The Effect of Process Parameters on the Mechanical and Optical Properties of Cast Film

# The Effect of Process Parameters on the Mechanical and Optical Properties of Cast Film

By

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**A Project Report** 

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#### ABSTRACT

This project will examine the effect of process parameters on the properties of a semi-crystalline cast film. The objective was to conduct the experiment on a commercial scale extruder. The process parameters studied were the chill roll temperature, annealing roll temperature, film thickness and line speed. The intent of this project was not to develop a deterministic model for the casting process, but only to investigate the effect of process parameters on the properties of cast films manufactured on a commercial extrusion line.

The film properties evaluated were the tensile strength at break, Young's modulus, elongation at break, and haze. Only the properties in the machine direction (MD) were evaluated. The experimental data was first analyzed by plotting the average film properties against the average normalized process parameters. A second analysis was done with the experimental data by using multivariate data analysis (MVDA). Two multivariate data analysis (MVDA) projected methods were used, these were the partial projection to latent structure (PLS) by means of partial least squares, and the principal component analysis (PCA). The results from the first and second analysis showed that the changes in process parameters affected the properties of the cast films. It is conjectured that the effect of process parameters on semi-crystalline cast film properties are related to the percentage of crystallinity and crystal size. The manipulation of process parameters would change the percentage of crystallinity and crystal size, which in turn modify the properties of cast film.

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## **TABLE OF CONTENTS**

	Page
ABSTRACT	iv
ACKNOWLEDGEMENTS	vi
TABLE OF CONTENTS	vii
LIST OF FIGURES	ix
LIST OF TABLES	xi
LIST OF ABBREVIATIONS	xii

ł

CHAPTER 1 INTRODUCTION	
CHAPTER 2 REVIEW OF THE LITERATURE	9
2.1 Introduction	9
2.2 Publications	10

СНА	PTER 3 DESCRIPTION OF EXPERIMENT	22
3.1	Introduction	22
3.2	Experimental Procedures	23
3.3	Mechanical and Optical Characterization of the Cast Film Samples	28
3.4	Experimental Data Analysis	32

CHAPTER 4 MULTIVARIATE DATA ANALYSIS		53
4.1	Introduction	53
4.2	Process Parameters-Structure- Properties (PP-S-P) Relationship	54
4.3	Principal Component Analysis (PCA)	55

4.3.1	PCA on the X's (Process Parameters)	56
4.3.2	PCA – Score and Loading Plots for the Process Parameters	57
4.3.3	PCA on the Y's (Film Properties)	61
4.3.4	PCA – Score and Loading Plots for the Film Properties	63
4.4	Projection to Latent Structures (PLS) Analysis on the X's and Y's	66
4.4.1	PLS- Score and Loading Plots	67
4.4.2	PLS-Regression Coefficient Plots of the Film Properties	71

СНА	PTER 5: DISCUSSION, CONCLUSIONS, RECOMMENDATIONS	80
5.1	Discussion and Conclusions	80
5.2	Recommendations for Further Work	85

REFERENCES	 	 86

A	PPENDIX A	89
	Unit variance scaled and mean centered of the experimental data	89
	Process parameters, calculated score values	95
	Film properties, calculated score values	101
	Film properties and Process parameters, calculated score values	107

Figure 3.1	Sketch of the casting unit, showing casting rolls, coat-	25
	hanger die, and air knife	
Figure 3.2	Plot of average tensile strength at break against average	33
	normalized chill roll temperature	
Figure 3.3	Plot of average Young's modulus against average	34
	normalized chill roll temperature	
Figure 3.4	Plot of average tensile strength at break (MD) against	35
	average normalized annealing roll temperature	
Figure 3.5	Plot of average Young's modulus against average	36
	normalized annealing roll temperature	
Figure 3.6	Plot of average log (haze) against average normalized chill	37
	roll temperature	
Figure 3.7	Plot of average log (haze) against average normalized	38
	annealing roll temperature	
Figure 3.8	Plot of average elongation at break against average	39
	normalized chill roll temperature	
Figure 3.9	Plot of the elongation at break (MD) against average	40
	normalized annealing roll temperature	
Figure 3.10	Plot of average tensile strength at break against average	41
	normalized film thickness	
Figure 3.11	Plot of average Young's modulus against average	42
	normalized film thickness	
Figure 3.12	Plot of average elongation at break against average	43
	normalized film thickness	
Figure 3.13	Plot of average log (haze) against average normalized	44
	film thickness	
Figure 3.14	Plot of average tensile strength at break against	
	average normalized line speed	45

normalized line speedFigure 3.16Plot of average elongation at break against average normalized line speed47Figure 3.17Plot of average log (Haze) against average normalized line speed48Figure 4.1Flow chart for Process Parameters-Structure- Properties (PP-S-P) Relationship55Figure 4.2Model overview plot of the PCA on the Process Parameters57Figure 4.3PCA - Score plot for the Process Parameters58Figure 4.4PCA - Loading plot for the Process Parameters59Figure 4.5Model overview plot of the PCA on the Film Properties62Figure 4.6PCA - Loading plot for the Process Parameters59Figure 4.7PCA - Loading plot for the Film Properties64Figure 4.8Overview plot of the PLS on the Process Parameters and Film Properties65Figure 4.10PLS - Score plot on the Film Properties67Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for Young's modulus75Figure 4.13Regression coefficient plot for haze77Figure 4.14Regression coefficient plot for haze77Figure 4.14Regr	Figure 3.15	Plot of average Young's modulus against average	46
Figure 3.16 Plot of average elongation at break against average normalized line speed 47   Figure 3.17 Plot of average log (Haze) against average normalized line speed 48   Figure 4.1 Flow chart for Process Parameters-Structure-Properties (PP-S-P) Relationship 55   Figure 4.2 Model overview plot of the PCA on the Process Parameters 57   Parameters 58   Figure 4.3 PCA - Score plot for the Process Parameters 59   Figure 4.4 PCA - Loading plot for the Process Parameters 62   Figure 4.5 Model overview plot of the PCA on the Film Properties 62   Figure 4.3 PCA - Score plot for the Film Properties 64   Figure 4.4 PCA - Loading plot for the Film Properties 65   Figure 4.4 PCA - Loading plot for the Film Properties 65   Figure 4.7 PCA - Loading plot for the Film Properties 65   Figure 4.8 Overview plot of the PLS on the Process Parameters and Film Properties 67   Figure 4.10 PLS - Score plot on the Film Properties 67   Figure 4.11 Regression coefficient plot for tensile strength at break 73   Figure 4.12 Regression coefficient plot for percentage elongation at break		normalized line speed	
normalized line speed48Figure 3.17Plot of average log (Haze) against average normalized line speed48Figure 4.1Flow chart for Process Parameters-Structure- Properties (PP-S-P) Relationship55Figure 4.2Model overview plot of the PCA on the Process Parameters57Figure 4.3PCA - Score plot for the Process Parameters58Figure 4.4PCA - Loading plot for the Process Parameters59Figure 4.5Model overview plot of the PCA on the Film Properties62Figure 4.6PCA - Loading plot for the Process Parameters64Figure 4.7PCA - Loading plot for the Film Properties65Figure 4.8Overview plot of the PLS on the Process Parameters and Film Properties66Figure 4.9PLS - Score plot on the Film Properties67Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79	Figure 3.16	Plot of average elongation at break against average	47
Figure 3.17 Plot of average log (Haze) against average normalized line speed 48   Figure 4.1 Flow chart for Process Parameters-Structure- Properties (PP-S-P) Relationship 55   Figure 4.2 Model overview plot of the PCA on the Process Parameters 57   Figure 4.3 PCA - Score plot for the Process Parameters 58   Figure 4.4 PCA - Loading plot for the Process Parameters 59   Figure 4.5 Model overview plot of the PCA on the Film Properties 62   Figure 4.6 PCA - Score plot for the Film Properties 64   Figure 4.7 PCA - Loading plot for the Film Properties 65   Figure 4.8 Overview plot of the PLS on the Process Parameters and Film Properties 66   Figure 4.9 PLS - Loading plot on the Film Properties 67   Figure 4.10 PLS - Loading plot on the Process Parameters and Film Properties 68   Figure 4.11 Regression coefficient plot for tensile strength at break 73   Figure 4.13 Regression coefficient plot for percentage elongation at break 76   Figure 4.14 Regression coefficient plot for haze 77   Figure 4.14 Regression coefficient plot for haze 77   Figure 4.14 Regression		normalized line speed	
speedFigure 4.1Flow chart for Process Parameters-Structure- Properties (PP-S-P) Relationship55Figure 4.2Model overview plot of the PCA on the Process Parameters57Figure 4.3PCA - Score plot for the Process Parameters58Figure 4.4PCA - Loading plot for the Process Parameters59Figure 4.5Model overview plot of the PCA on the Film Properties62Figure 4.6PCA - Score plot for the Film Properties64Figure 4.7PCA - Loading plot for the Film Properties65Figure 4.8Overview plot of the PLS on the Process Parameters and Film Properties66Figure 4.9PLS - Score plot on the Film Properties67Figure 4.10PLS - Loading plot for tensile strength at break73Figure 4.11Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79	Figure 3.17	Plot of average log (Haze) against average normalized line	48
Figure 4.1Flow chart for Process Parameters-Structure- Properties (PP-S-P) Relationship55Figure 4.2Model overview plot of the PCA on the Process Parameters57Figure 4.3PCA - Score plot for the Process Parameters58Figure 4.4PCA - Loading plot for the Process Parameters59Figure 4.5Model overview plot of the PCA on the Film Properties62Figure 4.6PCA - Score plot for the Film Properties64Figure 4.7PCA - Loading plot for the Film Properties65Figure 4.8Overview plot of the PLS on the Process Parameters and Film Properties66Figure 4.9PLS - Score plot on the Film Properties67Figure 4.10PLS - Loading plot on the Process Parameters and Film 		speed	
Properties (PP-S-P) Relationship57Figure 4.2Model overview plot of the PCA on the Process Parameters57Figure 4.3PCA - Score plot for the Process Parameters58Figure 4.4PCA - Loading plot for the Process Parameters59Figure 4.5Model overview plot of the PCA on the Film Properties62Figure 4.6PCA - Score plot for the Film Properties64Figure 4.7PCA - Loading plot for the Film Properties65Figure 4.8Overview plot of the PLS on the Process Parameters and Film Properties66Figure 4.9PLS - Score plot on the Film Properties67Figure 4.10PLS - Loading plot for the Process Parameters and Film Properties68Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process79	Figure 4.1	Flow chart for Process Parameters-Structure-	55
Figure 4.2Model overview plot of the PCA on the Process Parameters57Figure 4.3PCA - Score plot for the Process Parameters58Figure 4.4PCA - Loading plot for the Process Parameters59Figure 4.5Model overview plot of the PCA on the Film Properties62Figure 4.6PCA - Score plot for the Film Properties64Figure 4.7PCA - Loading plot for the Film Properties65Figure 4.8Overview plot of the PLS on the Process Parameters and Film Properties66Figure 4.9PLS - Score plot on the Film Properties67Figure 4.10PLS - Loading plot on the Process Parameters and Film Properties68Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79		Properties (PP-S-P) Relationship	
ParametersFigure 4.3PCA - Score plot for the Process Parameters58Figure 4.4PCA - Loading plot for the Process Parameters59Figure 4.5Model overview plot of the PCA on the Film Properties62Figure 4.6PCA - Score plot for the Film Properties64Figure 4.7PCA - Loading plot for the Film Properties65Figure 4.8Overview plot of the PLS on the Process Parameters and Film Properties66Figure 4.9PLS - Score plot on the Film Properties67Figure 4.10PLS - Loading plot on the Process Parameters and Film Properties68Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for Percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79	Figure 4.2	Model overview plot of the PCA on the Process	57
Figure 4.3PCA - Score plot for the Process Parameters58Figure 4.4PCA - Loading plot for the Process Parameters59Figure 4.5Model overview plot of the PCA on the Film Properties62Figure 4.6PCA - Score plot for the Film Properties64Figure 4.7PCA - Loading plot for the Film Properties65Figure 4.8Overview plot of the PLS on the Process Parameters and Film Properties66Figure 4.9PLS - Score plot on the Film Properties67Figure 4.10PLS - Loading plot on the Process Parameters and Film Properties68Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process79		Parameters	
Figure 4.4PCA – Loading plot for the Process Parameters59Figure 4.5Model overview plot of the PCA on the Film Properties62Figure 4.6PCA - Score plot for the Film Properties64Figure 4.7PCA – Loading plot for the Film Properties65Figure 4.8Overview plot of the PLS on the Process Parameters and Film Properties66Figure 4.9PLS - Score plot on the Film Properties67Figure 4.10PLS - Loading plot on the Process Parameters and Film Properties68Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process79	Figure 4.3	PCA - Score plot for the Process Parameters	58
Figure 4.5Model overview plot of the PCA on the Film Properties62Figure 4.6PCA - Score plot for the Film Properties64Figure 4.7PCA - Loading plot for the Film Properties65Figure 4.7PCA - Loading plot of the PLS on the Process Parameters and Film Properties66Figure 4.8Overview plot of the PLS on the Process Parameters and Film Properties67Figure 4.9PLS - Score plot on the Film Properties67Figure 4.10PLS - Loading plot on the Process Parameters and Film Properties68Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79	Figure 4.4	PCA – Loading plot for the Process Parameters	59
Figure 4.6PCA - Score plot for the Film Properties64Figure 4.7PCA - Loading plot for the Film Properties65Figure 4.7PCA - Loading plot for the Film Properties66Figure 4.8Overview plot of the PLS on the Process Parameters and Film Properties66Figure 4.9PLS - Score plot on the Film Properties67Figure 4.10PLS - Loading plot on the Process Parameters and Film Properties68Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for Young's modulus75Figure 4.13Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79	Figure 4.5	Model overview plot of the PCA on the Film Properties	62
Figure 4.7PCA – Loading plot for the Film Properties65Figure 4.8Overview plot of the PLS on the Process Parameters and Film Properties66Figure 4.9PLS - Score plot on the Film Properties67Figure 4.10PLS - Loading plot on the Process Parameters and Film Properties68Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79	Figure 4.6	PCA - Score plot for the Film Properties	64
Figure 4.8Overview plot of the PLS on the Process Parameters and Film Properties66Figure 4.9PLS - Score plot on the Film Properties67Figure 4.10PLS - Loading plot on the Process Parameters and Film Properties68Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for Young's modulus75Figure 4.13Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79	Figure 4.7	PCA – Loading plot for the Film Properties	65
Film Properties67Figure 4.9PLS - Score plot on the Film Properties67Figure 4.10PLS - Loading plot on the Process Parameters and Film Properties68Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for Young's modulus75Figure 4.13Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79	Figure 4.8	Overview plot of the PLS on the Process Parameters and	66
Figure 4.9PLS - Score plot on the Film Properties67Figure 4.10PLS - Loading plot on the Process Parameters and Film Properties68Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for Young's modulus75Figure 4.13Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79		Film Properties	
Figure 4.10PLS - Loading plot on the Process Parameters and Film Properties68Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for Young's modulus75Figure 4.13Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79	Figure 4.9	PLS - Score plot on the Film Properties	67
PropertiesPropertiesFigure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for Young's modulus75Figure 4.13Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79	Figure 4.10	PLS - Loading plot on the Process Parameters and Film	68
Figure 4.11Regression coefficient plot for tensile strength at break73Figure 4.12Regression coefficient plot for Young's modulus75Figure 4.13Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79		Properties	
Figure 4.12Regression coefficient plot for Young's modulus75Figure 4.13Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79	Figure 4.11	Regression coefficient plot for tensile strength at break	73
Figure 4.13Regression coefficient plot for percentage elongation at break76Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79	Figure 4.12	Regression coefficient plot for Young's modulus	75
breakFigure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79	Figure 4.13	Regression coefficient plot for percentage elongation at	76
Figure 4.14Regression coefficient plot for haze77Figure 4.15Variables influence on projection (VIP) plot for process parameters79		break	
Figure 4.15Variables influence on projection (VIP) plot for process79parameters	Figure 4.14	Regression coefficient plot for haze	77
parameters	Figure 4.15	Variables influence on projection (VIP) plot for process	79
		parameters	

