LLDPE respectively. From these two graphs, it can be seen that the Dispersive Surface Energy (DSE) is almost identical for all the grades of BN whereas the polar component varies. A relationship between the Polar Surface Energy (PSE) or Total Surface Energy (SE) and the Critical Shear Rate (CSR) can be observed for majority of the BN grades. A higher value of PSE (and SE) adversely affects the CSR whereas, a lower value of PSE and SE helps the extrusion process in obtaining a higher CSR. The two exceptions to this general trend are AS 427 and AS 429 grades of BN. Interestingly, both these grades of BN have significant degree of agglomeration, which prevents their uniform distribution within the base polymer.
Table 6.4: Comparison of Surface Energy of BN powders using Direct Measurement and Capillary Rise Method

<table>
<thead>
<tr>
<th>BN Grade</th>
<th>Surface Energy Component</th>
<th>Surface Energy (mJ/m²) by Direct Measurement</th>
<th>Surface Energy (mJ/m²) by Capillary-Rise Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 431</td>
<td>Dispersive</td>
<td>37.3</td>
<td>Not Available</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>12.2</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>49.5</td>
<td>&quot;</td>
</tr>
<tr>
<td>AS 612</td>
<td>Dispersive</td>
<td>34.9</td>
<td>44.4</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>8.9</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>43.8</td>
<td>55.0</td>
</tr>
<tr>
<td>CTF5</td>
<td>Dispersive</td>
<td>35.8</td>
<td>36.9</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>11.3</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>47.1</td>
<td>50.1</td>
</tr>
<tr>
<td>AS 614</td>
<td>Dispersive</td>
<td>37.4</td>
<td>24.0</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>14.9</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>52.3</td>
<td>33.0</td>
</tr>
<tr>
<td>AS 429</td>
<td>Dispersive</td>
<td>36.9</td>
<td>23.1</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>29.1</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>66.0</td>
<td>39.4</td>
</tr>
<tr>
<td>AS 428</td>
<td>Dispersive</td>
<td>37.1</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>23.0</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>60.1</td>
<td>33.0</td>
</tr>
<tr>
<td>AS 430</td>
<td>Dispersive</td>
<td>37.2</td>
<td>20.4</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>25.3</td>
<td>30.1</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>62.5</td>
<td>50.5</td>
</tr>
<tr>
<td>CTUF</td>
<td>Dispersive</td>
<td>36.9</td>
<td>28.0</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>26.5</td>
<td>33.8</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>63.4</td>
<td>61.8</td>
</tr>
<tr>
<td>AS 427</td>
<td>Dispersive</td>
<td>37.1</td>
<td>17.0</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>16.6</td>
<td>33.0</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>53.7</td>
<td>50.0</td>
</tr>
</tbody>
</table>
THE EFFECT OF SURFACE PROPERTIES OF BORON NITRIDE ON POLYMER PROCESSABILITY

Fig. 6.5: Surface Energy of BN Samples

Fig. 6.6: Critical Shear Rate of BN Samples
Thus if the above two grades of BN having agglomerations, are ignored then a correlation of critical shear rate as a function the surface energy can be obtained. Specifically it can be seen from Figure 6.7 that the critical shear rate for the onset of melt fracture can be correlated with either the inverse of polar surface energy (black circle) or the inverse of the total surface energy (white triangles).

![Fig. 6.7: CSR vs. 1/SE for BN Samples](image-url)
Linear regression coefficients for Total Surface Energy and Polar Surface Energy plots are 0.90 and 0.89 respectively.

Although the surface energy values obtained by the two methods are significantly different, it is interesting to note that the correlation made by Seth et al (2001) about the ratio of dispersive to polar surface energy and CSR is still being validated. It was observed by him that higher the ratio of dispersive to polar surface energy, higher is the CSR for onset of melt fracture. As per our above observations, CSR is favored by the lower polar surface energy and since the dispersive component is unchanged for all the grades of BN, it can be inferred that higher ratio of dispersive to polar surface energy favors higher CSR.

6.3 Comparison of BN with Fluoropolymers

From the above observations, it can be inferred that the lower polar surface energy enhances BN as a processing aid, thus increasing the CSR for the appearance of melt fracture. However, when it is tried to extend this apparently obvious generalization to other successful processing aids like fluoropolymers, an intricate relationship between surface energy and the performance of processing aids in terms of critical shear rate is observed. In other words, this generalization can not be made for all the processing aids.

