THE EFFECT OF MULTIPLE EXTRUSION PASSES DURING THE RECYCLING OF HIGH DENSITY POLYETHYLENE

By

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ABSTRACT

Plastics recycling has received significant attention within the past decade. Positive or negative, the attention has provided an impetus for the plastics industry to advance recycling technology. High density polyethylene blow moulding resins have been identified as a primary material for solid waste minimization and recycling. This thesis is concerned with the effects of multiple extrusion passes on the processing and product application properties of high density polyethylene blow moulding resins. The objective is to provide a comprehensive analysis on the system of properties as they are affected by multiple extrusion passes.

A justification for this present work is provided by a description of the current state of plastics recycling in terms of the history, legislation and technology. The role of political and global market pressures, relative to legislative initiatives such as the Green Dot program in Germany, the 3 R's legislation in Ontario, the content legislation in California and the decision to ban products such as polystyrene foam clamshell packaging, and the impact of these events on the research initiatives in plastics recycling is discussed.

An experimental study into the effect of multiple extrusion cycles on the properties of a virgin homopolymer, virgin copolymer, natural post consumer and mixed colour post consumer blow moulding resin was conducted. Rheological properties such as shear and elongational viscosity and elastic modulus were studied in the context of changes experienced during recycling. The G' - G" (elastic storage and loss modulus) cross-over point was used to measure relative changes in the polydispersity index and molecular weight distribution. It is also shown how parameters such as the Bagley correction factor, extrudate swell and sag are sensitive to the effect of multiple extrusion passes. Strength properties such as tensile strength and environmental stress crack resistance were measured. A rationale for the significant decrease in the environmental stress crack resistance of the virgin copolymer resin is presented. The results are analyzed in terms of known degradation mechanisms such as chain scission and cross-linking, and their relationship to the Phillips and Ziegler-Natta catalyst systems. Principal component analysis, a multivariate statistical technique, was applied to this plastics recycling study to provide data based support in the identification of those responses, within a system of correlated responses, which are most affected by multiple extrusion passes.

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Nomenclature

a	stress crack length parameter
a(t)	time dependant stress crack length parameter
A_p	pore area
A	cross sectional area
PC	principal component
E	Young's Modulus
F_e	elongational force
G	energy release rate
G_{crit}	critical energy release rate
$G(\omega)$	stress relaxation modulus
$G_c(\omega)$	terminal zone crossover modulus
$G''(\omega)$	loss modulus
$G'(\omega)$	storage modulus
K	stress intensity factor
K(t)	time dependant stress intensity factor
K_{crit}	critical stress intensity
L	die length
L/D	length to diameter ratio
L/R	length to radius ratio

M_i	molar mass
M_n	number average molecular weight
M_w	weight average molecular weight
m	power law coefficient
n_B	Bagley correction factor
n	power law index
n_i	number of moles
PI	polydispersity index
dp/dx	pressure gradient
ΔP	pressure drop
ΔP_e	entrance pressure drop
Q	mass flowrate
R	radius
s_i	standard deviation of response
s^2_i	variance and of the ith variable
s_{ij}	covariance between the ith and jth variables
t	time
$t_{L/D,\text{shear rate}}$	normalized swell ratio at a given L/D and shear rate
$\dot{U}$	flow rate of aggressive media
V	volume flowrate
w_i	total molecular mass
y_{ij}	obseved response
y_j	average response
z_{ik}	principal component loading

α	level of significance
$\dot{\xi}$	rate of elongation or stretch rate
$\dot{\gamma}$	shear rate
$\dot{\gamma}_{true}$	Rabinowitsch corrected shear rate at die wall
η	dynamic viscosity
η_e	elongational viscosity
η_f	fluid viscosity
μ	shear flow viscosity
ρ_{ij}	correlation between the ith and jth variables
ρ_m	melt density
σ_f	critical plane stress
σ	plane stress
τ	shear stress
τ_w	shear stress at wall
ω	rotational velocity

To the memory and professionalism of A. Zahavich Sr., P.Eng.

Chapter 1 - Introduction

In recent years there has been a profusion of public interest in the environment, especially in the area of solid waste reduction. Situations such as the tire fire near Hagersville, Ontario, Canada in the late 1980's and the rapid decline in landfill capacity, have inspired governments and industry to draft waste management legislation and to invest in recycling programs. It is a global phenomenon and no one region or country has a monopoly on recycling expertise, though some are more advanced in dealing with specific solid waste problems.

Increasing legislative and market pressure is being applied to the plastics industry not just in packaging but in all applications of products containing polymeric materials. This pressure is being exerted to ensure that polymeric materials are being used efficiently and with a minimum amount of damage to the environment. The polymer industry and research community must respond to the pressure quickly with solutions that allow consumers to take advantage of the best properties and benefits of polymers.

Recycling is only one phase of the "4-R's": Reduce, Reuse, Recycle and Recover. The use of polymeric materials in a product application begins with the definition of the performance requirements of the product. Not knowing the characteristics of a batch of reclaimed polymer may lead to over-designing a product, out right exclusion of the recycled material in an application and inefficiencies in the waste management system. Since recycling represents an opportunity for waste diversion or delayed entry, a systematic research approach is necessary to expedite the optimization of plastics recycling. An engineering research contribution that identifies the effects of multiple extrusion passes during recycling, on the processing and physical property characteristics used to describe recycled resins, could encourage the use of reclaimed polymers in a greater number of value added applications. It would also assist designers and processors in meeting PCR content requirements imposed by political, economical and environmental forces.