Table1.1	Relationship between processing conditions and film	13
	properties	
Table 3.1	Average normalized process parameters for each	31
	experimental run	
Table 3.2	Average film properties for each experimental run	32
Table 3. 3	Summary of the effect of process parameters on the cast	49
	film properties, and a comparison of the trend plot results	
	to other investigators' results.	
Table 4.1	Loading vectors p1 and p2 for the process parameters	60
Table 4.2	Loading vectors p1 for the film properties	65
Table 4.3	Loading vectors w*c(1) and w*c(2) for the process	69
	parameters and film properties	
Table 4.4	PLS coefficient values of the process parameters for the film	73
	properties	
Table A.1	Unit variance scaled and mean centered of the experimental	89
	data	
Table A.2	Process parameters, calculated score values t1 and t2,	95
	principal component analysis (PCA)	
Table A.3	Film properties, calculated score values t1 and t2, principal	101
	component analysis (PCA)	
Table A.4	Film properties and Process parameters, calculated score	107
	values t(1) and t(2), Projection to Latent Structures (PLS)	

### LIST OF ABBREVIATIONS

Roll #1	Chill Roll
Roll #2	Annealing Roll
Roll # 3	Final cooling Roll
RT #1	Chill Roll Temperature
RT #2	Annealing Roll Temperature
TSAB	Tensile Strength at break
YMOD	Young's Modulus
ТНК	Film Thickness
EL%	Percentage Elongation at break (Elongation)
% HZ	Percentage Haze (Haze)
LOG (Haze)	Logarithm (base 10) of percentage haze
LSpd	Line Speed
ASTM	American Society for Testing and Materials
MD	Machine Direction
TD	Transverse Direction
PLS	Partial Least Squares Projections to Latent Structure
MVDA	Multivariate Data Analysis
PCA	Principal Component Analysis
X/Y Plot	Plot of Process Parameter (X) against Film Property (Y)

#### **CHAPTER 1**

#### **INTRODUCTION**

The objective was to investigate the effect of process parameters on the mechanical and optical properties of cast films that were made on a commercial extruder. The process parameters studied were changed simultaneously, instead of one parameter at a time. There were two analyses done with the experimental data. The first analysis consisted of plotting trend plots of the average film property against the average normalized process parameter. The second analysis of the data was done with multivariable data analysis to show the weighted effect of the process parameters on the film properties.

The parameters that were studied included the film thickness, line speed, chill roll temperature, and annealing roll temperature. The film properties that were studied were the haze, elongation at break, tensile strength at break, and Young's modulus. Only the machine direction (MD) mechanical properties were evaluated. The experimental work for this project was different from that outlined in the open literature; other investigators' experiments were conducted on laboratory extruders. The experiments either involved changing one variable at a time or designing of experiments in which the parameters were evaluated at three response levels. Other investigators analyzed their experimental data by plotting only trend plots of the process parameters (X's) against the film properties (Y's). The X/Y trend plot analysis was suitable for experiments in which one variable was changed at a time. In experiments in which more parameters were changed simultaneously, the effect of the process parameters on the film properties should not be demonstrated only by plotting X/Y trend plots. Such experiments would require multivariable data analysis to be used to show the combined effect of the X's on the Y's. In this project, the experiment involved increasing and decreasing process parameters at the same time, to find out what effect that would have on the film properties.

It will be shown later that the changes in the process parameters affected the properties of cast film. Another way, in which this investigation was different from that of the other investigations, was that there was no work done by the other investigators to demonstrate the combined effects of chill and annealing roll temperatures on cast film properties. There were only generalizations of

2

annealing temperature effect on the properties of semi-crystalline polymers, but no experimental work to demonstrate the combined effects of the chill and annealing roll temperatures.

The word film has been used thus far; it is necessary at this point to give a definition of the meaning of film, the application of cast film, and a general description of a cast extrusion process that is used for making cast film. A film is usually defined as a material that is less than 0.010 inch or 250 microns [Veazey, E.W., 1992]. Cast polymer films are used in diverse applications such as packaging, building construction, agriculture, medical supplies, clothing, and automotive.

A cast extrusion process is used for making cast film. The polymers that are mostly used for making cast film are polyethylene, polypropylene, polyesters, polyamides, polyvinyllidene chloride, and fluorocarbon [Hecht, J. L., 1968]. A cast film process involves the melting of a thermoplastic resin by an extruder, followed by forcing the melt through a flat die, which molds or shapes the melt into a film, and a cooling or quenching process is used to cool or quench the melt into a solid film [Klauber, M., 1992].

A cast extrusion process can be done either by co-extrusion (more than one extruder) or by mono-extrusion (one extruder). Co-extrusion is the process of extruding two or more polymers through the same die to produce a multi-layered film [Butler, I. T., 1992, Jerdee, G., 2000, and Myers, A.M., 2000].

In a typical cast film extrusion manufacturing process, the equipment involved is:

- A resin handling system for metering resin into an extruder
- An extruder (twin or single screw) with or without a vent port, the vent port being used for moisture removal
- A melt pump for metering polymer melt to a die
- A filter for removing gel particles and other contaminants
- A die (T-Slot or Coat hanger) for shaping the molten polymer into a thin flat film
- A chill roll for cooling the molten polymer into a solid film
- An air knife or vacuum box or air chamber for pinning the molten melt to the surface of the chill roll
- An annealing roll for reheating the film for stress relieve
- A final cooling roll for cooling the film to room temperature
- A beta gauge for on-line film thickness measurement

- Corona treatment equipment for film surface treatment
- A winder for winding up the film into rolls
- A waste film reclaiming system (choppers and blowers) for edge trim plus other film waste recycling

The above pieces of equipment are the basic requirements for a typical mono (single) cast film extrusion process. The same basic equipment is required for co-extrusion, except in co-extrusion, a multi-layer die or multi-layer feed block when a single layer die is used [Butler, I. T., 1992].

Another important factor in cast film extrusion is to make the film so it will successfully perform in the required application. How does the process parameters affect the film properties? Understanding the property-structureprocess parameter relationship of cast film can be a challenging task. A good understanding of property-structure-process parameter relationship of cast film, is very important to cast film manufacturers in commercial operations.

Engineers who develop cast film are faced with the challenge of understanding the property-structure-process relationship. In the development of semicrystalline cast film for example, engineers must understand how to balance the property-structure-process parameter relationship, so that the film will perform successfully in the required application.

The percentage of crystallinity of the film is also important to know. Crystallinity is an important morphology that is related to the film's structure. The film's structure is influenced by the process parameters that are used to cast the film [Macauley, N.J., 1998 and Millar, B., 2003].

Properties including density, barrier, coefficient of friction, optics, impact strength, tensile strength, Young's modulus, elongation at break, and yield strength, are affected by the percentage of crystallinity. The effect of crystallinity on the desired properties of a cast film has to be taken into consideration in order to produce a film that will successfully perform in the required application. The desired percentage of crystallinity is obtained by manipulating the process parameters to get the desired properties of cast film.

Reprocessing, overheating, recycling or any further processing of polymer will potentially increase the percentage of crystallinity. Enough control or care must be taken when processing semi-crystalline polymers, to ensure crystallinity is not drastically increased. As polymer becomes more crystalline due to further

6

reprocessing, the melting point and tensile strength increased. The tensile strength can increase to the extreme that the polymer becomes brittle and lose properties that it was originally designed to have for the application. Therefore process parameters must be carefully chosen to ensure properties are maintained for subsequent applications.

In this project, it is shown that process parameters such as chill roll temperature, annealing roll temperature, line speed and thickness, influenced the following properties; tensile strength, Young's modulus, haze, and elongation at break, of a cast film.

The other thing worth mentioning is the difference between cast and blown film [Ivey, J., 2000]. Although the present work is not on the blown film process, some readers may want to know the difference between cast and blown film.

Cast film is cooled faster than blown film; the faster cooling causes one directional molecular orientation in the film. The molten polymer is usually drawn down from the die gap dimension to the desired film thickness. The film properties are generally more optimized in the machine direction, rather than the transverse direction, because more molecular orientation is in the machine direction. In the blown film process, the film is blown into a bubble by air. The film is cooled slowly by air while the bubble is drawn upward. The upward drawing in the machine direction (MD), the transverse direction (TD) stretching due to bubble blowing, and the slower cooling, allow enough time for the molecules to orient in both the machine and transverse directions. This slower cooling allowed more time for increased crystallinity, and larger crystals to grow. This increase in crystallinity makes blown film hazy, dull (low gloss), tough, and better in puncture resistant than cast film. Cast film, on the other hand, is clear with high gloss, lower modulus, and good puncture resistance.

In cast film extrusion, when the polymer-melt from the die took longer to cool, or cast at higher temperatures, the film becomes stiffer (higher modulus), hazier (cloudy) and duller (lower gloss), than when the film was to cast at lower temperatures. Higher casting temperatures caused the melt to take longer to cool, and as a result caused more and larger crystals to grow in the film structure, and as such influenced the mechanical and optical properties of the film.

#### **CHAPTER 2**

#### **REVIEW OF THE LITERATURE**

#### **2.1 Introduction**

There is scant literature available demonstrating the effect of process parameters on the mechanical and optical properties of cast film. The information in the available literature shows that cast extrusion process parameters affect the mechanical and optical properties of cast film. Some of the previous investigations described the experimental procedures that were used by other investigators, to demonstrate the effect of process parameters on the properties of cast film. Some of the references only gave generalizations about the effect of process parameters on the properties of cast polymer film.

The effect of process parameters on the properties of cast film relates to the modification of the crystal structure [Millar, B., 2003]. In the casting of a polymer melt, the control of the degree of crystallinity takes place by manipulating critical process parameters to get the desired film properties [Degroot, J.A., 1994] and [Leephakpreeda, T., 2004].

9

### **2.2** Publications

The effect of chill roll temperature, line speed, thickness and melt temperature on the elastic modulus in the machine direction (MD), elongation at break (MD), tensile strength (MD), yield strength (MD), total impact energy (MD), and shrinkage (MD) of cast polypropylene sheet was investigated by Macauley [Macauley, N.J., 1998]. In Macauley's experiment, one process parameter was changed at a time. Macauley reported that the increase in chill roll temperature caused elastic modulus (MD) to increase, while other properties like tensile strength at break (MD), elongation at break (MD), total impact energy (MD) decreased. The increase in the line speed caused the elastic modulus (MD) and shrinkage (MD), and crystallinity to increase, and elongation at break (MD), total impact energy (MD), and yield strength (MD) to decrease.

The decrease in the sheet thickness caused the elastic modulus (MD), tensile strength at break (MD), shrinkage (MD), and total impact energy (MD) to increase, and elongation at break, and crystallinity to decrease. Macauley [Macauley, N.J., 1998] attributed the increase or decrease in the room temperature mechanical properties to increase or decrease by the percentage of crystallinity in the sheet structure.

Melt temperature rise affected the properties of cast film as reported by Myers

[Myers, A.M., 2000]. The increase in melt temperature caused the melt density and viscosity to reduce, which resulted in more melt flow to the end of the die, during casting. Coefficient of friction, neck-in, and gloss increased, as melt temperature was increased. Tensile strength and haze decreased, as melt temperature was increased. Myers also explained the effect of the increase in chill roll temperature on other cast film properties. Increase in chill roll temperature caused the cooling time and percentage of crystallinity to increase, which resulted in film's density, barrier properties, stiffness and optics to increase, and a reduction in the coefficient of friction and impact strength [Myers, A.M., 2000].

The major extrusion factors that affected cast film properties were summarized by Ivey [Ivey, J., 2001]. The effects of increasing chill roll temperature were as follows: quench time increased, crystallization slowed down and resulted in larger crystal growth; density, stiffness, film barrier properties, and optics were all increased, coefficient of friction and impact strength decreased. Ivey also explained how other factors such as melt temperature, die gap or draw ratio, air gap, and air knife or vacuum box setting and output rate affected film properties [Ivey, J., 2001]. The processing factors of cast polypropylene film had some effect on the mechanical properties of the film; the effect was more on the optical properties, heat-sealing temperature and coefficient of friction [Yamada, T., 1999]. Plots were shown to reflect the relationship between the coefficient of static friction against film thickness, percent haze against polymer temperature, and percent haze against chill roll temperature. The trends in those plots were as follows; as thickness was increased the coefficient of static friction decreased, as melt temperature was increased, the haze deceased, and as chill roll temperature was increased.

The effects of the parameters on the properties were based on the increase in crystallinity. The higher the casting temperature of the film, the crystallinity was higher in the film, resulting in higher heat-sealing temperature and haze [Yamada, T., 1999]. The film surface became uneven as the crystallinity was increased, which caused a decrease in the coefficient of friction.

The modulus of the film also increased as crystallinity was increased. The higher polymer melt-temperature caused percentage of crystallinity, modulus and haze to decrease, and impact strength to increase. The higher melt temperature caused less shear stress to be applied to the polymer in the die and more melt relaxation as the polymer exited the die. A table was used by Yamada to summarize the relationships between processing parameters and cast film properties. The table is shown below:

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Conditions	Direction	Tensile	Tensile	Tensile	Tensile strength	Tensile	Tensile	Haze
		Modulus	Modulus	strength	(at yield point)	strength	strength	
		(MD)	(TD)	(at yield point)	(TD)	(at break)	(at break)	
				(MD)		(MD)	(TD)	
Polymer	Increased	Decreased	Decreased	Decreased	Decreased	Increased	Increased	Decreased
Temperature					}			
(180 to 280°C)								
Output (kg/h)	Increased	No effect	No effect	No effect	No effect	Decreased	No effect	Gradual
10 to 80 kg/h)								Increased
Roll Temperature	Increased	Increased	Increased	Increased	Increased	Decreased	Decreased	Increased
(20 to 80 °C)								
Thickness	Increased	Decreased	Decreased	Decreased	Decreased	Increased	Decreased	Increased
(micron)								
(10 to 40 microns)				}				

Table 1.1 - Relationship Between processing Conditions and Film Properties by [Yamada, T., 1999]

The effect of cooling temperature on the mechanical properties of cast polyethylene film was investigated by Millar [Millar, B., 2003]. The experimental work was done with metallocene-catalyzed polyethylene and conventional polyethylene.

In Millar's experiment, one parameter was changed at a time. X/Y trend plots were plotted to show the corresponding effect of the parameters on the studied

film properties. Increasing the cast film temperature resulted in similar effects on the mechanical properties of both metallocene-catalyzed polyethylene and conventional polyethylene [Millar, B., 2003]. For the different resin types, increasing the chill roll temperature resulted in both Young's modulus and tensile break strength to increase and the percentage elongation at break to decrease. As the chill roll temperature or cooling temperature was increased, the cast film became cloudy (hazy). The cast film samples were glossy and clear at lower chill roll temperature. All these effects on the mechanical and optical properties were due to the increase in the percentage of crystallinity [Millar, B., 2003].