Figure 6.8 compares the surface energy of PTFE (a known processing aid for polyethylene extrusion) with BN grades AS 612 and CTUF with their critical shear rate values mentioned alongside. As can be seen PTFE has an extremely low surface energy
with no polar component. Therefore, from the above generalization, it is expected that PTFE should provide a greater critical shear rate than any of the BN samples. However, in practice, PTFE has a higher critical shear rate than CTUF but lower than the AS 612 sample. In other words, PTFE is effective in eliminating SMF but has little effect on the GMF.

In order to understand the role of surface energy clearly in the above two cases, it was decided to find out the possible interactions of these processing aids with the polymer melt and the die wall during the extrusion process. First, the surface energy of the die material and the LLDPE were obtained. Table 6.5 lists the surface energy of these materials along with BN – AS 612 (better grade BN) and CTUF (worse grade BN) for comparison.

![Surface Energy and CSR values](image)

**Fig. 6.8:** Comparison between surface energy of BN and Fluoropolymer and their performance in terms of critical shear rate. CSR values reported by *Rosenbaum, 1998; Seth, 2001*
THE EFFECT OF SURFACE PROPERTIES OF BORON NITRIDE ON POLYMER PROCESSABILITY

Having obtained surface energy data for all the materials involved in the extrusion process, the Young and Good – Girifalco equation (2-25) was used to find the level of interaction between any two materials at a given time. Substituting the values of surface energy components for any two materials into equation (2-25) provides a calculated contact angle between them. This contact angle might not have any physical significance for two interacting solids, however, it can be quite useful in comparing relative affinity between two interacting surfaces. Table 6.6 indicates the results of this analysis. It can be observed that $\cos \theta$ value for LLDPE and PTFE is the smallest. This is indicated as 0 affinity in Table 6.6. The relative affinity between other surfaces is estimated from their $\cos \theta$ value as a percentage of the minimum $\cos \theta$ value of 0.39, found for LLDPE / PTFE interface.

**Table 6.5: Surface energy of different materials involved in m-LLDPE extrusion**

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Energy Component</th>
<th>Surface Energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN – AS 612</td>
<td>Dispersive</td>
<td>34.9</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>43.8</td>
</tr>
<tr>
<td>BN – CTUF</td>
<td>Dispersive</td>
<td>36.9</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>26.5</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>63.4</td>
</tr>
<tr>
<td>PTFE</td>
<td>Dispersive</td>
<td>17.7</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>17.7</td>
</tr>
<tr>
<td>mLLDPE</td>
<td>Dispersive</td>
<td>27.6</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>31.7</td>
</tr>
<tr>
<td>SS Die</td>
<td>Dispersive</td>
<td>43.1</td>
</tr>
<tr>
<td></td>
<td>Polar</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>58.1</td>
</tr>
</tbody>
</table>
Table 6.6: Level of interactions between different surfaces involved in the extrusion

<table>
<thead>
<tr>
<th>Material 1</th>
<th>Material 2</th>
<th>COS $\theta$</th>
<th>Affinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE</td>
<td>PTFE</td>
<td>0.39</td>
<td>0</td>
</tr>
<tr>
<td>LLDPE</td>
<td>BN-1</td>
<td>1.34</td>
<td>244</td>
</tr>
<tr>
<td>LLDPE</td>
<td>BN-6</td>
<td>1.67</td>
<td>328</td>
</tr>
<tr>
<td>PTFE</td>
<td>SS Die</td>
<td>2.12</td>
<td>444</td>
</tr>
<tr>
<td>BN-1</td>
<td>SS Die</td>
<td>1.30</td>
<td>233</td>
</tr>
<tr>
<td>BN-6</td>
<td>SS Die</td>
<td>0.89</td>
<td>128</td>
</tr>
</tbody>
</table>

It may also be noted that for some combinations of surfaces, the $\cos \theta$ value is greater than 1. This has no mathematical significance, and it can be possible due to the values of surface energy used in the model. A high $\cos \theta$ means a very high affinity between the two interacting surfaces and the use of relative affinity term helps in quantifying the degree of interaction between these surfaces.