A number of studies and articles have documented the levels of the components in solid waste (Nir, 1990, Leaversuch,1989, Rathje, 1989). Paper and paperboard are consistently estimated to contribute about 38% (by weight or volume) to the municipal solid waste (MSW) stream. In comparison, plastics contribute 7% by weight and 18% by volume. The typical breakdown in terms of resins is polyethylene (PE) 63%, polystyrene (PS) 11%, polypropylene (PP) 10%, polyethylene terephthalate (PET) 7%, poly vinyl chloride (PVC) and other materials such as polycarbonates (PC) 10%. It is estimated that 83% of all plastics produced and almost 100% of the plastics used in packaging are thermoplastic materials which can be remelted and reformed or reused.

In 1993 in the United States, about 19 billion lb. (8.6 million MT.) of plastic was used in packaging. At the same time, it was estimated that of the 75 billion lb. (34 million MT.) of plastic produced in the US, 1220 million lb., (555 thousand MT.) approximately 2%, was recycled. Within 5 years recycling rates for some plastics rose to a level of 20%-30% (Modern Plastics, 1994). With volumes of materials such as those presented above the waste management problem can seem overwhelming. At the same time, the lack of data on plastics recycling, in particular the effects of multiple extrusion passes, has damaged the credibility of the plastics industry and the confidence of processors who must incorporate recycled resins into their products. Therefore, at this stage, any level of research advancing the recycling technology of any polymer is significant.

This research project focused on the study of the effects of multiple extrusion passes during recycling of HDPE blow moulded bottle resin because it represents one of the largest volume of polymers in packaging which would fall into the waste stream. Three primary themes were used to guide the research. First, designed experiments (DOE) were to be an integral part of the program. Second, the use of relatively inexpensive, standard analytical techniques was a priority in the selection of responses. Third, the results were to have a direct and immediate practical application to current industrial processes. In considering such a broad area as multiple extrusions, it was critical to develop a comprehensive plan and a systematic experimental research strategy which minimized the total number of experimental runs yet did not compromise the opportunity for studying the effects of the factors on the responses. The strategy also had to account for the multivariate nature of the polymer extrusion system. Given this overview, the specific objectives established for this research project were:

i) to investigate, develop and test a systematic experimental methodology which is sensitive enough to measure significant effects experienced during multiple extrusion experiments;

ii) to identify the physical and rheological characteristics of HDPE homopolymer and copolymer blow moulding bottle resin which undergo the greatest change during multiple extrusion recycling which may cause a reclaimed material to be deemed as unfit for use in its primary application;

iii) to provide a description of the fundamental mechanisms that lead to changes in the characteristics of HDPE blow moulding bottle resin during multiple extrusion recycling.

This dissertation presents a detailed overview of the plastics recycling system in chapter 2. The background of HDPE, in terms of basic polymerization and the processing history of a typical molecule is described in chapter 3. In chapter 4 the properties which describe the characteristics of HDPE and how they may be affected by multiple extrusions is presented. Chapter 5 is devoted to the use of statistically designed experiments, the applicability of multivariate analytical techniques to multiple extrusion experiments and a detailed description of the experimental procedure, test equipment and analytical procedures. In chapter 6 the outcomes of the experimental work are described. An analysis and discussion of the results are presented in Chapter 7. Finally, in chapter 8 the conclusions and recommendations for further research are presented.

The significant contributions from this thesis are:

- the identification of the swell ratio as the response which changed the greatest during multiple extrusion passes, up to 8 passes, in a study using a virgin homopolymer, produced with a Phillips based catalyst system;
- the identification of the polydispersity index, swell ratio and environmental stress crack resistance as the responses most affected by multiple extrusion passes up to 4 passes in an experimental study using virgin

HDPE homopolymer and copolymer and post consumer natural and mixed colour bottle HDPE;

- the expansion of previously reported work which demonstrated an effect of the initial polymerization process (Phillips versus Ziegler catalyst systems) and the predominant degradation mechanism (crosslinking versus chain scission)
- the measurement of a significant decline in environmental stress crack resistance and melt strength for a Ziegler based catalyst, virgin copolymer HDPE, resulting from 4 extrusion passes.
- the observation of changes in post consumer HDPE properties, during multiple extrusion passes, consistent with changes in virgin HDPE.
- the development of models for the decay of environmental stress crack resistance and growth of the polydispersity index for a virgin copolymer as a result of multiple extrusion cycles.
- the application of principal component analysis (PCA) to analyze a large number of correlated response variables which undergo changes during multiple extrusion passes in recycling.

Chapter 2 - Recycling Plastics

2.1 Milestones in plastics recycling

The history of the development and application of polymeric materials is relatively short compared to materials such as wood and metal. Today, plastics represent roughly two thirds of all materials consumed annually per person (Richardson, 1989). It is projected that by the year 2010 demand for polyethylene alone will double to 70 million tonnes/year.

Until recently, it has been widely assumed that recycling or the reuse of plastics was non-existent. However, the recycling of industrial scrap has been a common operating procedure virtually since the development of each specific polymer. A condensed chronological history of plastics and plastics recycling follows:

1840's - sulfur vulcanization developed by Goodyear
1850's - first rubber reclamation process developed
1860's - cellulose nitrate used as a replacement for ivory and tortoise shell
1920's - concept of long molecules and polymers proven
1930's - high pressure process for polyethylene developed by ICI

- commercialization of synthesis of nylon by Du Pont de Nemours & Co.