Millar also reported [Millar, B., 2003] that as die gap was increased, the crystallinity of the film increased for the different line speeds, or haul off rates. An increase in die gap and line speed resulted in an increase in the draw down ratio of the melt in the section between the die lip and the surface of the chill roll. The increase crystallinity was due to the effect of strain-induced crystallization, due to the increase in draw down ratio. Millar showed that the increase in line speed (haul off rate) at constant die gap resulted in an increase in the break strength. The die gap increase was shown to have more effect in increasing the tensile strength at break, than the line speed increased.

14

Millar reported [Millar, B., 2003] on the effect of the increase in line speed and die gap on the tear strength and percentage shrinkage. There was more significant increase in the TD tear strength, than the MD tear strength, as line speed and die gap were increased. The same trend was illustrated for all the different resins that were used in the investigation.

The percentage shrinkage increased as line speed and die gap were increased. The increase in percentage shrinkage was attributed to the molecular orientation increase, in the MD direction, during the film casting. The MD shrinkage was found to have more increase than the TD shrinkage. The TD percentage shrinkage was decreased with increased die gap and increased line speed or haul off rate. This was due to less orientation in the (TD) transverse direction as mentioned by Millar [Millar, B., 2003].

The effect of processing parameters on cast LLDPE stretch film properties was investigated by Degroot [Degroot, J.A., 1994]. The processing parameters were melt temperature, air gap and line speed. A design of experiment was used to study three levels of responses for the processing parameters. The increases in melt temperature and air gap, were the main parameters to have caused an increase in elongation (Ultimate Stretch) and a decrease in tensile strength (load retention), of the stretch films.

The increase in the line speed was shown to have a minor effect on these properties. Degroot concluded that, it was possible to get a wide variety of stretch film properties from a single resin, by changing the fabrication conditions of the cast film.

Degroot's investigation showed that higher melt temperature, longer air gap, and slower line speed, resulted in better film extensibility and lower tensile strength. The relationship between the MD shrinkage and tensile strength of the stretch film were established; the MD shrinkage decreased as the elongation decreased and the tensile strength increased [Degroot, J.A., 1994].

The induced stress in the stretch film and the viscosity decreased, as melt temperature was increased. The increase in melt temperature caused a reduction in the molecular orientation in the film. The orientation in the film also reduced when the air gap was increased, which resulted in smaller extensional rate and lower extensional stresses, in the molten film. The higher extensibility resulted from the lower amorphous and crystalline phases orientation in the film [Degroot, J.A., 1994]. Peacock [Peacock, A.J., 2000] discussed the effects of cooling temperature and orientation on polyethylene cooling from the melt. The higher temperature caused longer cooling and increased the percentage of crystallinity in semi-crystalline polymer film. This increase in percentage of crystallinity resulted in an increase in the modulus of the film.

Orientation or stresses on polymer melt during cooling, induced additional crystallization in the melt. Increased orientation caused molecular alignment to increase. Increased orientation is related to the increase in the line speed. This increase in orientation caused Young's modulus and tensile strength at break to increase and elongation at break to decrease, all these were related to the increase in crystallinity [Peacock, A.J., 2000].

Optical properties, such as haze, were affected by the increase in crystallinity, film thickness and orientation in film samples [Peacock, A.J., 2000]. Rapid cooling or low temperature resulted in low percentage of crystallinity, which reduced the haze for high-density polyethylene, while slow cooling or high cooling temperature increased the haze. "High density polyethylene generally exhibits greater internal haze than low density polyethylene because its range of spherulitic sizes (crystal sizes) more closely match the wavelengths of visible light"[Peacock, A.J., 2000].

The other factor that affects the haze is orientation. Depending on the processing conditions and the molecular structure, haze can either increase or decrease [Peacock, J.A., 2000]. The effect of orientation on haze is complicated by crystal structure and the degree of crystallinity. It is not possible to make a general comment on how orientation affects haze during crystallization; haze could either increase or decrease.

The effect of annealing temperature on the physical properties of a semicrystalline polymer is explained by [Scheetz, A.H., 1995]. "Annealing is a heat treating process designed to reduce residual stresses and to allow materials to approach thermodynamic equilibrium while maintaining properties" [Scheetz, A.H., 1995].

Conventional annealing takes place between the glass transition temperature and below the melting point of a semi-crystalline polymer. Annealing caused crystallinity to increase, residual stress to reduce, and changes in physical properties. The property changes are the increase in tensile strength and modulus, lower elongation at break and toughness, improved dimensional

18

stability (less warping or shrinkage of finished product), and stabilized optical properties [Scheetz, A.H., 1995].

The effect of post-extrusion annealing of low-density polyethylene sheets significantly increased the crystallinity [Hindeleh, A.M., 1990]. The annealing of the sheets increased the transmission of light in the visible region.

The polyethylene sheet samples were annealed in an oven at different annealing temperatures. The sheets were not cast by the investigators, but by local cast sheet manufacturers. The work was done to investigate what effect the increase in the percentage of crystallinity of LDPE sheets, had on the transmission of light, in the visible region for sheets that were used as covers in agricultural greenhouses [Hindeleh, A.M., 1990].

An increase in orientation caused a greater degree of molecular alignment and crystallization, which increased molecular interaction, resulting in higher tensile strength [Kohan, M.I., 1964]. The molecular weight of a polymer is a secondary requirement in the determination of the degree of crystallinity. The crystallization time is longer for a higher molecular weight polymer, than one with a lower molecular weight. Annealing a polymer helped the polymer to reach the crystalline structure required for equilibrium in the degree of crystallinity, after quench cooling from the melt. "It is only when the polymers are carefully annealed that anything approaching an equilibrium degree of crystallinity occurs" [Reding, F.P., 1964]. The degree of crystallinity is the only factor that determines and controls the stiffness modulus of thermoplastics (condensation and addition) between their glass transition temperature and melting point [Reding, F.P., 1964].

The control of crystal structure is very important in the casting of polymeric film from the melt. Models are developed to simulate on line control of crystal structure, by obtaining process data from the process, and used this data through an on-line control loop to manipulate casting temperature to control crystal structure, while casting polymeric film [Leephakpreeda, T., 2004].

The crystal thickness with the temperature of crystal formation, when further annealing at a higher temperature, increased the thickness more [Rodriguez, F., 1989]. For example " A polyethylene crystal with a thickness of 10 nm may be formed at 100<sup>o</sup>C. Heating the crystal at 130<sup>o</sup>C for several hours will increase the thickness to about 40 nm". Crystallinity acts as massive cross-link similar to

covalent cross-link in polymer networks. The crystalline cross-links in semicrystalline polymers prevent the movement of the amorphous network [Rodriguez, F., 1989].

In conclusion, the review of the literature has indicated that limited papers are available on this subject, and as such more work is required in this area of polymer science and engineering. The comparison of previous works was important and it will help to lay the foundation for further work. The information from the literature showed that process parameters play a significant role in determining the properties of semi-crystalline cast film, casting from the melt. The next chapters will discuss the experimental procedures.

#### **CHAPTER 3**

#### **DESCRIPTION OF EXPERIMENTAL DATA**

#### **3.1 Introduction**

The experiment was conducted on an industrial scale extruder. In the production process, the process parameters were changed concurrently, rather than consecutively. The data from the experiment were analyzed and showed that the process parameters affected the properties of the film. The first analysis of the data was done with X/Y trend plots of the average normalized process parameters against the average of film properties. From the analysis of the X/Y trend plots, it was not possible to see how the process parameters influenced the changes in the film properties. In order to see how the process parameters affected the film properties, multivariate data analysis (MVDA) was used later in Chapter 4.

In the experiment, the throughput, die gap and air gap were kept constant. The line speed was used to get the different film thicknesses required for the experiment. The casting temperatures were set according to the type of products and film thicknesses. The casting temperatures for the chill roll and annealing roll were increased, as the film thickness was decreased. At the start of the experiment, the thick films were cast first, and then followed by the thin films in descending order. Ten to thirty (10-30) cast film samples were collected for each experimental run. The film samples were tested in the laboratory for the haze, tensile strength at break (MD), Young's modulus (MD) and elongation at break (MD). Details of the cast extrusion process, the film properties characterizations, and the analysis of the experimental data are explained below in the following sections.

#### **3.2 Experimental Procedures**

A cast extrusion production line was used to make the film samples. The cast line was equipped with a resin feed system, a 120 mm diameter twin-screw extruder with a vent port, and a coat hanger die with flexible lips for gauge control.

The width of the die was 102 inches or 2590.8 mm. There was a casting unit with three main process rolls, and small auxiliary rolls (4 inches in diameter) to keep the film in contact to the main casting rolls, an on-line thickness gauge measurement/control system for average thickness control, and a winder for winding up the film into rolls.

The casting roll diameters were 24 inches (609.6 mm) with a face length of 105 inches (2667 mm). The casting rolls were doubled walled cylinders with a heat transfer fluid flowing through the gaps. To get some basic information on casting rolls design, consult [Puhalla, M., 2000].

The polymer cast was a semi-crystalline polymer. The throughput was kept constant at 600 kg/hr for the experiment. The line speed was set at different speeds, to get different film thicknesses. The air gap was kept constant between the die lip and the chill roll's surface. The die gap was set constant at 0.0355 inch (0.902 mm). The changing of the line speed was used to get the different film thicknesses, at the constant throughput and die gap.

The resin feeder was used to meter the resin pellets into the extruder. There was no other resin or additive metered into the extruder. The molten polymer melt temperature was kept constant by keeping the screw speed constant. A thermocouple located at the exit of the extruder, measured and monitored the melt temperature.

The molten polymer entered a metering pump after leaving the extruder. The metering pump was located close to the end of the extruder exit. The metering
pump (gear pump) pumped the polymer melt from the extruder through the filter into the coat-hanger die. The polymer melt left the die, and contacted the chill roll's surface (roll #1). The die was located close to the chill roll. The distance (air gap) from the lip of the die to the chill roll's surface was approximately 1-1.5 inches.

Figure 3.1 shows a sketch of the polymer melt leaving the die, making contact with the chill roll's surface, and the air knife blowing air to lay the melt to the chill roll's surface.



Figure 3.1: Sketch of the casting unit, showing the casting rolls, coat hanger die, and air knife

Air blowing at high velocity from the air knife, laid the melt to the chill roll's surface. Air blowing at high velocity from edge pinning jets, were used to pin the edge of the film to the chill roll's surface. The film necked-in, or shrunk in width in the transverse direction, as it was drawn down from the die gap dimension (0.0355 inch) to the required film thickness. The film's edge, usually called the "edge bead", was silted off and recycled into the process. A knife cutter, before recycled into the process, cut the edge beads.

The melt was cooled to the set temperature of the chill roll. The different film thicknesses in the experiment were cast using different casting temperatures (chill and annealing). The main process rolls were wrapped about 70% of their circumferences with the film. The film thicknesses that were cast were 115, 102, 76, 60, 51, 44, 32, 25, and 19 microns. The line speed was from 90 - 620 feet per minute (0.457 - 3.15 meters per second) for the various film thicknesses.

At the beginning of the experiment, the film thickness was high (115 microns) at that time the line speed was low, the speed held constant for sampling, and then the line speed was increased to get the next thickness (102 microns), line speed held constant, film samples were collected, the line speed was increased again to get the other film thickness (76 microns), speed held constant, film samples were collected, so on and so forth for the rest of the experimental run. The film left the chill roll (roll #1) to the annealing roll (roll #2). Roll #2 was used to reheat the film a few degrees above the set chill roll temperature. The reheating or annealing of the film released the induced stress in the film. The induced stress was developed from the extruding of the resin in the extruder and shaping of the melt into a flat film inside the die. The reheating of the film also controlled the crystal growth in the film structure, shrinkage, and dimensional stability of the film during storage. The film left the heat setting or annealing roll to the final cooling roll (roll #3). The final-cooling roll cooled the film to room temperature, before it left the casting unit to the other downstream equipment.

The film left the casting unit to the other downstream equipment. The film thickness was measured in-line with the beta-gauge [Harris, H.E., 2004]. The beta-gauge was transversely located on a frame support. The film thickness was measured in the gap between the source and detector of the beta-gauge. The beta-gauge traveled in the transverse direction (TD), measuring the thickness as the film traveled in the machine direction (MD). The thickness data was send to the gauge controller. The controller communicated with the heater on the bolts on the die lip [Whiteman, R., 2000].

The bolt holder with the adjustable bolt and heater was 1 inch wide, and about 8 inches in length. The bolt holders were placed evenly across the width of the die

lip. The die lip was flexed about +/- 0.5-1.0 micron with either expansion or contraction (heating or cooling) by the adjustable bolts to control the average film thickness. To control the average film thickness, the bolts were flexed according to how low or high a spot on the film, localized thickness that was measured across the film. After the beta-gauge, the film then entered the winder and wound up.

The film samples that were collected and tested for haze, tensile strength at break (MD), Young's modulus (MD) and elongation at break (MD). The film samples collected were 180 samples or 180 observations, the break down is as follows: 20 samples each for 115, 102, 76, 60, 51, 32, and 25 micron, 30 samples for 19 micron and 10 samples for 44 micron. There were 9 experimental runs, run #1 was 115 microns, in this run, 20 samples were collected; run # 2 was 102 microns, 20 samples were collected, so on and so forth for the other runs. The test methods that were used for testing the film samples are explained below.

## 3.3 Mechanical and optical characterization of the cast film samples

Definition of properties:

1. Tensile strength at break is the tensile stress, in pounds per square inch (psi), at the instant of rupture of the test film or specimen based on the original crosssectional area of the specimen, ASTM method D-882 2. Elongation at break is the increase in length of a 1-inch section in the center of the test specimen, measured at the instant of rupture, expressed as a percentage of the original 1-inch length, ASTM method D-882

3. Tensile modulus of elasticity (Young's Modulus) is a measure of the stiffness of thin plastic films and sheets. By choosing a point on the tangent to the linear portion of the load-extension curve, and dividing the tensile stress by the corresponding strain gave Young's Modulus. The strain used as a standard is 1 % strain, ASTM method D-882

4. Haze is the percentage of the total transmitted light that is passing through the specimen, scattered from the incident beam by more than 2.5 degrees, ASTM method D-1003-95.

As mentioned above, the tensile strength at break and elongation at break were tested according to the testing conditions defined in the ASTM test method D-882. The test specimens' shapes were defined according to ASTM Method D-638. The specimens were strips of uniform width, about 50 mm (millimeters) longer than the grip separation used. For the testing of the tensile modulus, elongation at break and Young's modulus, 5 specimen samples were tested for each film sample. The average value of the 5 samples was found and recorded.

The tensile modulus or Young's modulus was tested with the ASTM method D-

882. The tensile modulus test was done at a constant rate of grip separation. The crosshead speed for the jaws was 500 mm/minute. The initial jaw separation was 50 mm. The mechanical properties tested for the films were only in the machine direction (MD). A PC-controlled INSTRON was used to measure the tensile properties of the film samples.

The percent haze (haze) indicated the clarity of the film by determining the scattering of light as it passed through the film. The measurement was obtained by using a Pacific Scientific XL-211 Haze guard System. The test was conducted according to the ASTM method D-1003-95. The logarithm (base 10) of the percentage haze was found; the data was recorded as LOG (haze) or log of haze in Table 3.2.