Figure 6.9 shows the above relative affinity values in the form of a schematic diagram. It can be seen that PTFE has very high affinity for die wall but extremely low affinity for the extruding polymer. Thus during the extrusion process, PTFE migrates towards the wall and allows LLDPE melt to slip over its surface – thereby eliminating the sharkskin effectively. This inference is in agreement with the microscopic flow visualization observations made by Migler et al (2001).
BN - AS 612 sample has approximately equal affinity for both die wall as well as extruding LLDPE polymer and therefore it can provide effective lubrication at both the surfaces because of its lubricious, layered lattice structure. The die wall lubrication helps to eliminate the SMF and the polymer melt lubrication helps in overcoming polymer - polymer melt friction in the die entrance region for controlling the GMF.

BN - CTUF sample has a very high affinity for the LLDPE and therefore it can provide effective lubrication within the polymer melt because of its lubricious nature. However, due to its poor affinity for the die wall, it fails to lubricate the die surface during extrusion process and therefore fails prematurely as processing aid by the occurrence of SMF.

Having obtained this background about the surface energy and relative affinity among different interacting materials in the extrusion process, the important differences in the behavior of fluoropolymers (FP) and BN can be summarized as follows.
• FP is a low surface energy, non polar in nature. BN powders have moderate surface energy and are mildly polar.

• FP has high affinity for die wall, whereas BN has relatively low affinity for wall and higher affinity for the extruding polymer depending on its polarity.

• Lubricating effect of FP is because of their low surface energy and non polar nature. Whereas the lubricating effect of BN is due to their layered lattice structure.

• FP eliminates sharkskin but fails to overcome GMF. Low surface energy BN, which survives sharkskin, goes long way in extending the GMF. Higher surface energy BN however, fails prematurely in the sharkskin region.

• In short, FP behaves as an external lubricant between the polymer melt and the die wall (useful for instability in the die exit region). Whereas BN is more effective as an internal lubricant for removing friction from the bulk of the polymer melt (useful for instability in the die entrance region).

6.4 Combination of BN and Fluoropolymer

From the above hypothesis, it appears that in general the strength of BN lies in lubricating the polymer melt and eliminating the gross melt fracture. The high surface energy grade of BN (CTUF) fails to lubricate the die wall and hence fails prematurely in the sharkskin region. However, this grade of BN has higher affinity to PE melt and it is likely that it may be able to eliminate the gross melt fracture effectively if sharkskin melt fracture is taken care of by an independent processing aid.
THE EFFECT OF SURFACE PROPERTIES OF BORON NITRIDE ON POLYMER PROCESSABILITY

In order to test this hypothesis, it was decided to test the two grades of BN, one with low surface energy (CTF5) and the other being higher surface energy (CTUF) in combination with fluoropolymer (Dynamar – FX 9613) in capillary rheometry using the crosshead die at 163 °C. BN was compounded within the LLDPE melt using master batch technique as explained in section 5.2.1 whereas fluoropolymer was dry mixed with the sample. Capillary rheometry experiments for extrusion studies are explained in section 5.2.1. The results of these tests are depicted in the Table 6.7 to show the effectiveness of the combined processing aid in eliminating melt fracture in LLDPE.

Table 6.7: Effect of combining BN and fluoropolymer in LLDPE extrusion at 163 °C

<table>
<thead>
<tr>
<th>Processing Aid</th>
<th>Shear Rate (s⁻¹)</th>
<th>327</th>
<th>655</th>
<th>982</th>
<th>1309</th>
<th>1636</th>
<th>1964</th>
<th>2291</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td></td>
<td>SS</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>0.1% D</td>
<td></td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>SS</td>
<td>SS</td>
<td>SSS</td>
<td>SSS</td>
</tr>
<tr>
<td>0.1% D + 0.1% BN1</td>
<td></td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>SS</td>
<td>SSS</td>
<td>SSS</td>
</tr>
<tr>
<td>0.1% D + 0.5% BN1</td>
<td></td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>MS</td>
<td>SS</td>
<td>SS</td>
</tr>
<tr>
<td>0.1% D + 0.1% BN2</td>
<td></td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>MS</td>
<td>SS</td>
<td>SS</td>
<td>SS</td>
</tr>
<tr>
<td>0.1% D + 0.5% BN2</td>
<td></td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>MS</td>
<td>SS</td>
<td>SS</td>
<td>SS</td>
</tr>
</tbody>
</table>

D Dynamar – FX 9613  S Smooth
BN1 CTF5              MS Minor Streaks
BN2 CTUF             SS Sharkskin
                      SSS Severe Sharkskin
                      G Gross Melt Fracture
Based on the above experiment of combining BN with fluoropolymer as processing aid, following three important observations can be made.