1940's - recycling of scrap plastics incorporated into industrial processes

- rapid expansion in the development of new polymers during war

- expansion of recycling industry to minimize raw material costs

- total U.S. plastics production 734 million lbs (333×10^3 t)

1960's - decline of virgin resin prices impacts recycling industry profits

- increase of landfill and incineration of plastics waste

- total U.S. plastics production 18.5 billion lbs (3.3×10^6 t) of which 78% is thermoplastics

1970's - OPEC oil embargo drives up feedstock prices

- renewed interest in recycling

- pyrolysis of plastics considered as possible alternative fuel source

1980's - post consumer plastics recycling promoted by governments

- commingled systems developed in Europe

- curbside collection and separation programs initiated

- materials recovery facilities (MRF's) established

- PET bottle recycling program developed

1990's - aggressive world wide government legislation enacted

- sophisticated automated sorting systems developed

2.1.1 Thresholds and the 4 R's

The 4 R's program (Reduce, Reuse, Recycle and Recover) was a marketing program initiated by governments and industry in response to declining landfill capacity around the world. The objective was to encourage methods, other than permanent disposal, for solid waste. Some governments such as the one in Ontario during the early 1990's conveniently dropped the 4th R for political reasons to reinforce their ban on incineration. The objectives of the 4 R's initiative are realistic provided each part is managed properly. Reduction of waste should be the primary goal but a point will be reached where elimination of a product or material is the only alternative. Banning or the complete elimination of a material may not always be beneficial because the process may begin to impinge on the gains made in other areas such energy conservation or resource management. Reusing products or materials also has a threshold. Refilling bottles is an example where this threshold exists. A bottle can only survive a certain number of refilling trips before it breaks or cannot be used again. Therefore, the material in the bottle such as glass or plastic, leaves the reuse phase and enters the recycling stream. Recycling implies that the materials in a product are reformed into another product and not necessarily in the same application. Again there are limitations as to how far recycling can be taken. Property changes due to processes such as heat histories which degrade plastics or screening which reduces fibre size for paper, will end the period of recycling for a particular material. Once the recycling threshold has been reached, the final stage is recovery. Recovery is meant to imply the complete and total breakdown of a material at the molecular level. Incineration, pyrolysis, waste to energy, evaporation, oxidation and irradiation are examples considered to be recovery processes.

2.1.2 Alternatives for disposal

When a product containing polymeric materials is considered unfit for use the industrial, commercial, institutional or household consumer of the product will decide on the next event the polymer will experience. The consumer will either direct the product into the general trash stream for permanent disposal or into a recycling stream.

The general trash stream leads to a landfill, incineration or to a waste to energy system. The distinction between the latter 2 outcomes lies in how the latent energy in the polymer is used. In a waste to energy system heat is generated and can be used in industrial processes or transferred into district heating systems. In Scandinavian countries district heating is an integral part of the waste system and plastics are often described as "frozen natural gas" in reference to the feedstock used in making plastics and their calorific values. In contrast, incineration involves burning trash with no recovery of the heat energy.

Recycling represents the last opportunity for delaying or diverting polymeric materials from permanent disposal and consists of 2 parts, reclamation and reprocessing. Reclamation is concerned with the collection and separation of products and/or their constituent materials. Reprocessing involves the forming of reclaimed polymeric materials into useful products either independently or with virgin polymers. In the past 10 years post consumer recycling has been the target for large improvements to aid in the reduction of municipal solid waste (MSW). The definition of "post consumer" has been the subject of many debates but it has been generally agreed that post consumer refers to the household consumer.

2.2 The reclamation system

If a product is directed into a recycling stream it is collected and sent to a dismantling and/or separation centre. Dismantling centres separate multicomponent products such as automobiles, computers or some household appliances, into sub-component bins or if possible into specific material bins (Brooke, 1990). At an automobile dismantling centre HDPE washer and coolant bottles may be sorted directly into an HDPE bin, whereas dashboards and instrument panels, which are made of plastics with imbedded metallic subcomponents, are separated into an instrument panel bin. Even a seemingly pure stream of single material components may require higher levels of separation depending on the materials they may have contained. An example of this is HDPE and its use not just in coolant and washer bottles but also its use in gasoline tanks. The HDPE gasoline tanks are usually separated from the other HDPE components because of the residual gasoline trapped in the polymer structure.

When considering packaging, most products directed for recycling are collected and sent directly to a specific materials recycler or to a material recovery facility (MRF). In many jurisdictions materials such as polystyrene or corrugated cardboard are picked up directly at industrial, commercial and institutional (ICI) waste generators by recyclers. This bypasses the MRF and optimizes collection costs. Other materials and other polymers are being considered for this model if volumes are economically feasible.

2.2.1 The reclamation system for post consumer household packaging

Household packaging reclamation is typically done in conjunction with general trash collection. Various collection schemes have been piloted and are in place including curbside collection and drop off depots. One of the first and most successful is the Blue Box program initiated in Ontario. Regardless of the system, it has been demonstrated that collection costs and resale revenues are the two most critical factors in the planning of a reclamation program (Canadian Plastics, 1990, Bond, 1990).