The average of the film properties and the normalized process parameters are shown below in the next section. The film samples collected were 180 samples. The break down was as followed; 20 samples each for 115, 102, 76, 60, 51, 32, and 25 micron, 30 samples for 19 micron and 10 samples for 44 micron. Experimental run #1 was for the 115 microns film samples, #2 for 102 microns, #3 for 76 microns, #4 for 60 microns, #5 for 51 microns, #6 for 44 microns, #7 for 32 microns, #8 for 25 microns and #9 for 19 microns. Each film sample was tested for mechanical and optical properties, and the average of the film

properties and the normalized process parameters are shown in the tables below. Dividing by the minimum value among the data normalized the process parameters for each experimental run

Experimental	Avg. Normalized	Avg. Normalized	Avg. Normalized	Avg. Normalized
Run	Film Thickness	Chill Roll Temp	Annealing Roll Temp	Line speed
1	5.95	1.00	1.00	1.00
2	5.21	1.03	1.01	1.14
3	3.90	1.08	1.02	1.53
4	3.08	1.14	1.03	1.93
5	2.61	1.20	1.09	2.28
6	2.25	1.23	1.12	2.65
7	1.64	1.27	1.18	3.63
8	1.28	1.36	1.39	4.63
9	1.00	1.38	1.41	5.97

Table 3.1 shows the average normalized process parameters for each experimental run

The average film properties per experimental run are shown in Table 3.2. Only the machine direction (MD) mechanical properties were measured.

Experimental Run	Average Young's Modulus ( MPa )	Average Tensile Strength at break ( MPa )	Average Elongation at break (%)	Average LOG (Haze)
1	601.60	105.42	462.44	1.55
2	612.01	114.55	429.75	1.22
3	630.49	118.03	425.26	0.78
4	661.80	122.24	419.29	0.53
5	703.59	126.77	408.01	0.41
6	718.73	128.85	397.49	0.37
7	727.31	130.86	390.02	0.19
8	735.53	145.39	388.79	0.16
9	746.81	147.35	376.63	0.10

Table 3.2 shows the average film properties for each experimental run

#### **3.4 Experimental Data Analysis**

The data in Table 3.1 and 3.2 were used to plot X/Y trend plots of the average normalized process parameters against the average film properties. The trend plots (Figure 3.2 to 3.17) have shown what was observed in the experiment. These plots do not show the weighted effects of the process parameters on the film properties. From the observations in trend plots, one may conclude that the process parameters all had equal contributive effect on the film properties. The conclusion must not be drawn that all the process parameters had equal contributive effect on the film properties at the same time, and therefore their effects would be different. Later on in Chapter 4, multivariable data analysis will be done, to show the multivariable effect the process parameters had, on the film properties

The trend plots for the film properties are shown below. The tensile strength at break and Young's modulus show an increasing trend, and the elongation at break and hazes show decreasing trends for the number of film samples that were tested. The decrease in the film thickness and the increase in line speed, plus the increase in the annealing and chill roll temperatures, contributed to the increased or decreased trends that are shown in the trend plots, Figure 3.2 to 3.17

Figure 3.2 shows the trend plot of the average tensile strength at break (MD), against the average normalized chill roll temperature.



Figure 3.2: Plot of average tensile strength at break against average normalized chill roll temperature

The figure shows the tensile strength at break, increased as the chill roll temperature was increased. The increase in the tensile strength at break (MD) as the chill roll temperature was increased, was similar to that reported by [Millar, B., 2003], but different from that reported by [Macauley, N.J., 1998] and [Yamada, T., 1999]. They reported that tensile strength at break reduced, as chill roll temperature was increased.

Figure 3.3 shows the plot of the average Young's modulus (MD), against the normalized chill roll temperature. As the chill roll temperature was increased, the Young's modulus (MD) increased.



Figure 3.3: Plot of average Young's modulus against average normalized chill roll temperature

The increase in the Young's modulus as the chill roll temperature was increased, was similar to that reported by [Macauley, N.J., 1998], [Millar, B., 2003], [Yamada, T., 1999], [Myers, A.M., 2000], and [Ivey, J., 2001].

Figure 3.4 shows the plot of the average tensile strength at break (MD), against the average normalized annealing roll temperature.



Figure 3.4: Plot of average tensile strength at break (MD) against average normalized annealing roll temperature

The tensile strength at break (MD) increased as the annealing roll temperature was increased. The rise in the tensile strength at break (MD) as the annealing roll temperature was increased, was similar to that reported by [Scheetz, A.H., 1995].

Figure 3.5 shows the plot of the average Young's modulus (MD), against the average normalized annealing roll temperature.



Figure 3.5: Plot of average Young's modulus against average normalized annealing roll temperature

The increase in the annealing roll temperature caused the Young's modulus to increase; this increased trend was similar to that reported by [Scheetz, A.H., 1995].

Figure 3.6 shows the plot of the average log of haze; against the average normalized chill roll temperature.



Figure 3.6: Plot of average log of haze against average normalized chill roll temperature

Figure 3.6 shows the haze decreased as the chill roll temperature was increased. The decrease in the haze as the chill roll temperature was increased, was not in agreement with that mentioned by [Yamada, T., 1999 and Millar, B., 2003]. According to [Yamada, T., 1999 and Millar, B., 2003] as the chill temperature was increased, the haze of the film increased. Figure 3.7 shows the plot of the average log of haze, against the average normalized annealing roll temperature.



Figure 3.7: Plot of average log of haze against average normalized annealing roll temperature

Figure 3.7 shows that as the annealing roll temperature was increased, the haze of the film decreased. This decreased trend in the haze was not similar to that reported by [Scheetz, A.H., 1995].

Figure 3.8 shows the plot of the average elongation at break (MD), against the average normalized chill roll temperature.



Figure 3.8: Plot of average elongation at break against average normalized chill roll temperature

The figure shows the elongation at break (MD) decreased, as the chill roll temperature was increased. This reducing trend that is shown in the plot was similar to that reported by other investigators.

Figure 3.9 shows the plot of the average elongation at break, against the average normalized annealing roll temperature



Figure 3.9: Plot of average elongation at break (MD) against average normalized annealing roll temperature

The elongation at break decreased as the annealing roll temperature was increased. Figure 3.9 shows the same decreased trend in the elongation at break, as in Figure 3.8. Both Figure 3.8 and Figure 3.9 show the same decreased trend in the elongation at break, as chill roll and annealing roll temperature were increased. [Macauley, N.J., 1998], [Millar, B., 2003] and [Yamada, T., 1999] reported that the elongation at break decreased, as the chill roll temperature was increased. [Scheetz, A.H., 1995] reported that elongation at break decreased.

Figure 3.10 shows the plot of the average tensile strength at break (MD), against the average normalized film thickness.



Figure 3.10: Plot of average tensile strength at break against average normalized film thickness

Figure 3.10 shows the tensile strength at break increased, as the film thickness was decreased. The plot in Figure 3.10 agreed with that reported by [Macauley, N.J., 1998], but was opposite to that reported by [Millar, B., 2003] and [Yamada, T., 1999]. [Macauley, N.J., 1998] reported that tensile strength at break increased, as the sheet thickness was decreased. [Millar, B., 2003] and [Yamada, T., 1999] reported that tensile strength at break increased, as the sheet thickness was decreased. [Millar, B., 2003] and [Yamada, T., 1999]

Figure 3.11 shows the plot of the average Young's modulus (MD), against the average normalized film thickness.



Figure 3.11: Plot of average Young's modulus against average normalized film thickness

Figure 3.11 shows that, as the film thickness was reduced, the Young's modulus (MD) increased, the trend was similar to that reported by [Macauley, N.J., 1998] and [Yamada, T., 1999].

Figure 3.12 shows the plot of the average elongation at break (MD), against the average normalized film thickness.



Figure 3.12: Plot of average elongation at break against average normalized film thickness

As the film thickness was decreased, the elongation at break (MD) decreased. The decrease in the elongation, as the film thickness was reduced, was similar to that reported by [Macauley, N.J., 1998].

Figure 3.13 shows the plot of the average log of haze, against the average normalized film thickness. The figure shows that as the film thickness was decreased, the haze of the film decreased.



Figure 3.13: Plot of average log of haze against average normalized film thickness

The decrease in the haze as the film thickness was decreased, was similar to that reported by [Yamada, T., 1999].

Figure 3.14 shows the plot of the average tensile strength at break (MD), against the average normalized line speed. The figure shows that as the line speed was increased, the tensile strength at break (MD) increased.



Figure 3.14: Plot of average tensile strength at break against average normalized line speed

The increase in the tensile strength at break (MD) with the increase in the line speed, was in agreement with that reported by [Millar, B., 2003], but was not in agreement with that reported by [Yamada, T., 1999]. Yamada reported that tensile strength (MD) at break decreased, when output rate was increased.

Figure 3.15 shows the plot of the average Young's modulus (MD), against the average normalized line speed. The figure shows that as the line speed was increased, the Young's modulus increased.



Figure 3.15: Plot of average Young's modulus against average normalized line speed

The increase in the Young's modulus, as the line speed was increased, was similar to that reported by [Macauley, N.J., 1998], but opposite to Yamada's report. [Yamada, T., 1999] reported that there was no effect on Young's modulus (MD), when output rate was increased.

Figure 3.16 shows the plot of the average elongation at break (MD), against the average normalized line speed.



Figure 3.16: Plot of average elongation at break against average normalized line speed

Figure 3.16 shows the elongation at break (MD) decreased, as the line speed was increased. The same trend was reported by [Macauley, N.J., 1998].

Figure 3.17 shows the plot of the average log of haze, against the average normalized line speed. The figure shows that as the line speed was increased, the haze decreased.



Figure 3.17: Plot of average log of haze against average normalized line speed

The decrease in the haze as the line speed was increased, did not agree with that reported by [Yamada, T., 1999]. [Yamada, T., 1999] reported that as output rate was increased, the haze increased.

The table below Table 3.3 summarized the effects of the process parameters on the cast film properties. The table also shows the comparison of the experimental results, to the results of the other investigators.

Process	Change	Effect on Film Property	Comparison to the work of other
r ai ameters		1. Increased Tensile strength at break (MD)	1. Agreed with [Millar, B., 2003], not agreed with [Macauley, N.J., 1998] and [Yamada, T., 1999]
Chill roll Temperature	Increased	2. Increased Young's modulus (MD)	<ol> <li>Agreed with [Macauley, N.J., 1998] [Millar, B., 2003], [Yamada, T., 1999], [Myers, A.M., 2000] and [Ivey, J.A., 2001]</li> </ol>
		3. Decreased haze	<ol> <li>Not agreed with [Millar, B. 2003], [Yamada, T., 1999], [Myers, A.M., 2000] and [Ivey, J.A., 2001]</li> </ol>
		4. Decreased elongation at break (MD)	4. Agreed with [Macauley, N.J., 1998], [Millar, B., 2003] and [Yamada, T., 1999]
		1. Increased Tensile strength at break (MD)	1. Agreed with [Scheetz, A.H., 1995]
Annealing Roll Temperature	Increased	2. Increased Young's modulus (MD)	2. Agreed with [Scheetz, A.H., 1995]
		3. Decreased haze	3. Not agreed with [Scheetz, A.H., 1995]
		4. Decreased elongation at break (MD)	4. Agreed with [Scheetz, A.H., 1995]
Film Thickness	Decreased	1. Increased Tensile strength at break (MD)	1. Agreed with [Macauley, N.J., 1998], Not agreed with [Yamada, T., 1999], and [Millar, B., 2003]
		2. Increased Young's modulus (MD)	2. Agreed with [Macauley, N.J., 1998] and [Yamada, T., 1999]
		3. Decreased haze	3. Agreed with [Yamada, T., 1999]
		4. Decreased elongation at break (MD)	4. Agreed with [Macauley, N.J., 1998]
		1. Increased Tensile strength at break (MD)	1. Agreed with [Millar, B., 2003], not agreed with [Yamada, T., 1999]
Line Speed	Increased	2. Increased Young's modulus (MD)	2. Agreed with [Macauley, N.J., 1998], not agreed with [Yamada, T., 1999]
		3. Decreased haze	3. Not agreed with [Yamada, T., 1999]
		4. Decreased elongation at break (MD)	4. Agreed with [Macauley, N.J., 1998]

Table 3. 3: Summary of the effect of process parameters on the cast film properties, and a comparison of the trend plots results to the other investigators' results.

In conclusion, the entire trend plots showed that the film properties were affected by the changes in the process parameters. In this experiment, all the process parameters, varied simultaneously. The increase in the chill and annealing roll temperatures, and the increase in line speed that resulted in a decrease in the film thickness, affected the properties of the film in different magnitude and direction or weighted effect.

It is not possible to see the weighted effect of how the process parameters affected the mechanical and optical properties of the films, unless further analysis is done with multivariable data analysis (MVDA). The combined effect of the changes in the process parameters caused the changes in the film properties. Not only one process parameter caused the change, but also at the same time, one parameter might have more weight effect than another parameter. In Chapter 4, multivariable analysis will be done to show or indicate how the weighted effect of the process parameters, contributed to the changes in the film properties.

Most of the results obtained from the analysis were similar to those of other investigators, however there were some differences. The fundamental difference in the experimental procedures from the other investigators was that, the procedures were conducted on a commercial production line. A commercial line is more of a multivariate and dynamic system than a laboratory experimental

system. On a production line, process parameters are changed simultaneously or move up and down together. In this experiment, the chill roll and annealing roll temperatures, the line speed and the film thickness were changed at same time, for each experimental run. In comparison to other investigator's work, one parameter was changed at a time, plus there were no work done to show the combined effect of the chill roll temperature, annealing roll temperature, film thickness and line speed on the properties of cast film.

If the experimental procedures were involved in changing one process parameter at a time, then the simple X/Y plot analysis would be suitable. Because the process parameters were varied, all together at the same time, it would be interesting to see if an alternative analysis such as multivariate data analysis would detect any correlation among the process parameters and the properties of the films.

Two multivariate data analysis methods will be used in Chapter 4. These methods are the principal component analysis (PCA) and partial least squares projections to latent structures (PLS). PLS and PCA are multivariate statistical analytical methods use for multivariable data analysis on data, from systems or processes with many variables changing at the same time. PLS is used to perform analysis between X and Y variables in any multivariate system, and PCA is used for

analysis among X variables. Multivariate analysis is capable of dealing with multiple variables, and is able to deal with the multiple variation or changes that are happening simultaneously in a system.

#### **CHAPTER 4**

### **MULTIVARIATE DATA ANALYSIS**

## **4.1 Introduction**

Multivariate data analysis was used to analyze the data from the experiment in Chapter 3, to show the relationship between the film properties and the process parameters. The multivariate projection method that was used was the projection to latent structures (PLS), by means of partial least squares. The SIMCA-P +10.0 was the multivariate data analysis software from Umetrics Academy that was used to analyze the experimental data. To find more information on Umetrics Academy consult the website, <u>www.umetrics.com</u>.

The other projection method was the principal component analysis (PCA). This method was also used in the analysis. PCA is normally used for analysis among X variables or same data set, while PLS method is used for analysis between X and Y variables. To get more information on the PLS and PCA methods, consult [Eriksson, L., 2001].

The key advantage of multivariable data analysis (MVDA) projection methods is its ability to analyze multivariate systems, or to reduce the multivariate dimensions of a complex problem into small dimensional spaces of about three

dimensions [Eriksson, L., 2001].

The multivariable data software performs analyses by developing new variables from the original variables. The new variables are called the scores or latent variables. MVDA projection method used the latent variables, or scores, to analyze data set. The new latent variables made it easier to see sudden shifts in a process data set, and easily identified variables that are contributing to a system's disturbance, and or process problems, and also variables interactions.

PLS method is used to develop predictive model between X's and Y's [Eriksson, L., 2001]. The X's could be process parameters and the Y's film properties, or quality properties of a product. In cast film for example, Y properties are tensile strength, modulus, elongation, gloss, haze and impact strength etc. The Y variables are usually obtained by off line testing in a laboratory.