- It may be observed that Dynamar – FX 9613 alone is quite effective in eliminating sharkskin up to 982 s$^{-1}$.
- When Dynamar is combined with low surface energy BN (CTF5), there is significant increase in the critical shear rate from 982 to 1309 s$^{-1}$. Addition of the high surface energy BN (CTUF) has minor improvement on melt fracture as the sharkskin observed by Dynamar alone at 1309 s$^{-1}$ is converted into minor streaks.
- At very high processing rate (1964 s$^{-1}$ and higher) Dynamar alone and combination of Dynamar and CTF5 show very severe sharkskin – close to gross melt fracture. However, combination of Dynamar and high surface energy BN (CTUF) is able to reduce the severity of sharkskin at these high shear rates.

Thus it may be inferred that when low surface energy BN (CTF5) is combined with an effective external lubricant such as fluoropolymer (Dynamar – FX 9613), sharkskin elimination capacity of the combination is improved. Whereas combining high surface energy BN (CTUF) with fluoropolymer (Dynamar – FX 9613) can be effective in reducing the severity of sharkskin or gross melt fracture at very high processing rates.

6.5 Conclusion

Surface energy data obtained using direct contact angle measurements are consistent and especially useful for relative comparison of different grades of BN as compared to Washburn’s capillary rise method.
Surface energy plays an important role in determining the suitability of a given BN sample as a successful PPA. It is the polar component of surface energy which influences the critical shear rate during extrusion process. The dispersive components of all the BN samples tested were found to be similar, implying that it has little effect on CSR during extrusion.

Although surface energy values obtained by direct contact angle measurement are quite different from those estimated by the capillary rise method, it indirectly confirms the conclusion drawn by Seth et al (2001) about the ratio of dispersive to polar surface energy as a governing factor for the performance of BN in extending the critical shear rate.

When performance and surface energy of BN are compared with those of fluoropolymers (PTFE), interesting observations are made, emphasizing the importance of surface energy in their interaction with the polymer melt and the extruding wall which, in turn decides its suitability as a polymer processing aid. More specifically,

- Low surface energy and low polarity are desired for effective interaction with die wall in the sharkskin region.
- Higher surface energy and polarity are helpful for positive interaction with polymer melt in the GMF region.
- Lubricious nature of BN along with an optimum balance of surface energy and polarity makes AS-612 and CTF5 successful in both sharkskin and GMF regions.
Combination of low surface energy BN (CTF5) with fluoropolymer (Dynamar – FX 9613) is effective in extending the CSR as they effectively eliminate the sharkskin.

High surface energy BN (CTUF) when combined with floropolymer (Dynamar – FX 9613) does not extend the CSR as it is not effective in eliminating sharkskin. However, it does reduce the severity of melt fracture at very high processing rates.
7 Adsorption Capacity of Boron Nitride

7.1 Introduction

In order to understand and explain the different behaviour of different grades of BN, it was thought to carry out adsorption experiments of PE onto the BN particles so that the adsorption capacity of BN can be studied and correlated to their performance in extrusion experiments.

It is observed and believed that the grades of BN which are effective as processing aids, are effective in eliminating gross melt fracture in the die entrance region, where they lubricate the bulk of polymer melt. Therefore, it may be assumed that these grades of BN should have better affinity for polymer melt. This affinity of BN for polymer melt may be quantified with the help of adsorption experiments by trying to measure the adsorption capacity of each BN sample to selectively adsorb mLLDPE from its solution.

Thus the main objective of the adsorption experiment was to study the selective adsorption or removal of mLLDPE from its solution using different samples of BN.