In 1990 a computer model was developed to project the cost and viability of using curbside collection (Cornell, 1990). Eastman Chemical, a high volume producer of PET used in beverage bottles, donated the software and rights to the program to the Council for Solid Waste Solutions (CSWS), Washington DC. The CSWS administered the program and advised municipalities on the best approach for setting up collection programs. This program had some success in promoting the recycling of plastic bottles.

The extent of household collection for plastic materials is restricted to bottles and in some cases film. The materials for bottles are typically PET and HDPE, though PVC is also inadvertently collected because it is often used in similar applications as PET and HDPE. Polyethylene is the only material involved in the collection of films and is typically found in grocery carry out sacks and shrink wrap.

2.2.2 Legislation, public issues and reclamation

Scientists, engineers and designers often are guided by government regulation, who are in turn driven by public pressure. The impact of social pressure and policy cannot be ignored, especially in relation to this work. Recycling plastics is one of the highest profile yet least well defined in terms of government legislation. The type of reclamation system used and its success is largely dependent on the jurisdiction and social policies of the day in that jurisdiction. The effect of public pressure cannot be underestimated and its power is best illustrated by the following example. Prior to 1988 immense pressure was being applied to governments to ban plastics from packaging. In 1988 a number of studies were published which showed the effect of a plastics ban. One of the more prolific studies was done in Germany. A chart summarizing the results from that study is shown in Figure 2.1.

Other examples of the influence of public pressure on plastics recycling involve the TETRA PAK© and MacDonald's restaurant "clamshells". The TETRA PAK, a multilayer, multimaterial container was

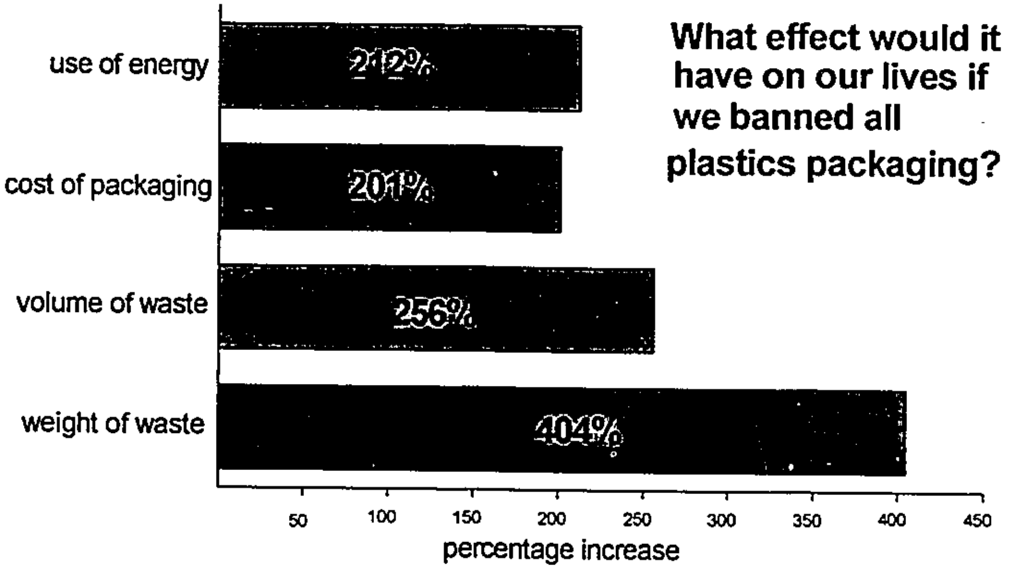


Figure 2.1: Effect of banning plastics packaging summary
German Society for Research into Packaging Markets

targeted for banning because of its complex materials structure of paper, plastic and aluminium foil. This product, originally developed in the 1960's, was designed for transporting large quantities of fresh milk to underdeveloped countries without the need for refrigeration or preservatives. In the late 1970's juice companies saw an opportunity to reduce transportation costs by using a downscaled version commonly referred to as a juice box. Since the product could not be reused or effectively recycled, with the plastic component being the prime reason given for its non-recyclability, it was considered a burden on the solid waste system. Public pressure almost eliminated it from the store shelves in early 1991 but the manufacturers and juice companies fought back with aggressive advertising (Lynch, 1990, Deloitte, 1991). This case clearly demonstrates the conflicts within the 4 R's hierarchy. While the TETRA PAK was designed for source reduction, arguments were made that it did not fit the criteria for reuse and recycling.

A move by MacDonald's Canada in 1990 virtually shut down the Canadian Polystyrene Recycling Association (CPRA) facility in Mississauga, Ontario. A switch by MacDonald's Canada from polystyrene foam "clamshell" containers back to wax paper wrappers for hamburgers was done in response to pressure to reduce the volume of packaging generated by the clamshells (Today's Generation, 1991). This was done in spite of the industries' efforts to recycle the plastic. This example demonstrates the dilemma faced by researchers and investors to advance the recycling of plastics. A plan to reclaim and reprocess the packaging was developed and actually being implemented, then the primary source of stock for recycling was eliminated.

The previous examples illustrate how public pressure influences the recycling of plastics. However, the greatest effect is from government regulation. World-wide, governments in the late 1980's and early 1990's took aggressive action to control waste through legislation. However, there is no consistent standard and this makes plastics recycling and research into recycling a challenge. The differences in regulations between regions, such as states and provinces, within countries are just as great as the differences between countries.