## 4.2 Process Parameters-Structure- Properties (PP-S-P) Relationship

From what has been demonstrated in the literature, the parameter changes affected the polymer percentage of crystallinity, the change in the crystallinity determined the properties of the film. The manipulation of the process parameters determined the type of film structure that is obtained after casting. Figure 4.1 shows a simple flow chart. In the first box are the process parameters, these parameters, when changed, influenced the crystal structure in the second box; this change influenced the changes in the film properties, in the third box.

It will be shown when the principal component analysis (PCA) on the Y variables or film properties was performed. The PCA analysis only generated one component. The one component was an indication that the properties were influenced by only one factor, the percentage of crystallinity and crystal size, as speculated by other investigators. This was the hypothesis that was proven when the PCA on Y was performed.



Figure 4.1: Flow chart for process parameters-structure-properties relationship. The change in the process parameters affected the percentage of crystallinity and crystal size in the film; this caused the film properties to change

## 4.3 Principal Component Analysis

The multivariable data analysis started with a principal component analysis (PCA) on the X's only, followed by an analysis on the Y's only. The final analysis was the PLS analysis on the X's and Y's. The PCA and PLS analysis

showed the number of components that were responsible for the changes in the process parameters and film properties.

The experimental data were entered into an Excel worksheet. Then, the data were imported into the multivariate data analysis software, SIMCA-P +10.0. The software performed the following data preprocessing; mean centering and unit variance scaling of the data. The mean centering of the data and unit variance scaling were done by finding the mean for each column, then subtracting it from each column, and dividing by the standard deviation of the column to get the unit variance. The unit variance scaling was done to put the variables on the same footing, because the variables had different units. The mean centered and unit variance scaled experimental data are shown in Table A.1, in appendix A.

# 4.3.1 Principal Component Analysis on the Process Parameters

The PCA on the process parameters only showed the two components that were responsible for explaining the variability and predictability of the data, as shown in Figure 4.2.



Figure 4.2: Model overview of the PCA on the process parameters. The two components explained the variability  $(R^2)$  and predictability  $(Q^2)$  of the data

The principal component analysis (PCA) on the process parameters (X's) only gave two components. For this model, the total variability ( $R^2X$ ) was 99.13 % and predictability ( $Q^2X$ ) 97.3% for the two components. The first principal component was very significant, because it explained 94.65 % of the total variation of the data. The second component was not significant, because it only explained 4.48 % of the total variation. The high values of variability and predictability mean that the first component dominated the model; this means the process parameters had strong correlations. The process variables all had strong influence on the PCA model.

### 4.3.2 PCA - Score and Loading Plots for the Process Parameters

In PCA analysis, the first principal component (PC1) explained the maximum source of the variations in the data set. If the first component is not sufficient, a second component (PC2) is calculated that explained the rest of the variations. In this case most of the variations were explained by the first component and a small percentage by the second component.

The score plot in Figure 4.3 shows the data pattern for the experimental runs. The scores were the co-ordinate values of the observations or rows that were projected on the components planes. The plotting of the components scores was done in the score plot, Figure 4.3. The clusters in the plot are the experimental runs



The calculated score values for t1 and t2 are shown in Table A.2 in Appendix A.

Figure 4.3: PCA score plot of t1 plotted against t2. The plot represents 99.13 % of the total variation in process parameters. The first component explained majority of the variation, 94.65%.

For principal component one (PC1) and principal component two (PC2), the scores were t1 and t2 respectively. The process parameters data had two sets of score values, one score along PC1 and the other along PC2. The score plot was a

map of the data set for the process parameters. There were several separate clusters in the plot, notice that in Figure 4.3 that there are different size clusters in all four quadrants. Variables that are similar are close together and those that are not similar in properties are far away from each other. Clusters that are close to the origin of the plot have similar average properties or effects.

The pattern that is shown in Figure 4.3 is easier to interpret by looking at the loading vector plot, Figure 4.4.



Figure 4.4: PCA loading plot of p1 plotted against p2. The first component explained most of the variation; this means that the four variables or parameters had strong correlations.

Table 4.1 shows the values of the loading vectors p1 and p2 for the process parameters.

Process Parameters	p(1)	p(2)
ТНК	0.488187	0.734636
RT#1	-0.511036	-0.178234
RT#2	-0.496929	0.557813
LSpd	-0.503564	0.342618

Table 4.1: Loading vectors p1 and p2 for the process parameters

It was important to know which variables or parameters were influential to the PCA model and how they were correlated. The loading plot gave this information; the loading vectors were p1 and p2. They gave the magnitude and direction of the score values, t = p1\*x1 + p2\*x2. The loading plot shows the relationships amongst the four process parameters.

In Figure 4.3, the clusters in the first and second quadrants are influenced by the film thickness; RT#1 is responsible for the clusters near to the origin and in the third quadrant, and the LSpd and RT#2 is responsible for the clusters in the fourth quadrant. The process parameters that gave the same or similar information are nearer or closer together, and are positively correlated. RT#2, RT#1 and LSpd are close or near together; these parameters were increased during the experiment. Variables or parameters in diagonally opposed quadrants are negatively correlated. When one variable is increased, the other variable decreased.
Film thickness is negatively correlated with the chill roll temperature RT#1, when the film thickness was decreased; the chill roll was increased, during the experimental runs. The loading plot shows how the process parameters were changing during the experimental runs.

The distance the process parameters or variables from the plot origin, meant that they have strong influence on the model. Film thickness, chill roll temperature, annealing roll temperature and line speed all had a strong influence on the PCA model; they are all far away from the origin of the plot.

## 4.3.3 Principal Component Analysis on the Film Properties

A principal component analysis was done only on the film properties (Y's). The analysis only gave one principal component that explained 83.46 % and 73.35 % of the total variability and predictability respectively, as shown in Figure 4.5.



Figure 4.5: Model overview of the PCA on the film properties. The one component explained all of the variability  $(R^2)$  and  $(Q^2)$  predictability of the data

This component represented the only component that influenced the changes in the Y variables. As speculated by other investigator, the manipulation of the X variables influenced the percentage of crystallinity and crystal size, which in turn influenced the film properties. The benefit of MVDA is that it can extract the latent variables from the measured variables. The measured variables were the film properties in this case; the latent variables were the percentage of crystallinity and crystal size.

The percentage of crystallinity and crystal size would change based on how much the process parameters changed, during the cooling and annealing processes of the film. Process parameter must be carefully chosen based on the final film properties required for an application. The high percentage of the variability  $(R^2X)$  meant that the crystallinity had a strong correlation or influence on the film properties. The hypothesis has proven that the change in the crystallinity and crystal size was the main factor that influenced the changes in the film properties.

## 4.3.4 PCA-Score and Loading Plots for the Film Properties

The score plot in Figure 4.6 shows how the film properties changed over the experimental runs, as the change in the process parameters caused the change in the latent variable, percentage of crystallinity and crystal size, in the film samples.

Figure 4.6 shows the score plot for the one component, t1 against number of observations. It further illustrates how the properties changed as the line speed, film thickness, chill roll and annealing roll temperatures, changed the percentage of crystallinity and crystal size in the film structure, which in turn affected the film properties. The calculated score values for t1 are shown in Table A.3 in Appendix A.



Figure 4.6: PCA score plot of t1 plotted against number of observations. The plot represents 83.46% of the total variation in the film properties

The properties were below average or at the centerline until 80 samples were reached, at which point they started to increase for the rest of the samples tested. The pattern seen here is best explained with the loading plot in Figure 4.7.



Figure 4.7: PCA loading plot of p1, one component explained most of the variation in the film properties

Table 4.2 show	s the values	of the	loading	vectors r	ol for	the film	properties
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Film Properties	p(1)
TSAB	0.509931
YMOD	0.512774
EL%	-0.496417
Haze	-0.480211

Table 4.2: Loading vectors p1 forthe film properties

As shown in the score plot, there were some properties that were below the centerline, as the experiment progressed, some properties started to increase. The loading plot shows that elongation at break and the haze were decreasing, trending below the centerline in the score plot, and the Young's modulus and tensile strength at break were increasing, trending above the centerline as shown in the score plot.

The next section below will discuss the PLS analysis of the data. This involves the analysis of X and Y to find out the relationship with MVDA regression analysis.

## 4.4 Projection to Latent Structures (PLS) Analysis on Process Parameters and Film Properties (X's and Y's)

The relationship between the four process parameters and the four film properties was modeled by PLS. Two components were generated. The components explained 84.6% and 84.41% of the total variability ( $R^2Y$ ) and predictability ( $Q^2Y$ ) respectively. The PLS components are shown in Figure 4.8.



Figure 4.8: Model overview of the PLS model based on the film properties. The two component models explained 84.6% of the total variability ( $R^2Y$ ) and 84.41% predictability ( $Q^2Y$ ).

The first component was more significant than the second component. The first component explained 73.46 % and the second component 11.14 % of the total variation. The high variability ( $R^2Y$ ) meant that the first component dominated

the model; this meant that the variables were correlated.

#### 4.4.1 PLS - Score and Loading Plots

The PLS score plot below was plotted for score values of t1 and t2, component one and two. The score plot is shown in Figure 4.9. The plot shows nine clusters; these are the experimental runs. Several different film samples were taken from each run; the cluster means same or similar properties peculiar to each run. The calculated score values for t1 and t2 are shown in Table A.4 in Appendix A.



Figure 4.9: PLS score plot of t1 plotted against t2. The plot represents 84.6 % of the total variation in the film properties. The first component explained majority of the variation, 73.46%.

The pattern starts from the third quadrant down to the fourth, then to the first and up to the second quadrant. The process parameters were changed in each experimental run as the experiment progressed. The variables responsible for the pattern in the score plot is seen clearer in the PLS weights or loading plot as shown in Figure 4.10. The plot in Figure 4.10 shows, film thickness, haze and elongation at break diagonally opposite to tensile strength at break, Young's modulus, and chill roll temperature. These variables are responsible for the pattern in the third, fourth and first quadrants, and the annealing roll and line speed influenced the pattern in the second quadrant.



Figure 4.10: PLS loading plot of W\*C (1) against W\*C (2). The first component explained most of the variation.

The component weights showed how the variables combined to develop the model relationship between the X's and Y's. The weight for X is denoted by w<sup>\*</sup>, and, for Y by c. The PLS weight or loading plot was the plot of the components' weights (w<sup>\*</sup>c) combined for the X's and Y's. The plot shows w<sup>\*</sup>c (1) plotted against w<sup>\*</sup>c (2). The plot shows the relationship between the film properties and the process parameters. Table 4.3 shows the values of the loading vectors w<sup>\*</sup>c (1) and w<sup>\*</sup>c (2) for the process parameters and film properties.

Process Parameters and Film Properties	w*c(1)	w*c(2)
ТНК	-0.532929	0.745021
RT#1	0.521093	-0.158386
RT#2	0.461867	0.55256
LSpd	0.480757	0.343568
TSAB	0.495169	-0.0379766
YMOD	0.472455	-0.517054
EL%	-0.418143	0.431696
Haze	-0.368259	1.42702

Table 4. 3: Loading vectors w\*c(1) and w\*c(2) for the process parameters and film properties

In Figure 4.10, the distance the variables are from the plot origin is an indication of how much influence they had on the model. All the variables in this model are far from the plot origin, which meant that they had strong influence on the model or strong correlations. How close or far, the variables are from each other meant something. Closer meant that variables had stronger correlation, and the further apart the variables were meant they had less influence on each other. The chill roll temperature, tensile strength at break, and Young's modulus are closer or nearer together, they gave the same information and were correlated.

The chill roll temperature had a stronger influence on the tensile strength at break (TSAB) and the Young's modulus (YMOD); it is closer to those properties as shown in the Figure 4.10.

Annealing roll temperature and line speed had stronger positive influence on the tensile strength at break, than on the Young's modulus; they are closer or nearer to the tensile strength at break. Thickness had a strong negative influence on the tensile strength at break and Young's modulus; it is diagonally opposite to them, as shown Figure 4.10. In the experiment, when the film thickness was high, the chill and annealing roll temperature were low. The plot does not show line speed to be negatively correlated to film thickness, as would be expected, since the line speed was used to get the different film thicknesses. The line speed is positively correlated with the annealing roll and chill roll temperature.

In the experiment, when the film was thin, line speed was high, because the line speed was increased to get the thin film; the chill roll and annealing roll temperatures were also increased at the same time, the plot in Figure 4.10 shows this to be the case. The film thickness positively correlated with the elongation at break and the haze. The previous data analysis in Chapter 3 has shown that when the film thickness was high, the haze and elongation at break were high.

As the film thicknesses were decreased over the experimental runs, the haze and the elongation at break decreased. Remember that at the start of the experiment, the film thickness were high (115 microns), at that point the line speed was low, the speed held constant for sampling, and then the line speed was increased to get

70

the next thickness (102 microns), line speed held constant again, film samples were collected, then the line speed was increased again to get the other film thickness (76 microns), speed held constant, film samples were collected, so on and so forth for the rest of the experimental runs.

The PLS weights or loading plots summarized the trends in one plot, the tensile strength at break and the Young's modulus increased, and the haze and elongation at break decreased, when the film thickness was decreased by increasing the line speed, and the chill roll and annealing roll temperatures were increased. To get more information from the loading plot, the PLS model generated PLS regression coefficients ( $B_{PLS}$ ) plots. The solution to the PLS model is given in latent variables format with scores, with the weights relating to the coefficient in the model. The PLS model,  $Y = B_1X_1 + B_2X_2 + B_3X_3 + ..., B_NX_N$ , where  $B = W^*C$ . The regression model is plotted for each Y response (film property) against the process parameter. The plot for each response is scaled and centered for the variables.

### 4.4.2 PLS – Regression Coefficient Plots of the Film Properties

The PLS method generated simplified coefficient plots that summarized the relationships or trends and provided quick illustrations of how much the process parameters influenced the films' properties. The plots show the magnitudes and directions of the coefficients for the process parameters. The PLS coefficient plots show how each film property was affected by the process parameters, or the weighted effect of the process parameters on the film properties.

The plots were developed by the software from the relationship equation between Y's and X's,  $Y = B_1X_1 + B_2X_2 + B_3X_3 + B_4X_4$ , where B's are the coefficients for the process parameters. The regression coefficient plot for each film's property is shown in Figure 4.11 - 4.14. These plots are mean centered and unit variance scaled, showing the value of the coefficients on the y-axis and the corresponding process parameters (X's) on the x-axis (centre line). The negative coefficients bar below the centre line meant that the parameter had a negative influence on the film property. The negative influence meant that as the process parameter was increased, the film property decreased. The positive coefficients bar above the centre line meant that the parameter had a positive influence on the film property. The positive influence meant that as the process parameter was increased, the film property increased. The values of the process parameters' coefficients for the film properties are shown in Table 4.4.

Process Parameters (X's)	Tensile strength at break (TSAB), coefficient for the X's	Young's modulus (YMOD), coefficient for the X's	Elongation at break (EL %), coefficient for the X's	Percentage haze (%HZ), coefficient for the X's
Film Thickness	-0.292	-0.637	0.544	1.259
(THK)				
Chill Roll	0.264	0.328	-0.286	-0.418
Temperature (RT#1)				
Annealing Roll	0.208	-0.067	0.045	0.618
Temperature (RT#2)				
Line Speed (LSpd)	0.225	0.049	-0.053	0.313

Table 4.4: The values of the coefficients for the process parameters and film properties. These coefficients were used to develop the relationship equations for the film properties (Y's) and the process parameters (X's).