7.2 Experimental Details

The adsorption experiment involved three steps: 1) Preparation of a solution of mLLDPE. 2) Mixing of the solution with a specific grade of BN and providing sufficient standing time for the mixture to reach adsorption equilibrium. 3) Separation of BN particles and adsorbed mLLDPE from the solution by filtration. The adsorbed PE can be estimated from the change in weight of the BN.
PE is soluble in some of the solvents such as n-hexane, carbon tetra chloride and diphenyl ether above their theta temperatures – ranging between 130 – 160 °C. Diphenyl ether (DPE) was chosen for dissolving PE since n-hexane and CCl₄ turn into vapours at the desired theta temperature and atmospheric pressure.

A low concentration solution (1 – 3 %) of mLLDPE was then prepared in a glass flask with closed lid at a controlled temperature of 160 °C in an oven. A higher concentration of PE makes the solution extremely viscous and difficult to handle as a liquid. Temperature control of the solution was also critical throughout the experiment, since the PE precipitates back into solid phase below the theta temperature of 160 °C.

PE solution was mixed with a fixed amount of different grades of BN powders. Adsorption of PE on BN was allowed by maintaining the mixture at controlled temperature for sufficiently long time (24 hours) with frequent stirring in between.

After allowing the mixture to be in contact for a residence time of about 24 hours, the solution was filtered at 160 °C to separate out the solid BN particles and any adsorbed PE. A filter assembly, made of steel was fabricated for the filtration purpose as shown in the Figure 7.1. The filter can be split into two halves and a suitable filtering media can be used for the filtration process. In this case, Whatman® filter papers have been used as filtering media. Before the filtration process, the assembled filter is kept in the oven for at least 30 minutes at 160 °C to get it conditioned to the operating temperature. This will
prevent the dissolved PE from precipitating by coming in contact with the cooler walls of the filter. Even during the filtration process, the filter assembly is kept in the oven.

![Filter Assembly Diagram](image)

**Fig. 7.1:** Filter assembly used for separating BN and adsorbed mLLDPE

Once filtration is over, the filter media is taken out of the filter assembly. The DPE solvent is then evaporated from the filter media at slightly higher temperature in the same oven. The amount of PE adsorbed on BN can be estimated by measuring the weight gain over the initial weight of BN and the dry filter media.

Experiments were performed for 3 different concentrations of PE in DPE and with 5 grades of BN powders. Finally, the adsorption isotherm was generated by plotting the amount of PE adsorbed on BN vs. the equilibrium concentration of PE in DPE.

**7.3 Results and Discussion**

The results of the adsorption experiments can be compared for the 5 samples of BN by generating the Freundlich isotherm on a log – log scale (Figure 7.2) so that it can be approximately represented as a straight line using Freundlich’s equation (2-31).
\[
\ln Q_e = \ln K_F + n \ln C_e
\]  
(2-31)

where,

\(Q_e\) = Adsorption density at equilibrium (mg of adsorbate per g of adsorbent)

\(C_e\) = Concentration of adsorbate in solution at equilibrium (mg/l)

\(K_F\) and \(n\) are the empirical constants, dependent on several environmental factors

**Fig. 7.2:** Freundlich Adsorption Isotherm for BN
Freundlich index for the five specific grades of BN powders are determined from the above Adsorption Isotherm and listed in the following Table 7.1 along with the dispersive and non-dispersive components of surface energy of these samples and the corresponding critical shear rate for onset of gross melt fracture.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Critical Shear Rate ($S^{-1}$)</th>
<th>$\gamma^D$ (mJ/m$^2$)</th>
<th>$\gamma^{ND}$ (mJ/m$^2$)</th>
<th>Freundlich Index ($n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 612</td>
<td>1049</td>
<td>34.9</td>
<td>8.9</td>
<td>1.24</td>
</tr>
<tr>
<td>CTF5</td>
<td>926</td>
<td>35.8</td>
<td>11.3</td>
<td>1.52</td>
</tr>
<tr>
<td>AS 614</td>
<td>617</td>
<td>37.4</td>
<td>14.9</td>
<td>1.46</td>
</tr>
<tr>
<td>CTUF</td>
<td>155</td>
<td>36.9</td>
<td>26.5</td>
<td>1.64</td>
</tr>
<tr>
<td>AS 427</td>
<td>70</td>
<td>37.1</td>
<td>16.6</td>
<td>1.33</td>
</tr>
</tbody>
</table>