The types of legislation to reduce and minimize waste vary from deposit laws to volume or weight restrictions with packaging receiving a significant amount of attention. Content or composition legislation which establishes a minimum amount of recycled resin content is one of the most popular regulations being considered for implementation. However, outside global forces can have disastrous effects on well intentioned plans. The aluminium recycling industry is one case where uncontrollable global economics had a significant effect. This successful industry was severely undermined when aluminium was dumped into the market by the Russians in 1993 (Uxa, 1993). In this case the price of aluminium dropped by 50% which seriously threatened the viability of aluminium can recycling. The following is a sample of some of the government programs in place or anticipated in Canada, the United States, Europe and Japan at the time of writing this thesis:

Canada

The provinces of Ontario and Quebec are proposing or have passed the most comprehensive waste management legislation. In Ontario, all companies with over 50 employees must conduct regular waste and packaging audits and have waste and packaging reduction action plans. Source reduction and recycling content are considered part of the action plans. A ban on incineration is also in place in Ontario.

Across the country Blue Box or Blue Bag municipal collection programs for post consumer recyclables, including PET and HDPE, are a way of life. Though in some areas, plastics are not part of the collected materials. In 1994-95 a number of subsidy programs in place to assist in the start up of the collection programs reached a "sunset" phase and alternative funds for the programs had to be found. In an attempt to avoid content legislation and address the funding problem, the Canadian Industry Packaging Stewardship Organization (CIPSO) has developed a Canadian Industry Packaging Stewardship Initiative (CIPSI). The initiative proposes to administer a levy on packaging scaled according to the type of material. The levy would then be used to assist in the funding of the collection programs and to aid in market development for recycled materials.

United States

By mid 1992, 39 states had enacted legislation with recycling targets, 33 having specific recycling rates to be achieved by specific dates and with penalties for non-compliance. However, in anticipation of regulations, recycling rates increased significantly just between 1990 and 1991. For some resins such as those used in HDPE bottles the rates doubled while for other more "recycling mature" resins such as PET the rate increased by 50%.

While the writing and passage of legislation progressed, serious contradictions or barriers to economic feasibility emerged. For example, a number of states chose to ignore the reality of the fourth R, recovery, and banned or restricted any waste to energy facilities. This tends to inhibit the accelerated return of plastics back to their original constituents. In comparison, paper, when it reaches its threshold in recycling will find its way into its recovery phase in the form of compost.

The recession in the early 1990's drove virgin resin prices down to levels, which in most cases were less than the cost necessary for recycled resins to break even. As the price for virgin resin climbed back up in late 1994, early 1995, a new scenario emerged. The increase in virgin resin prices coupled with aggresive content legislation increased the demand PCR and also drove up the price for that material to the point where the collection, sortation and reprocessing costs for recycled resins were being recovered. As of the spring of 1995 the most aggressive states in terms of content legislation were Oregon and California. In the spring of 1994 the courts in Washington State ruled that a pyrolysis project for plastics did not fall within the recycling legislation and was considered incineration.

Europe

In general, the European community endorsed a resolution to reduce the levels of the waste stream, harmonize standards of treatment and disposal, reduce the level of movement between countries and to assign liability. Similar to Ontario, audits are an integral part of the program. Companies which are in compliance are allowed to display a nationally approved symbol which enhances the marketability of the product in terms of its environmental effects. The role of incineration and waste to energy varies significantly from country to country. In the UK, 20% of waste is incinerated or used in waste to energy systems, in France 32%, 50% in Sweden, and over 60% in Denmark and Switzerland. In 1990 about 7% of plastics were recycled in Western Europe, by the year 2000 a recycling rate of 60% is targeted.

The most aggressive packaging collection legislation was established in Germany in 1993. Under the Dual System, packaging that is used for a product is returned back to the retailer who returns it the manufacturer for recycling. To participate, producers pay a fee to market a "Green Dot" product. The fees are used to subisidize the cost of collection, transportation and separation. The success of the collection aspect of the program was overwhelming, to the point where market development severely lagged supply. It was been suggested that reclaimed plastics were flooding into other countries from Germany.

Japan

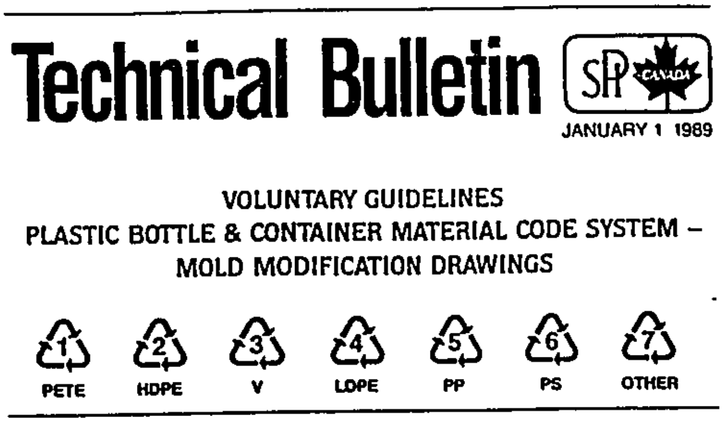
Japan is under intense domestic pressure to act on its MSW problems. The increase in the amount of waste generated per year has increased from 1-2% in the 1970's and 1980's to 4% in the early 1990's. The Japanese waste system was based on incineration. Therefore, a large amount of research is directed towards waste to energy as opposed to recycling (Akoh, 1985). Tokyo's municipal incinerators handle 80% of the burnable waste the city produces with the remainder landfilled. Roughly 5% of the current plastics production is recycled.