Figure 4.11 shows the PLS coefficient plot for the tensile strength at break against the process parameters. It shows the process parameters that affected the tensile strength at break in the machine direction (MD). The statistical importance of each coefficient is shown as 95% confidence intervals



Figure 4.11: Regression coefficient plot of unit variance scaled and mean centered plot for tensile strength at break (TSAB) in the machine direction (MD)

The figure shows that the chill roll temperature (RT#1), line speed (LSpd) and annealing roll temperature (RT#2) have positive coefficients, which means they had positive effects on the tensile strength at break. The film thickness (THK) has a negative coefficient, which means it had a negative effect on the tensile strength at break. The magnitude of the coefficients has given an indication of the sensitivity of the tensile strength at break to these process parameters.

All the process parameters' coefficients were of almost equal values; therefore they were all-important to the changes in the tensile strength. As the line speed was increased, and thickness was decreased, and the chill roll and annealing roll temperatures were increased, the tensile strength at break increased. It was not possible to single out any one variable to have more effect on this property than another variable, because they all had almost the same equal values, or equal effects on the tensile strength. This figure shows that these casting conditions were critical to this film property.

Figure 4.12 shows the PLS coefficient plot for the Young's modulus against the process parameters. The plot shows that the Young's modulus was more responsive to changes in the film thickness (THK) and chill roll temperature (RT#1), and was least responsive to the changes in the annealing roll temperature - (RT#2) and the line speed (LSpd).

74



Figure 4.12: Regression coefficient plot of unit variance scaled and mean centered plot for Young's modulus (YMOD) in the machine direction (MD)

The decrease in the film thickness, and the increase in the chill roll temperature mostly contributed to the increase in the Young's modulus. The other two parameters were also increased, but their contributions to the increase in the modulus were very small. Thickness had a significant negative influence, chill roll temperature a medium positive influence, annealing temperature a very small negative influence, and line speed a very small positive influence. Figure 4.13 shows the PLS coefficient plot of elongation at break against the process parameters. The decrease in the elongation at break was mostly influenced by the changes in the film thickness and the chill roll temperature, and was least affected by the annealing roll temperature and line speed.



Figure 4.13: Regression coefficient plot of unit variance scaled and mean centered plot for elongation at break (EL%) in the machine direction (MD)

The film thickness had a very large positive effect, the chill roll temperature a large negative effect, the annealing roll temperature a very small positive effect and the line speed a very small negative effect. The decrease in the film thickness, and the increase in the chill roll temperature contributed mostly in causing the decrease in the elongation at break. Although, the annealing roll temperature and the line speed were increased, their contributions were very small. Figure 4.14 shows the PLS coefficient plot for the haze against the process parameters. The film thickness had a very large positive influence on the haze, the chill roll temperature a medium negative influence, the annealing roll temperature a large positive influence, and the line speed a less than medium positive influence.



Figure 4.14: Regression coefficient plot of unit variance scaled and mean centered plot for haze

The haze was mostly affected by the changes in the film thickness. The process parameters are shown to have some significant effect on the haze. All these parameters are important to the changes in the haze.

From the PLS coefficient plots; the process parameters had different magnitude and directional effect on the film properties. As per speculation by other investigators, the changes in the process parameters affected the percentages of crystallinity and crystal size in the cast film. Therefore the change in the film structure would affect the film properties. Any change in the process parameters, would result in change in the film properties. The magnitude of the change in the film properties would depend on the magnitude of the change in the process parameters. In this experiment, all the process parameters were changed at the same time, therefore the effect on the film properties had to be based on the combined effects of the changes in the process parameters.

The PLS coefficient plots also show that the process parameters had different weighted effects on the film properties. The plots show that the process parameters did not have equal effect on the properties. In the X/Y plots in Chapter 3, it was not possible to see the different weighted effect of the process parameters on the film properties.

The variable influence on projection (VIP) is a parameter that helped to give an indication of how important the X's are to the modeling of the Y's. A VIP greater than 0.8 means the predictor is important to the modeling of the Y's. The plot in Figure 4.15 shows the VIP for the process parameters.



Figure 4.15: Variables influence on projection (VIP) for the process parameters

The process parameters all have a VIP above 0.8; this means that all these process parameters were important to the model of the film properties. Therefore the conclusion cannot be drawn that one parameter was more important than another. All the process parameters played a critical role in changing the percentage crystallinity and crystal size in the film structure, which in turn changed the properties of the films.

#### **CHAPTER 5**

#### **DISCUSSION, CONCLUSIONS, and RECOMMENDATIONS**

#### **5.1 Discussion and Conclusions**

As per speculation by other investigators, the increase or decrease in process parameters will either increase or decrease film properties, because there is either an increase or decrease in the film percentage of crystallinity and crystal size. As mentioned before, the change in the crystal structure (increase or decrease in crystallinity) dictates or controls the properties of cast films [Leephakpreeda, T., 2004].

The trend plots in Chapter 3, shows that the tensile strength at break (MD) and the Young's modulus (MD) increased, while the haze and the elongation at break (MD) decreased. The tensile strength at break (MD) and the Young's modulus (MD) increased and the elongation at break (MD) decreased, due to the increase in the film crystallinity [Millar, B., 2003]. The increase in the chill roll temperature caused larger and stronger crystals to grow in the film structure. The polymer melt takes longer to cool at higher chill roll temperatures. The longer cooling allowed more time for more crystals to grow in the film structure [Macauley, N.J., 1998].

The increase in crystallinity increases the stiffness or modulus of semi-crystalline polymers [Reding, F.P., 1964]. The annealing of the film also caused more

crystals to grow and improve dimensional stability.

The elongation at break (MD) decreased, because the percentage of amorphous region in the film was reduced as crystallinity increased. This reduction in amorphous region in the film allowed less slippage and disentanglement to take place in the film structure [Millar, B., 2003].

Although the chill roll and annealing roll temperatures were increased, the haze still decreased, because the film thickness was decreased. The haze was influenced by the film thickness and the percentage of crystallinity and crystal size, hence, if these factors are reduced, the haze reduced [Peacock, J.A., 2000]. The multivariate data analysis (MVDA) confirmed that the haze was strongly influenced by the film thickness. The reduction in the film thickness affected the film properties, because of the increase in additional molecular-orientation in the film structure as the line speed was increased, as a result the percentage of crystallinity increased [Kohan, M.I., 1964].

The multivariate data analysis (MVDA) has shown that the annealing temperature affected the film properties in different magnitude and direction. The annealing of

81

the film was done after the chill roll cooled the film. The film was heated a few degrees above the chill roll temperature. The annealing process was used to relieve induced stress in the film and allowed it to reach the equilibrium degree of crystallinity and achieved optimum dimensional stability at room temperature [Reding, F.P., 1964].

Annealing or heat setting further increased the crystallinity and crystal size in the film. The annealing or reheating of the film allowed the crystals to grow larger and, to have more time for molecular alignment, interaction, and relief of induced shear stress [Reding, F.P., 1964]. Annealing process caused the following changes in semi-crystalline polymer properties, the tensile strength at break increased, Young's modulus increased, haze increased and elongation of break (MD) decreased [Scheetz, A.M., 1995].

From what has been shown so far, the process parameters affected the mechanical and optical properties of the cast films. The casting temperatures played a critical role in determining the properties of the film. The casting temperatures for each film thickness at a particular line speed, governed the film properties. As other investigators speculated, the casting temperature change caused modification in the percentage of crystallinity and crystal size of the film. The percentage of crystallinity and crystal size determined cast film's mechanical and optical properties.

The MVDA, PCA on the X, shows how the process parameters were correlated with each other. The PCA on the Y (film properties) shows only one principal component that was a strong indication that the changes in the properties were driven by one latent factor. MVDA is effective in showing latent variables by the number of components that are used to explain the percentage of the variation in the data. The hypothesis was that the crystallinity was the only factor that influenced the changes in the film properties. The hypothesis was proven in the PCA on the film properties, only one component are shown, that explained more than 50% of the variation.

The MVDA- PLS method gave an indication of the magnitude and direction of the effect of the process parameters on the properties of the film. The centered and normalized coefficients of the process parameters are shown in the regression coefficient plots for the film properties. The magnitude and sign of the coefficient for each process parameter shows the weighted effect on the properties. The positive coefficient means that the property would increase if the process parameter should increase. The negative coefficient means that the property would decrease if the process parameter should increase. All the process parameters were important to the film properties, although they affected the properties differently. As shown in PLS analysis, each parameter had an individual weighted effect on the film properties, see the PLS regression coefficient plots. Notice in the PLS regression coefficient plots, the chill roll temperature was shown to have a reasonably large positive or negative coefficient in all the plots for the properties. The chill roll temperature was critical in determining the crystal structure during the casting of the film.

In conclusion, this study confirmed that there is a relationship between process parameters and film properties. The film properties were dependent on the crystal size and percentage of crystallinity in the film, as per speculation by other investigators. The percentage of crystallinity and crystal size in the film were determined by the process parameters that were used to cast the film. The main objective of this project was to investigate how process parameters affect film properties, for films made on an industrial scale extruder. The study proved that changes in process parameters would affect the mechanical and optical properties of cast film.

#### **5.2 Recommendations for Further Work**

1. The above work could be repeated on a cast film production to investigate the effect of process parameters on more film properties such as gloss, tear strength, impact strength, dimensional stability, kinetic coefficient of friction, heat-sealing temperature and percentage of crystallinity. The tensile strength, yield strength, Young's modulus, haze and elongation to be included, as well as the machine and transverse directions for the mechanical properties. This would show the relationship among the property-process parameter and structure (percentage of crystallinity). The process parameters should include the melt temperature, along with the chill roll temperature, annealing roll temperature, film thickness, and line speed.

2. The development of a deterministic model should be looked into, as it could be used to predict film properties on a production line. The model could be used to predict film properties based on the input process parameters, or to predict process parameters based on the input film properties. Eventually comparison should be made between such a deterministic models in (MVDA) multivariable data analysis.

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# APPENDIX A

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Primary ID	THE	RT#1	RT#2	LSpd	TSAB	YMOD	EL%	Haze
1	1.89005	-1.39209	-0.93543	-1.11346	-1.42351	-1.6421	1.65845	2.51304
2	1.86593	-1.44424	-0.929939	-1.10976	-1.55278	-1.42772	1.89766	2.43412
3	1.85086	-1.41877	-0.957398	-1.10742	-1.71512	-1.17836	1.4202	2.76305
4	1.83578	-1.43211	-0.945499	-1.10506	-1.48241	-1.38426	1.57499	2.44434
5	1.82975	-1.43211	-0.929023	-1.10411	-1.61353	-1.52731	2.33019	2.46684
6	1.80564	-1.47092	-0.934515	-1.10029	-1.8742	-1.55148	1.57748	2.46684
7	1.80564	-1.40422	-0.966552	-1.10029	-1.64846	-1.81974	1.52509	2.45874
8	1.79961	-1.5073	-0.957398	-1.09932	-1.23348	-1.75689	2.0746	2.44836
9	1.79961	-1.39209	-0.947329	-1.09932	-1.60695	-1.28818	1.78952	2.5751
10	1.77549	-1.40422	-0.936346	-1.09543	-1.59238	-1.31312	1.17349	2.48985
11	1.77549	-1.49517	-0.947329	-1.09543	-1.57348	-1.1124	2.14996	2.5173
12	1.77247	-1.59218	-0.950076	-1.09494	-1.63925	-1.1124	1.72399	2.5173
13	1.76946	-1.42241	-0.957398	-1.09444	-1.99308	-1.28564	1.58761	2.86412
14	1.7574	-1.3254	-0.93543	-1.09247	-1.59891	-1.53939	1.55933	2.51304
15	1.7574	-1.37633	-0.916209	-1.09247	-1.51121	-1.59075	2.11392	2.48532
16	1.7574	-1.32297	-0.937261	-1.09247	-1.88004	-1.70578	1.30312	2.72553
17	1.75137	-1.54368	-0.928108	-1.09148	-1.57348	-1.34483	2.22205	2.46658
18	1.74836	-1.47092	-0.949526	-1.09098	-1.39086	-1.49106	1.52896	2.63314
19	1.7363	-1.47092	-0.947329	-1.08898	-1.53879	-1.40146	1.44982	2.48186
20	1.71519	-1.43211	-0.909801	-1.08545	-0.94894	-1.24891	1.58653	2.54999
21	1.40769	-1.18837	-0.957398	-1.02863	-1.06344	-1.007	0.439504	0.68369
22	1.37754	-1.16776	-0.967467	-1.02245	-0.955274	-2.03481	0.887992	0.702168
23	1.37754	-1.16776	-0.946414	-1.02245	-0.984265	-1.14224	0.488688	0.917643
24	1.36548	-1.16776	-0.881426	-1.01995	-1.08473	-1.33816	0.496323	1.01726
25	1.36247	-1.2005	-0.965636	-1.01932	-0.994253	-1.51523	0.043018	0.813038
26	1.36247	-1.13865	-0.939092	-1.01932	-0.908695	-1.77035	0.606618	0.927981

27	1.36247	-1.20244	-0.945499	-1.01932	-1.06076	-1.14772	0.750729	0.960762
28	1.35945	-1.18837	-0.947329	-1.01869	-0.685347	-1.10439	1.05881	0.619016
29	1.35945	-1.25507	-0.947329	-1.01869	-1.03177	-0.681477	0.476171	0.674451
30	1.35644	-1.25385	-0.930853	-1.01806	-0.987919	-0.862727	0.943926	0.68369
31	1.35644	-1.18594	-0.946872	-1.01806	-0.652215	-1.15116	0.792278	0.739125
32	1.35644	-1.17382	-0.939092	-1.01806	-1.04785	-0.84424	0.792278	0.711407
33	1.35644	-1.18607	-0.957398	-1.01806	-1.00619	-1.33682	0.0561248	0.915897
34	1.34136	-1.21626	-0.947329	-1.01488	-0.746202	-1.16081	1.01621	1.07406
35	1.33533	-1.27083	-0.925362	-1.0136	-0.731147	-1.77502	0.996551	0.720646
36	1.33533	-1.18716	-0.946872	-1.0136	-0.93939	-1.12405	0.314987	0.91828
37	1.33232	-1.2005	-0.945499	-1.01296	-0.619083	-1.43971	0.91958	0.68369
38	1.3293	-1.18594	-0.956116	-1.01232	-0.990599	-1.15271	0.246177	0.865978
39	1.3293	-1.18594	-0.947329	-1.01232	-1.02729	-0.923216	0.623624	0.912949
40	1.32629	-1.18837	-0.947329	-1.01167	-0.976079	-1.5624	0.872034	0.943494
41	0.611787	-0.837916	-0.922616	-0.812186	-0.579763	-0.811288	0.744241	-0.0846353
42	0.602743	-0.745754	-0.858543	-0.808877	-0.391106	-1.30267	1.16366	0.170356
43	0.599728	-0.825788	-0.762433	-0.807769	-0.55165	-1.05477	0.678706	-0.0944879
44	0.599728	-0.867019	-0.927193	-0.807769	-0.562856	-1.08254	-0.0599702	0.102855
45	0.596713	-0.812449	-0.947329	-0.806657	-0.568752	-1.08367	0.267606	-0.116427
46	0.593699	-0.828214	-0.73955	-0.805542	-0.980611	-0.83856	0.247356	-0.230983
47	0.590684	-0.865927	-0.670901	-0.804425	-0.885113	-0.84424	0.311186	-0.249461
48	0.587669	-0.825182	-0.776163	-0.803305	-0.837364	-0.98356	0.0626787	-0.2587
49	0.578625	-0.717863	-0.785317	-0.799926	-1.16332	-0.415643	0.373969	-0.221744
50	0.578625	-0.839127	-0.783486	-0.799926	-0.288739	-1.34606	1.15056	0.240222
51	0.572595	-0.85368	-0.772502	-0.797659	-0.680475	-0.521373	0.744241	-0.221744
52	0.572595	-0.867019	-0.772045	-0.797659	-0.698502	-0.958668	1.16366	-0.2587
53	0.56958	-0.814875	-0.886002	-0.796521	-0.566998	-1.2782	0.678706	-0.107096
54	0.56958	-0.85368	-0.931769	-0.796521	-0.577571	-1.09939	-0.0599702	-0.113082
55	0.56958	-0.890059	-0.947329	-0.796521	-0.593455	-0.828265	0.267606	-0.0900947
56	0.566566	-0.856104	-0.886002	-0.79538	-0.610605	-0.92156	0.247356	-0.107623