Table 7.1: Freundlich Index and SE for BN

These results show that the adsorption capacities of BN for PE are not as sensitive as their surface energy. It is also observed that the error associated with repeated adsorption experiments is sometimes in the excess of 20 % (more than the variations obtained between different grades of BN). However, it appears that in general, the extent of adsorption of PE onto BN surface is high. This validates the earlier inference made regarding the high affinity of BN for PE melt. It also suggests that during extrusion, PE molecules which are adsorbed on the surface of the BN particles, incorporate BN into the bulk of the polymer system forming a possible network. This network of PE and BN could help in smoothening the discontinuous flow streams observed in the die entry region (Figure 2.11) of grossly fractured extrudate.
7.4 Adsorption of Fluoropolymer on BN

Using the experimental technique outlined in section 7.3, it is also possible to test the adsorption capacity of BN for fluoropolymer such as Dynamar – FX 9613. Dynamar is soluble in acetone, therefore a low concentration solution of Dynamar (1 – 3 %) in acetone was prepared and was allowed to get adsorbed on the two grades of BN (CTF5 and CTUF). Filtration of BN and any adsorbed Dynamar was carried out at low temperature of about 5 °C to minimize evaporation of acetone during filtration. Adsorption isotherm for this experiment is shown in Figure 7.3.

![Freundlich Adsorption Isotherm for Fluoropolymer – BN](image)

**Fig. 7.3:** Freundlich Adsorption Isotherm for Fluoropolymer – BN
The Freundlich Index (n) for adsorption of Dynamar – FX 9613 on BN CTF5 and BN CTUF have been found to be 1.24 and 1.56 respectively. Again error associated with the repeated experiments is found to be higher, ~ 20%.

### 7.5 Conclusion

From the preliminary experiments carried out, it appears that adsorption experiments for low concentration solutions of m-LLDPE onto BN powders are not very effective in assessing the different grades of BN for their melt fracture eliminating capacities. However, the experiments imply that PE gets readily adsorbed onto the BN surface. It is also observed that the adsorption capacity of BN for fluoropolymer (Dynamar – FX 9613) is comparable to LLDPE.
8 Summary

LLDPE extrusion experiments were carried out using capillary rheometer in order to characterize the performance of different PPAs including a variety of BN samples in eliminating melt fracture. These experiments provided the basis for further analysis into surface properties of PPAs in order to understand their differing performances in overcoming melt fracture.

Two important surface properties namely surface energy and adsorption capacity of several BN grades were estimated. Surface energy was estimated using Washburn's capillary rise method as well as through direct contact angle measurement using the sessile drop images. It was observed that surface energy data obtained using direct contact angle measurements are consistent and especially useful for relative comparison of different grades of BN as compared to Washburn's capillary rise method.

Surface energy plays an important role in determining the suitability of a given BN sample as a successful PPA. It is the polar component of surface energy, which influences the critical shear rate during extrusion process. The dispersive components of all the BN samples tested were found to be similar, implying that it has little effect on CSR during extrusion.

Although surface energy values obtained by direct contact angle measurement are quite different from those estimated by capillary rise method, it indirectly confirms the conclusion drawn by Seth et al (2001) about the ratio of dispersive to polar surface
energy as a governing factor for the performance of BN in extending the critical shear rate.

When performance and surface energy of BN are compared with those of fluoropolymers, interesting observations are made, emphasizing the importance of surface energy in their interaction with the polymer melt and the extruding wall which, in turn decides its suitability as a polymer processing aid. More specifically,

- Low surface energy and low polarity are desired for effective interaction with die wall in controlling the sharkskin. This is the probable reason for the success of fluoropolymers in the SMF region.
- Higher surface energy and polarity are helpful for positive interaction with polymer melt in the GMF region.
- Lubricious nature of BN along with an optimum balance of surface energy and polarity makes AS-612 and CTF5 successful in both sharkskin and GMF regions. Whereas high surface energy BN samples such as CTUF, AS-430 etc. fail prematurely in overcoming sharkskin.