2.2.3 The importance of education in reclamation

Often the plastics industry is requested or is motivated to provide information on processing, product design or polymer science. The educators, institutional, industrial or otherwise, confidently deliver their message because it has been extensively researched and is supported with data. Plastics recycling education faces a number of formidable barriers, including: minimal data on the successes of recycling; the complexity of polymer science; the magnitude of the types and combinations of polymeric materials; the adaptability of polymer science in meeting the needs of narrowly focused, highly specialized product applications; the high visibility and exposure of plastics in products; the perceptions associated with advantages and disadvantages of using polymeric materials (Ehrig, 1992).

It is imperative that consumers, designers and plastics producers work together to consolidate complex scientific information into some form that is understood by students and consumers who could use the knowledge. An example of the significance of this type of consolidation is available in a recent study on the life cycle of a coffee cup which compared 3 different materials and the impact they have on the environment in this application (Van Ejik, 1992). Scientifically sound in its conclusions, the importance of this study lies in the presentation of its results. While the data indicates that a reusable ceramic cup has some advantages, the results are put into a form that is easily understood, specifically, the number of cups of coffee that must be consumed before a net benefit is realized. In this format, people can draw their own conclusion as to the practicality of using a ceramic or foamed polystyrene cup.

A scheme to reduce separation costs and promote the recycling of plastics was developed by the Society of Plastics Industries (SPI) of both Canada and the United States in 1989. However, the labelling system and concurrent education program was not clear or easily understood (SPI, 1989). A coding system initially for plastic bottles, tubs and trays was introduced. The intent of the system was to provide a standard identification method for source separation of plastic containers. The system is shown in Figure 2.2 a. The inability for the public to modify their habits is often suggested as the downfall for system. However, the codes in many cases became difficult to read because they were soiled or hidden in a crushed container. The SPI in both Canada and the United States has been reviewing the system and plans to introduce a new system for all applications of plastics. It would be integrated into the ISO system and be supported by ASTM (Figure 2.2 b).

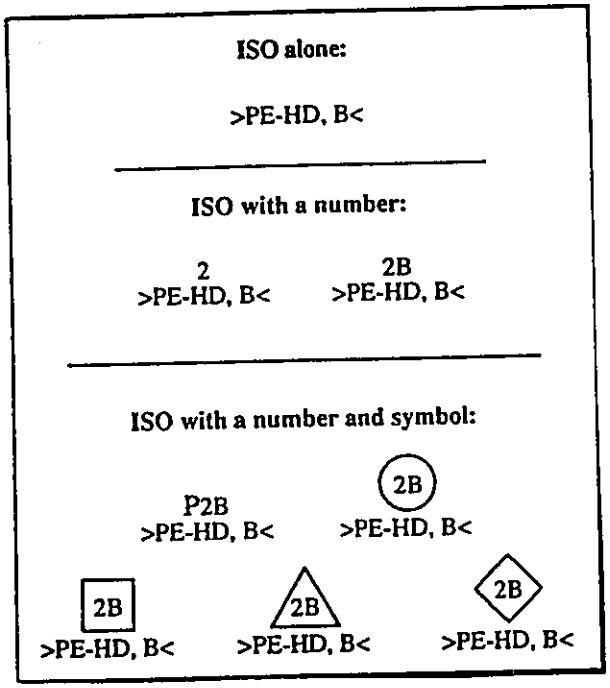


Technical Bulletin

JANUARY 1 1989

VOLUNTARY GUIDELINES
PLASTIC BOTTLE & CONTAINER MATERIAL CODE SYSTEM –
MOLD MODIFICATION DRAWINGS

a) 1989 SPI system



ISO alone:

>PE-HD, B<

ISO with a number:

2
>PE-HD, B<

2B
>PE-HD, B<

ISO with a number and symbol:

P2B
>PE-HD, B<

2B
>PE-HD, B<

2B
>PE-HD, B<

2B
>PE-HD, B<

2B
>PE-HD, B<

b) proposed SPI/ISO system

Figure 2.2: SPI coding systems

The intention of the new system is to expand the source for recycled plastics beyond packaging and into applications such as automotive parts (SPI, 1994). The new codes appear even more complex than the old ones and would be a greater challenge for the consumer.

2.3 Separation technology

When a product is deposited into the recycling stream it becomes intermingled with any number of and any combination of other materials and products. Gross separation where identification is generally driven by the main constituent of the product (i.e. plastics, metals and paper) is relatively straightforward. For example, a pop bottle may be made of plastic or glass but the distinct difference in properties between the materials would make separation easy. In contrast, automotive fluff may have glass, polymeric and other materials yet when it is reduced to baseball sized chunks how can these materials be distinguished?

Hand separation was used in many community recycling pilot projects and continues but separation technology has progressed to the point where a few economically viable methods exist for gross separation and some "within material group" separation. Most of the gross separation technology is based on the established methods used in the mining mineral separation industry (Basta, 1989, Brewer, 1987, Wilder, 1990). Taking advantage of the different densities of the materials, flotation techniques combined with hydrocyclones and dryers are used to separate most metals, plastics and paper. A second stage may include the use of magnets for purifying the separated streams to a greater degree (Koch, 1990).

The recycling of polyethylene terephthalate (PET) pop bottles and high density polyethylene (HDPE) milk bottles showed growing success in the early 1990's. In terms of separation both bottles are highly distinguishable. If they are collected in a commingled stream, their densities are significantly different that floatation technology can work. More importantly, in most cases, both bottles are composed entirely of a single resin, excluding pigments and other additives. The latter point is significant because of the increased strength in the market for a 100% recovered PET and HDPE.