57	0.565059	-0.85368	-0.922616	-0.794808	-0.5631	-0.934019	0.311186	-0.0932055
58	0.560536	-0.812449	-0.774058	-0.793089	-1.07172	-0.627102	0.0626787	-0.230983
50	0.551/02	-0.801271	0 774332	0 789629	_0 758010	-0 033777	0 373060	-0.240222
	0.531492	-0.0712/1	0.774332	0.769029	-0.736919	-0.333777	1.15056	0.040222
OU	0.521344	-0.838885	-0.7/4332	-0.77/897	-0.038085	-0./2981	1.15056	-0.249401
61	0.126409	-0.543242	-0.757856	-0.588971	-0.583515	-1.05819	0.46657	-0.410679
62	0.117365	-0.449868	-0.757856	-0.583697	-0.354028	-0.850644	1.08293	-0.415765
63	0.117365	-0.421978	-0.721244	-0.583697	-0.48485	-0.385979	0.52814	-0.409768
64	0.117365	-0.450475	-0.796301	-0.583697	-0.702741	-0.305226	0.562808	-0.420468
65	0.111335	-0.415914	-0.886002	-0.580152	0.124436	-0.270643	0.640532	-0.415765
66	0.108321	-0.451081	-0.675478	-0.578371	0.0917904	-0.590852	0.115107	-0.406526
67	0.0992763	-0.489886	-0.73955	-0.572993	-0.038788	-0.298918	0.547636	-0.397287
68	0.0962616	-0.488673	-0.76701	-0.571188	-0.0100412	-0.91106	0.698367	-0.425004
69	0.0932469	-0.489886	-0.748703	-0.569377	-0.715556	-0.120918	-0.0552843	-0.421144
70	0.0902321	-0.421978	-0.689207	-0.567561	-0.721402	-0.109814	0.629555	-0.415765
71	0.0902321	-0.475334	-0.691954	-0.567561	-0.780845	-0.157048	-0.012687	-0.413149
72	0.0902321	-0.461631	-0.773966	-0.567561	-0.619814	-0.449488	0.495208	-0.422984
73	0.0872173	-0.437742	-0.76701	-0.565738	-0.43832	-0.105947	0.605143	-0.397287
74	0.0872173	-0.390449	-0.689207	-0.565738	-0.298629	-0.38355	0.781694	-0.238111
75	0.0751582	-0.448655	-0.748703	-0.558386	-0.870301	-0.116122	0.347985	-0.429293
76	0.0721435	-0.385598	-0.730397	-0.556533	-0.582005	-0.520974	0.651379	-0.411102
77	0.0691286	-0.452294	-0.691954	-0.554673	-0.0295303	0.0556066	0.498551	-0.406526
78	0.0691286	-0.44623	-0.691954	-0.554673	0.10787	-0.750956	0.0299112	-0.406526
79	0.0600844	-0.452294	-0.730397	-0.549057	-0.384724	-0.177348	0.308435	-0.413362
80	0.0480253	-0.448655	-0.76701	-0.541479	-0.331128	-0.11356	0.600065	-0.406526
81	-0.0816099	0.00972504	-0.400879	-0.453009	-0.193972	0.161577	-0.108629	-0.485582
82	-0.15095	0.0218513	-0.400879	-0.399716	-0.214679	0.30984	-1.49377	-0.497528
83	-0.153964	0.0909721	-0.391725	-0.397293	-0.151972	-0.00520815	0.159375	-0.494156
84	-0.172053	0.0145757	-0.400879	-0.382554	0.0581713	0.514774	-0.193268	-0.4712
85	-0.172053	0.0509546	-0.437492	-0.382554	-0.083711	-0.0902508	1.36027	-0.469665
86	-0.181097	0.0630809	-0.428339	-0.375055	0.0995865	0.683941	-0.0782219	-0.4712

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87	-0.181097	0.0727822	-0.345959	-0.375055	0.0586587	0.801753	-0.871193	-0.480439
88	-0.181097	0.0497417	-0.373419	-0.375055	-0.124931	_0.0102218	1.11451	-0.491364
89	-0.181097	0.010331	-0.373419	-0.375055	-0.226178	0.500153	-0.0915907	-0.485116
90	-0.184112	0.117651	-0.391725	-0.372536	-0.204447	0.53894	-0.248612	-0.461961
91	-0.184112	0.0448919	-0.373419	-0.372536	-0.00516891	0.381857	0.3645	-0.480439
92	-0.184112	0.0145757	-0.398133	-0.372536	0.103972	0.53894	-0.333808	-0.489678
93	-0.189539	0.00972504	-0.417355	-0.367977	0.0350764	0.307545	-0.0618382	-0.467309
94	-0.193156	-0.00482705	-0.364266	-0.364919	0.0961759	0.454357	0.167108	-0.480439
95	-0.196171	0.0473168	-0.391725	-0.36236	-0.191487	0.0834949	-1.97218	-0.498373
96	-0.202201	0.0800578	-0.373419	-0.357212	0.0265017	0.448315	0.191913	-0.480439
97	-0.205215	0.0364034	-0.400879	-0.354623	-0.18106	-0.0211098	-0.969496	-0.490011
98	-0.21426	-0.0412068	-0.336806	-0.346793	-0.072894	0.526857	0.862204	-0.4712
99	-0.232348	0.0145757	-0.400879	-0.330849	-0.101885	-0.0408911	0.561432	-0.484142
100	-0.235363	0.0642938	-0.464952	-0.328154	0.0494015	0.919565	-0.438664	-0.489678
101	-0.304703	0.24134	-0.20683	-0.263018	0.36854	0.563107	-1.61174	-0.480439
102	-0.386102	0.253466	-0.215067	-0.177964	-0.18642	0.986024	0.233069	-0.498917
103	-0.386102	0.237702	-0.205914	-0.177964	0.193623	0.200607	-0.333808	-0.489678
104	-0.407205	0.257105	-0.194931	-0.154201	0.106408	0.175425	-0.956389	-0.536829
105	-0.41022	0.253466	-0.20866	-0.150744	-0.221841	1.13369	0.321541	-0.494181
106	-0.413235	0.257105	-0.213237	-0.147272	0.0766867	0.256215	-0.858087	-0.528038
107	-0.413235	0.281358	-0.20683	-0.147272	0.0688907	0.686345	-0.923622	-0.52291
108	-0.416249	0.258317	-0.20866	-0.143783	0.475243	0.768523	0.000420737	-0.489678
109	-0.416249	0.253831	-0.225136	-0.143783	0.00433251	0.86919	-0.382336	-0.537146
110	-0.422279	0.275294	0.140995	-0.136757	-0.0280687	0.526857	0.349492	-0.4712
111	-0.7328	0.495996	0.148317	0.34019	0.222856	0.50269	-1.0252	-0.600548
112	-0.744859	0.494784	0.119027	0.364792	0.232601	0.309357	-0.176458	-0.57283
. 113	-0.747874	0.494784	0.148317	0.371037	0.40021	1.28811	-0.720463	-0.591309
114	-0.747874	0.495996	0.148317	0.371037	0.399723	0.816857	-0.87447	-0.563591
115	-0.750889	0.554203	0.151064	0.377321	0.0652848	0.658747	-0.792552	-0.58207
116	-0.750889	0.61726	0.15381	0.377321	-0.242061	0.605036	-0.661482	-0.563591
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117	-0.750889	0.554203	0.160217	0.377321	0.0883798	1.29531	-0.979327	-0.58207
118	-0.753904	0.496603	0.177608	0.383643	0.352948	0.418108	-0.461502	-0.57283
119	-0.753904	0.481444	0.171201	0.383643	-0.389645	0.81589	-0.497645	-0.563591
120	-0.756918	0.499634	0.151064	0.390005	-0.24328	0.284587	-0.890854	-0.554352
121	-0.759933	0.500846	0.140995	0.396406	0.0469657	1.19144	-0.825319	-0.58207
122	-0.762043	0.375944	0.119942	0.400911	0.047453	0.853107	-0.759784	-0.57283
123	-0.762948	0.491146	0.140995	0.402848	0.321765	0.937691	-0.352812	-0.58207
124	-0.765963	0.616048	0.181269	0.409329	0.162002	0.495803	-0.402619	-0.585765
125	-0.765963	0.448702	0.151064	0.409329	0.611084	0.765986	-0.317424	-0.58207
126	-0.768977	0.495996	0.23985	0.415852	0.586381	0.880899	-0.405896	-0.57283
127	-0.771992	0.494784	0.15381	0.422416	0.594177	0.729011	-0.923622	-0.57283
128	-0.778022	0.440214	0.157471	0.435668	0.352461	0.671857	-0.838426	-0.58207
129	-0.778022	0.517823	0.151064	0.435668	0.299353	1.27602	-0.256739	-0.58207
130	-0.778022	0.37837	0.160217	0.435668	0.647676	0.543653	-1.05469	-0.57283
131	-0.943834	1.15446	1.52131	0.880007	0.494684	0.560812	-0.664431	-0.570481
132	-0.949864	1.20903	1.4911	0.899734	1.20561	1.33644	0.0495719	-0.619026
133	-0.949864	1.28179	1.52131	0.899734	1.0381	0.45339	-0.268502	-0.563497
134	-0.955893	1.16053	1.46273	0.91977	0.914242	0.901441	-0.409172	-0.609787
135	-0.955893	1.22237	1.43161	0.91977	0.870391	0.508128	-0.382959	-0.609787
136	-0.955893	1.23571	1.54877	0.91977	0.846516	1.26974	-1.77558	-0.600548
137	-0.961923	1.2254	1.46273	0.940121	1.15737	0.479732	-0.686713	-0.600548
138	-0.961923	1.20903	1.45724	0.940121	1.574	1.18141	-0.509441	-0.563022
139	-0.961923	1.16295	1.53962	0.940121	1.01432	1.27651	-0.915168	-0.554352
140	-0.964938	1.29392	1.51216	0.950418	1.40459	1.01309	-1.18576	-0.553625
141	-0.967952	1.22722	1.53962	0.960796	1.53478	0.418953	-1.23131	-0.552348
142	-0.970967	1.23207	1.56708	0.971256	1.3663	1.09441	-0.706373	-0.571417
143	-0.970967	1.16053	1.4847	0.971256	1.46131	0.756682	-1.38237	-0.567565
144	-0.972173	1.10232	1.53046	0.975464	1.49829	1.1274	-0.767353	-0.549601
145	-0.976997	1.17265	1.4911	0.99243	1.42145	1.49352	-1.84111	-0.609787
146	-0.976997	1.22965	1.45724	0.99243	1.69625	1.36024	0.0168045	-0.609787

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147	-0.986041	1.28179	1.50483	1.02484	1.01559	0.50269	-0.369852	-0.600548
148	-0.986041	1.22843	1.47554	1.02484	1.43612	0.588965	-0.456391	-0.600548
149	-0.989056	1.25754	1.4911	1.03581	1.6524	0.478523	-0.333153	-0.609787
150	-0.995085	1.22843	1.53046	1.05804	1.48966	1.41945	-0.206015	-0.609787
151	-1.05538	1.29392	1.53046	1.30225	1.13233	0.989649	-1.03293	-0.600548
152	-1.06442	1.28179	1.45724	1.34271	1.58662	0.829545	-0.317424	-0.591309
153	-1.0795	1.28179	1.50483	1.41265	1.50594	1.10142	-0.942594	-0.609787
154	-1.08553	1.36183	1.51399	1.44155	1.42048	0.62002	-0.685272	-0.619026
155	-1.09457	1.58495	1.53046	1.48592	1.36737	1.26394	-0.743401	-0.609787
156	-1.10965	1.36668	1.55792	1.56277	1.21779	1.17936	-1.66417	-0.609787
157	-1.10965	1.35455	1.45724	1.56277	1.28259	1.27518	-0.80448	-0.600548
158	-1.11568	1.34364	1.51399	1.59457	1.66994	1.00342	-1.85753	-0.578282
159	-1.12171	1.36668	1.4847	1.627	1.44192	0.768523	-1.73625	-0.600548
160	-1.12171	1.22358	1.52406	1.627	1.45843	1.10529	-0.767321	-0.619026
161	-1.12472	1.46369	1.52131	1.64346	1.5876	1.51769	-1.12678	-0.609787
162	-1.12472	1.34242	1.57623	1.64346	1.43266	1.17936	-0.323978	-0.609787
163	-1.13075	1.41518	1.45724	1.67688	1.17589	1.26007	0.00369668	-0.609787
164	-1.13075	1.36668	1.50483	1.67688	1.24361	1.11894	-3.14525	-0.600548
165	-1.13376	1.40306	1.51216	1.69384	1.48299	0.819636	-0.863363	-0.609787
166	-1.13678	1.34242	1.52131	1.71098	1.15932	1.22769	-2.08359	-0.600548
167	-1.13979	1.36668	1.55792	1.72829	1.28795	1.08269	-0.769614	-0.600548
168	-1.13979	1.3594	1.50483	1.72829	1.2077	1.02892	-1.94171	-0.596883
169	-1.14582	1.36668	1.53962	1.76345	1.48177	1.26769	-0.595914	-0.609787
170	-1.14884	1.29392	1.56067	1.78131	1.42545	0.975753	-0.339148	-0.607015
171	-1.14884	1.34606	1.50483	1.78131	1.00297	1.19724	-0.849174	-0.600548
172	-1.16391	1.35455	1.57623	1.87345	1.48333	1.2492	-0.294486	-0.609787
173	-1.16693	1.34364	1.52222	1.89247	1.92038	1.2469	1.89	-0.584918
174	-1.16994	1.34485	1.55792	1.9117	1.63389	1.2063	-1.00226	-0.609787
175	-1.17296	1.34485	1.50392	1.93114	1.25238	1.30019	-1.45773	-0.600548
176	-1.17597	1.30604	1.53046	1.95079	1.42403	1.16051	-1.08661	-0.609787

177	-1.17597	1.38244	1.53595	1.95079	1.53473	1.30696	-1.85766	-0.592284
178	-1.18502	1.40306	1.59454	2.01105	1.18953	1.16727	-1.6314	-0.600548
179	-1.19707	1.40306	1.46456	2.09459	1.44708	0.607574	-0.787538	-0.615173
180	-1.21516	1.41518	1.4847	2.22728	1.33667	1.20352	-0.392789	-0.609787

Table A.1: Unit variance scaled and mean centered of the experimental data

Table A.2: Process parameters, calculated score values t1 and t2, principal component analysis (PCA)