Adsorption studies indicate that adsorption capacities of BN for PE are not as sensitive as their surface energy. It appears that adsorption experiments for low concentration solutions of mLLDPE onto BN powders are not very effective in characterising different grades of BN for their melt fracture eliminating capacities. However, overall results indicate that PE gets readily adsorbed to the BN surface. This could be a way of finding out other polymers for which BN might work as a processing aid.
THE EFFECT OF SURFACE PROPERTIES OF BORON NITRIDE ON POLYMER PROCESSABILITY

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THE EFFECT OF SURFACE PROPERTIES OF BORON NITRIDE ON POLYMER PROCESSABILITY

Nomenclature

- \( b \) Rabinowitsch correction
- \( D \) capillary diameter, m
- \( d \) tip diameter, m
- \( e \) Bagley end correction or energy
- \( F_d \) piston force, lb
- \( g \) gravitational acceleration, m/s\(^2\)
- \( G \) shear modulus, Pa
- \( G' \) storage modulus, Pa
- \( G'' \) loss modulus, Pa
- \( G^* \) complex modulus, Pa
- \( h \) gap between plates, m
- \( h \) liquid penetration distance in capillary, mm
- \( K \) power-law consistency index, MPa \( \cdot \) s\(^n\)
- \( K \) tortuosity constant
- \( K' \) geometric factor
- \( K_F \) Freundlich constant
- \( K_L \) Langmuir constant, l of adsorbent / mg of吸附质
- \( L \) capillary length or length of sample, m
- \( n \) power-law exponent
- \( n \) Freundlich index
- \( P \) absolute pressure, Pa
- \( P_a \) ambient pressure, Pa
- \( P_d \) driving pressure, Pa
- \( \Delta P_{\text{end}} \) Bagley correction, Pa
- \( \Delta P_{\text{ex}} \) exit pressure drop, Pa
THE EFFECT OF SURFACE PROPERTIES OF BORON NITRIDE ON POLYMER PROCESSABILITY

\( \Delta P_{\text{ent}} \) entrance pressure drop, Pa

\( Q \) volumetric flow rate, m\(^3\)/s

\( r \) capillary radius, m

\( R_b \) radius of barrel, in

\( T \) absolute temperature, K

\( t \) time, s

\( u \) melt velocity, m/s

\( u_s \) slip velocity, m/s

\( W_t \) total weight of column

\( \Delta w \) difference of penetration weight, gm

\( \Delta x \) plate displacement, m

Greek Letters

\( \alpha \) pressure coefficient of viscosity, Pa\(^{-1}\)

\( \beta \) geometrical parameter for shear stress distribution

\( \delta \) mechanical loss angle

\( \gamma \) shear strain

\( \dot{\gamma} \) shear rate, s\(^{-1}\)

\( \dot{\gamma}_A \) apparent shear rate, s\(^{-1}\)

\( \dot{\gamma}_{A,s} \) apparent shear rate, corrected for slip, s\(^{-1}\)

\( \dot{\gamma}_w \) wall shear rate, s\(^{-1}\)

\( \gamma_0 \) strain amplitude in oscillatory shear

\( \gamma_s \) surface energy of solid

\( \gamma_i \) surface tension of liquid

\( \gamma_{sl} \) interfacial tension between solid and liquid

\( \gamma_{lv} \) interfacial tension between liquid and vapor
THE EFFECT OF SURFACE PROPERTIES OF BORON NITRIDE ON POLYMER PROCESSABILITY

$\gamma_{sv}$  interfacial tension between solid and vapor
$\gamma^D$  dispersive component of surface energy, $\text{mJ/m}^2$
$\gamma^P$  polar component of surface energy, $\text{mJ/m}^2$
$\mu$  viscosity of liquid, $\text{mPa}\cdot\text{s}$
$\rho$  density of liquid, $\text{kg/m}^3$
$\theta$  liquid contact angle on solid surface
$\eta$  viscosity, $\text{Pa}\cdot\text{s}$
$\eta_0$  zero-shear viscosity, $\text{Pa}\cdot\text{s}$
$\eta^*$  complex viscosity, $\text{Pa}\cdot\text{s}$
$\sigma_c$  critical shear stress for the onset of melt fracture, $\text{Pa}$
$\sigma_w$  wall shear stress, $\text{Pa}$
$\sigma_0$  stress amplitude in oscillatory shear, $\text{Pa}$
$\omega$  frequency, $\text{rad/s}$ or specific volume, $\text{cm}^3/\text{g}$