The degree of separation for waste is dictated by the end use or application of the separated materials. The end use for a material is dictated by the acceptance of the product on the market. Regardless of whether the product uses recycled, virgin or both types of material, if the product performs, and is cost effective then the material used in the product is considered acceptable. The desire to have a highly separated, clean stream for reprocessing in packaging is often driven by the performance requirements consumers and marketing representatives place on products.

As an example, consider PET and PVC which are used in the beverage bottle market. Both are extremely different in their chemical and molecular structure but have similar strength properties and are used where high optic properties are required. To recycle 2 litre PET pop bottles back into 2 litre PET pop bottles there can be no PVC water or juice bottles. If 1 PVC bottle is left in a batch of 1 million PET bottles the entire lot of 1 million PET bottles will have to be used in a lower grade product application. This situation arises because 1-20 ppm of PVC in PET can drastically alter the intrinsic viscosity and colour of the recycled PET (Babinchak, 1990). A number of projects working towards solving the PVC identification problem were initiated (Modern Plastics, 1990). A heated belt was used by Refakt from Germany and The Centre for Plastics Recycling Research (CPRR) at Rutgers studied the use of x-ray fluorescence to identify chlorine in a highly automated rigid container sorting line. In the CPRR project a robot aligned the bottles in single file and 3-10 bottles/sec were bombarded. The line was programmed to "kick out" either the bottles containing chlorine or the other bottles. Usually 5 readings/bottle were taken and the estimated error was 0.3 ppm. Govoni S.p.A. of Italy in collaboration with ENICHEM and SOLVAY developed a similar process where an electromagnetic scanner was used to identify the chlorine. In a pilot project at the City of Akron, a physical characteristic of clear PVC, extrusion blow moulded bottles (a "smile" at the parison pinch off) was used for identification during separation (Summers, 1990).

In 1994, the most automated, commercially available process was part of a fully integrated bottle sorting system. Developed by Magnetic Separation Systems, Nashville, Tenn. it uses electromagnetic radiation and mechanical sorters after an optic system. In figure 2.3, a schematic of the system is shown. Plastic bottles which have been grossly separated from the reclamation stream are unbaled and singulated. Each bottle then passes through an optic and electro magnetic sensor where a polymeric "fingerprint" is recorded and compared to a databank. Optional colour identification is also done using video technology. The bottles are then sorted according to the information stored in a microprocessor. With this system, bottles of different polymers and colours can be sorted at a rate of 2300 kg/hr (5000 lbs/hr) (Kenny, 1993).

UNIT

DEBALER/SCREEN	SINGULATOR	SENSOR	EJECTOR

FUNCTION

STORE AND FEED BALES BREAK DOWN BALES INTO SEPARATE BOTTLES SCREEN OUT CONTAMINATES	ACCEPT BOTTLES AND OUTPUT INDIVIDUAL SPACED BOTTLES	IDENTIFY TYPE OF PLASTIC BOTTLE	EJECT BOTTLE ONTO OUTPUT CONVEYOR WITH AIR JETS

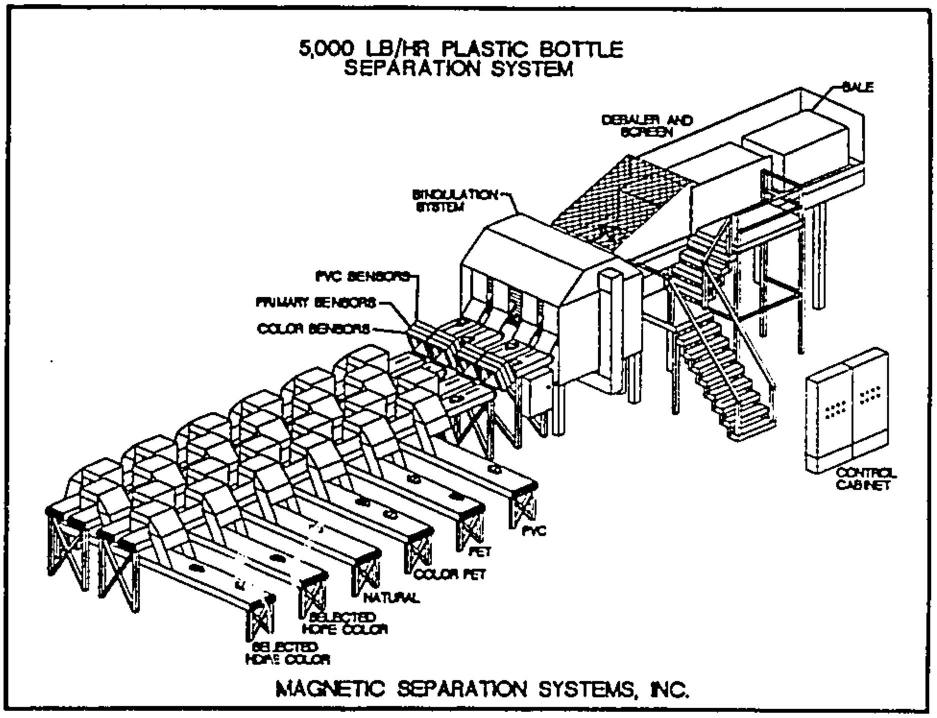


Figure 2.3: Bottle Sort© system

2.4 Cleaning reclaimed plastics

Once products made from plastics have been separated they are reduced in size by shredding or grinding and are cleaned prior to entering the reprocessing stage. A flow diagram for the QUANTUM Chemical HDPE bottle reclaiming system is shown in Figure 2.4. Most reclaimed plastics are cleaned to remove loose dirt, labels and ink. Pneumocyclones, hydrocyclones and dryers usually make up the cleaning system. Sometimes detergents are used but often hot water is the only cleaning agent.