<b>Observation ID</b>	t (1)	t(2)
1	2.65965	0.73333
2	2.66993	0.729237
3	2.66202	0.699109
4	2.65438	0.697858
5	2.64277	0.702944
6	2.65163	0.69039
7	2.63347	0.660632
8	2.67816	0.680011
9	2.61429	0.665094
10	2.60129	0.656998
in in	2.65323	0.667082
12	2.70245	0.680793
13	2.61761	0.644404
14	2.55024	0.631184
15	2.56671	0.650984
16	2.54991	0.629731
17	2.6547	0.670083
18	2.62644	0.643124
19	2.61846	0.636174
20	2.5679	0.635898

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21	2.28825	0.359468
22	2.26489	0.330146
23	2.25443	0.34189
24	2.21499	0.37014
25	2.27178	0.327003
26	2.22698	0.330787
27	2.26277	0.338582
28	2.2547	0.333055
29	2.28878	0.344942
30	2.27818	0.351918
31	2.25144	0.330879
32	2.24138	0.333058
33	2.25673	0.325029
34	2.2582	0.326042
35	2.27158	0.344031
36	2.23951	0.317119
37	2.24385	0.318267
38	2.2399	0.307756
39	2.23553	0.312658
40	2.23497	0.311096
41	1.59433	-0.194131
42	1.50932	-0.180327
43	1.50043	-0.114286
44	1.60337	-0.198843
45	1.58346	-0.221635
46	1.48623	-0.104756
47	1.46935	-0.0615729
48	1.4988	-0.129383
49	1.44239	-0.159103
50	1.50345	-0.136469
51	1.50135	-0.131401
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52	1.50794	-0.128768
53	1.53587	-0.203454
54	1.57845	-0.222067
55	1.60477	-0.224262
56	1.5549	-0.197929
57	1.57083	-0.219696
58	1.47286	-0.14691
59	1.50712	-0.138474
60	1.45972	-0.165939
61	1.01251	-0.434846
62	0.957725	-0.456325
63	0.925278	-0.440873
64	0.977139	-0.477662
65	0.999324	-0.537074
66	0.910311	-0.414977
67	0.954857	-0.448602
68	0.965503	-0.465733
69	0.954642	-0.456899
70	0.887986	-0.437407
71	0.916618	-0.429429
72	0.95037	-0.477619
73	0.932315	-0.479587
74	0.869484	-0.444617
75	0.919206	-0.47377
76	0.875479	-0.476378
77	0.888052	-0.444624
78	0.884953	-0.445704
79	0.899912	-0.470788
80	0.906543	-0.498122

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81	0.382517	-0.440512
82	0.315633	-0.475353
83	0.273069	-0.483951
84	0.300406	-0.48368
85	0.300009	-0.510587
86	0.281072	-0.511717
87	0.235178	-0.467494
88	0.260598	-0.478705
89	0.280738	-0.471681
90	0.232251	-0.502372
91	0.260336	-0.479192
92	0.28811	-0.487574
93	0.295196	-0.499857
94	0.272945	-0.46926
95	0.257183	-0.495209
96	0.225818	-0.493498
97	0.258997	-0.502363
98	0.25846	-0.456751
99	0.244934	-0.51026
100	0.248537	-0.556153
101	-0.0368592	-0.472348
102	-0.121531	-0.509761
103	-0.118023	-0.501846
104	-0.155665	-0.506539
105	-0.150196	-0.514579
106	-0.153002	-0.518806
107	-0.168579	-0.519555
108	-0.159124	-0.517488
109	-0.148644	-0.525879
110	-0.348035	-0.327495

The second static rest in a second state state of the		
111	-0.856226	-0.427456
112	-0.859327	-0.444008
113	-0.878499	-0.427745
114	-0.879119	-0.427961
115	-0.914865	-0.436865
116	-0.948454	-0.446572
117	-0.919414	-0.431759
118	-0.903275	-0.411841
119	-0.892345	-0.412713
120	-0.89631	-0.427223
121	-0.896621	-0.433077
122	-0.825628	-0.422566
123	-0.896379	-0.431356
124	-0.984958	-0.431146
125	-0.884428	-0.418168
126	-0.957473	-0.377052
127	-0.918875	-0.424796
128	-0.902424	-0.412916
129	-0.938902	-0.430323
130	-0.872184	-0.400362
131	-2.24986	0.250974
132	-2.27562	0.226728
133	-2.32781	0.230609
134	-2.24976	0.22198
135	-2.2659	0.193598
136	-2.33094	0.256575
137	-2.29611	0.21296
138	-2.28501	0.212815
139	-2.3024	0.26698
140	-2.36234	0.229633

And the second		
141	-2.3486	0.258179
142	-2.37146	0.274001
143	-2.29396	0.240801
144	-2.28967	0.27726
145	-2.31695	0.245039
146	-2.32925	0.215989
147	-2.40028	0.237703
148	-2.35846	0.230875
149	-2.38806	0.235914
150	-2.40689	0.266243
151	-2.59276	0.293945
152	-2.57496	0.262478
153	-2.64119	0.301918
154	-2.70414	0.29823
155	-2.85311	0.276212
156	-2.80127	0.34569
157	-2.74504	0.291687
158	-2.78662	0.331754
159	-2.80311	0.317991
160	-2.74955	0.36545
161	-2.88064	0.324547
162	-2.84596	0.376796
163	-2.84379	0.304472
164	-2.84265	0.339668
165	-2.87489	0.340865
166	-2.85856	0.360434
167	-2.89934	0.380252
168	-2.86924	0.351935
169	-2.91089	0.377658
170	-2.89463	0.406272

171	-2.89353	0.365833
172	-2.98711	0.424642
173	-2.96574	0.400765
174	-2.99526	0.424835
175	-2.97968	0.399156
176	-2.98441	0.425397
177	-3.02618	0.414844
178	-3.10059	0.457849
179	-3.08395	0.40511
180	-3.1758	0.446354

Table A.2: Process parameters, calculated score values t1 and t2, principal component analysis (PCA)

Table A.3: Film properties, calculated score values t1 and t2, principal component analysis (PCA)

Constant States of States	
Observation ID	t(1)
1	-3.59799
2	-3.63483
3	-3.51068
<b>4</b>	-3.42139
5	-3.9473
6	-3.71896
7	-3.71151
8	-3.73548
9	-3.60492
10	-3.26353
11	-3.64889
12	-3.47097
13	-3.83908

14	-3.58556
15	-3.82917
16	-3.7891
17	-3.7795
18	-3.49729
19	-3.41484
20	-3.13642
21	-1.60514
22	-2.30853
23	-1.77087
24	-1.97419
25	-1.69575
26	-2.11793
27	-1.96348
28	-1.73865
29	-1.43583
30	-1.74305
31	-1.6711
32	-1.70216
33	-1.66626
34	-1.99599
35	-2.12379
36	-1.65274
37	-1.83874
38	-1.63428
39	-1.74523
40	-2.18486
41	-1.04046
42	-1.52688
43	-1.11371

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44	-0.762952
45	-0.922637
46	-0.941907
47	-0.918935
48	-0.838226
49	-0.885507
50	-1.29326
51	-0.877312
52	-1.3012
53	-1.23005
54	-0.774187
55	-0.816914
56	-0.855029
57	-0.875803
58	-0.788261
59	-0.936101
60	-1.15097
61	-0.874564
62	-0.954646
63	-0.510563
64	-0.592336
65	-0.193641
66	-0.118089
67	-0.254131
68	-0.614878
69	-0.197206
70	-0.537042
71	-0.274011
72	-0.589257
73	-0.387462

the stand bull of the stand of	
74	-0.622658
75	-0.469932
76	-0.689864
77	-0.0388158
78	-0.149695
79	-0.241733
80	-0.329747
81	0.271048
82	1.02986
83	0.0780166
84	0.615843
85	-0.538688
86	0.666596
87	1.10422
88	-0.37577
89	0.419556
90	0.517354
91	0.242939
92	0.73023
93	0.430692
94	0.429783
95	1.16352
96	0.378841
97	0.61343
98	0.0312504
99	-0.119136
100	0.94963
101	1.50748
102	0.534432
103	0.602457

AND ADDRESS ADDRE	
104	0.876773
105	0.545897
106	0.850024
107	1.09668
108	0.871361
109	0.895649
110	0.308627
111	1.16872
112	0.639917
113	1.50619
114	1.32744
115	1.04403
116	0.785826
117	1.47494
118	0.898551
119	0.737357
120	0.730314
121	1.32411
122	1.1139
123	1.09956
124	0.818003
125	1.14148
126	1.22729
127	1.41039
128	1.21997
129	1.21393
130	1.40769
131	1.14361
132	1.57272
133	1.16573

The second statement of	
134	1.42438
135	1.18733
136	2.25257
137	1.46546
138	1.9317
139	1.8923
140	2.09022
141	1.87395
142	1.88296
143	2.09195
144	1.98698
145	2.69747
146	1.84695
147	1.24764
148	1.54928
149	1.54619
150	1.88258
151	1.88603
152	1.67597
153	2.09345
154	1.67972
155	2.00724
156	2.34468
157	1.99566
158	2.56589
159	2.27965
160	1.98864
161	2.43998
162	1.78896
163	1.53675

164	3.05767
165	1.89793
166	2.54342
167	1.88238
168	2.39397
169	1.99429
170	1.68708
171	1.83529
172	1.83597
173	2.83775
174	2.2421
175	2.31736
176	2.15347
177	2.65938
178	2.30337
179	1.73582
180	1.78656

Table A.3: Film properties, calculated score values t1, principal component analysis (PCA)

Table A.4: Film properties and Process parameters, calculated score values t(1) and t(2), Projection to Latent Structures (PLS)

<b>Observation ID</b>	t(1)	t(2)
1	-2.70002	0.729186
2	-2.71002	0.723782
3	-2.70028	0.694148
4	-2.69257	0.692416
5	-2.68129	0.697354
6	-2.68935	0.683812
7	-2.66939	0.655546

Characterized and the second		
8	-2.7152	0.672769
9	-2.65052	0.660086
10	-2.63704	0.651445
11	-2.68951	0.659781
12	-2.73949	0.671551
13	-2.65256	0.638538
14	-2.58448	0.627005
15	-2.60215	0.645693
16	-2.58407	0.62561
17	-2.69115	0.661472
18	-2.66129	0.636038
19	-2.65288	0.628954
20	-2.60239	0.629035
21	-2.30616	0.354553
22	-2.28103	0.325386
23	-2.27131	0.337019
24	-2.23366	0.364805
25	-2.28771	0.32143
26	-2.24322	0.326302
27	-2.27942	0.332864
28	-2.27102	0.327595
29	-2.30578	0.338159
30	-2.29563	0.345042
31	-2.26764	0.325435
32	-2.25773	0.327813
33	-2.27256	0.319638
34	-2.27409	0.319845
35	-2.28855	0.336574
36	-2.25488	0.311435
37	-2.25928	0.312281

and the second		
38	-2.25469	0.302084
39	-2.25063	0.30694
40	-2.24998	0.305299
41	-1.57926	-0.200333
42	-1.49523	-0.185127
43	-1.49041	-0.12121
44	-1.58799	-0.205719
45	-1.56671	-0.227353
46	-1.47682	-0.111909
47	-1.46262	-0.0698648
48	-1.48786	-0.136343
49	-1.42972	-0.163976
50	-1.49207	-0.143758
51	-1.49027	-0.139097
52	-1.49701	-0.136732
53	-1.52032	-0.209814
54	-1.56168	-0.228957
55	-1.58782	-0.231793
56	-1.53965	-0.205138
57	-1.55422	-0.22668
58	-1.46088	-0.153901
59	-1.4956	-0.147118
60	-1.4466	-0.173846
61	-0.983628	-0.440893
62	-0.927616	-0.460609
63	-0.896172	-0.444795
64	-0.945688	-0.481755
65	-0.964192	-0.540069
66	-0.882819	-0.419806
67	-0.925227	-0.453954

THE OWNER AND THE OWNER AND ADDRESS OF THE OWNER ADDRESS OF		
68	-0.934804	-0.470945
69	-0.924504	-0.462261
70	-0.859158	-0.441764
71	-0.88823	-0.434831
72	-0.918968	-0.482318
73	-0.900824	-0.483878
74	-0.840245	-0.448377
75	-0.888095	-0.478492
76	-0.844283	-0.479973
77	-0.858781	-0.449774
78	-0.855622	-0.450735
79	-0.869017	-0.475825
80	-0.873962	-0.503013
81	-0.35438	-0.439491
82	-0.285487	-0.474761
83	-0.242469	-0.482064
84	-0.269781	-0.483435
85	-0.267734	-0.509427
86	-0.248763	-0.510452
87	-0.205659	-0.466469
88	-0.230348	-0.477993
89	-0.250885	-0.471751
90	-0.200599	-0.500245
91	-0.230058	-0.478605
92	-0.25727	-0.48746
93	-0.263592	-0.499789
94	-0.243257	-0.469794
95	-0.225931	-0.494593
96	-0.194726	-0.492387
97	-0.227306	-0.502002

Contraction of the second s		
98	-0.22957	-0.458354
99	-0.21279	-0.510592
100	-0.213573	-0.555191
101	0.0661699	-0.469885
102	0.152954	-0.50778
103	0.148967	-0.500225
104	0.186822	-0.504788
105	0.181853	-0.512856
106	0.184911	-0.517014
107	0.200509	-0.517315
108	0.190941	-0.515725
109	0.180993	-0.524118
110	0.367873	-0.327287
111	0.881042	-0.425678
112	0.885136	-0.442202
113	0.903274	-0.426118
114	0.903905	-0.42631
115	0.940133	-0.434099
116	0.97426	-0.442569
117	0.94436	-0.429041
118	0.927024	-0.410383
119	0.916166	-0.411522
120	0.921009	-0.42559
121	0.921674	-0.431392
122	0.850155	-0.423267
123	0.921323	-0.429889
124	1.00973	-0.427437
125	0.908579	-0.417622
126	0.978973	-0.376058
127	0.943365	-0.4234

For A strategy where the strategy of the strat		
128	0.926204	-0.412672
129	0.963687	-0.428505
130	0.895246	-0.40136
131	2.23029	0.256929
132	2.25747	0.233882
133	2.30934	0.239048
134	2.23194	0.228277
135	2.24979	0.201285
136	2.31086	0.263911
137	2.27874	0.220501
138	2.26767	0.220059
139	2.28171	0.272877
140	2.34383	0.238252
141	2.32835	0.265309
142	2.3502	0.281062
143	2.27487	0.246874
144	2.26834	0.281929
145	2.29754	0.251276
146	2.3116	0.223535
147	2.38115	0.245972
148	2.33982	0.238238
149	2.36906	0.243753
150	2.38597	0.273255
151	2.56963	0.301863
152	2.55376	0.270485
153	2.6174	0.309584
154	2.68044	0.307402
155	2.83048	0.289674
156	2.77439	0.354591
157	2.72157	0.300877

the state of the s		
158	2.7606	0.340396
159	2.77788	0.327213
160	2.72149	0.371625
161	2.85486	0.335487
162	2.81704	0.38504
163	2.81927	0.314755
164	2.81598	0.348737
165	2.84808	0.350604
166	2.83056	0.368906
167	2.87004	0.388997
168	2.84172	0.360815
169	2.8817	0.38647
170	2.8637	0.413516
171	2.86508	0.374405
172	2.95481	0.432938
173	2.93493	0.409115
174	2.9629	0.433009
175	2.94891	0.4076
176	2.95201	0.432919
177	2.99435	0.423853
178	3.06594	0.466923
179	3.0525	0.414822
180	3.14155	0.456139

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Table A.4: Film properties and Process parameters, calculated score values t(1) and t(2), Projection to Latent Structures (PLS)