In comparison to degradation, which will be discussed in chapter 3, contamination is the presence of a compound or particulate which was not originally intended to be part of the material system. The effects of contaminants are typically measured subjectively in terms of visual, odour or other sensory means though they may also modify the physical or melt flow characteristics. Typical contaminants found during reclamation include particulates, chemical compounds and incompatible polymers. Particulates can range from dirt, cellulose, metals, severely oxidized polymers and gels. Gels occur naturally during polymerization and can be generated by degradation mechanisms. They are described as a highly cross-linked three dimensional network of polymer which is insoluble.

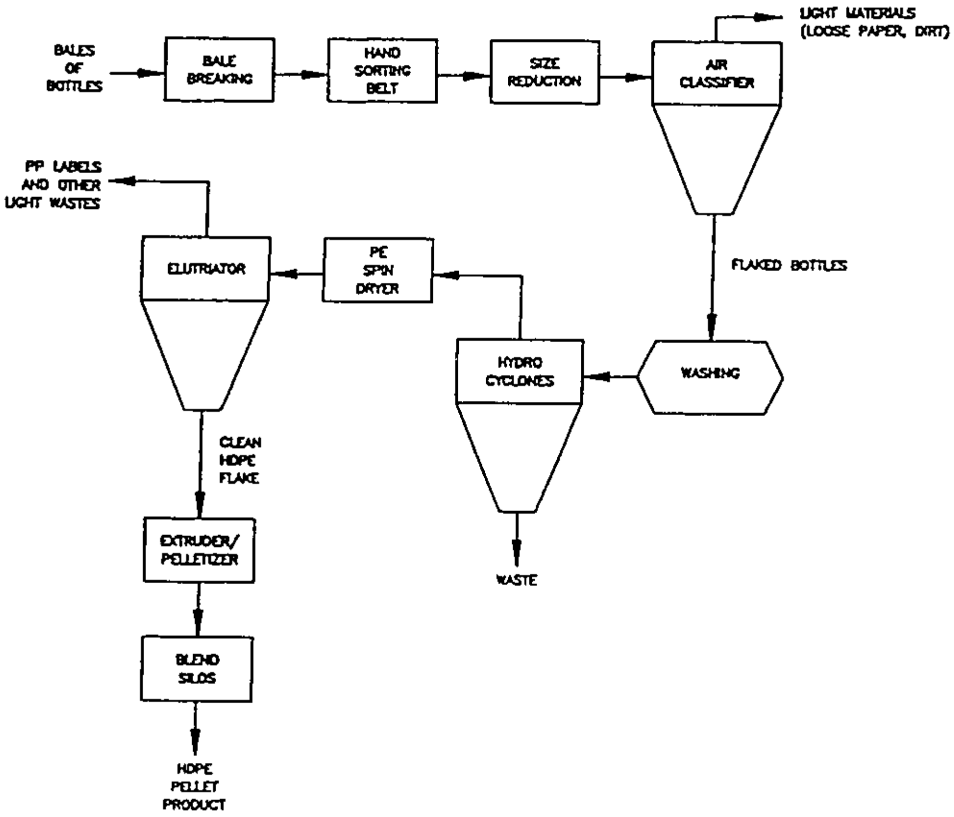


Figure 2.4: QUANTUM Chemical reclaiming process
(Reprinted with permission from author, Ehrig, 1992)

This network is very rigid and does not have the rotational or elastic properties of the original polymer molecule.

The possible chemical compounds found in reclaimed materials are limited only by the compounds either used in the product or by the environment to which the product is exposed (Ezrin, 1994). Buric acid, a by product of spoiled milk, is considered a contaminant because of the odour associated with it. Motor oil in bottles, perfumes used in detergents and tackifiers used in stretch film are also considered as contaminants in reclaimed material. Most of the compounds are residues that manage to migrate into amorphous regions of the polyolefin material. While they may not be strongly bonded to molecular chains, the highly random packing of the molecules tends to entrap the compounds. Some chemical compounds may be vented and most particulates can be screened out of a polymer during extrusion. However, even at elevated temperatures, with the polymer in a molten state, traces of the chemical compounds still remain within the polymer structure.

2.4.1 Closed loop reclamation

In order to accommodate the complexities and toxic nature of contaminants, closed loop systems are being developed. In one project, trials involving FDA approved products were initiated with a major US airline in 1993. A closed loop process is being tested where PS food trays are being collected from flights, ground and re-extruded back into food trays. The FDA has approved the trial based on the elimination of unidentified source material entering the reclamation stage. Similar, non-food application trials are ongoing in the agricultural industry. Banana bags in Costa Rica are part of a closed loop to prevent the insecticide laced bags from entering the post consumer recycling stream (Portugués, 1994). The bags are shredded and re-extruded back into new bags. A trial is also being run for HDPE bottles used for insecticides by farmers in the US (Denny, 1994). The farmers are trained to rinse the bottles which are collected regularly for disposal. At the time of the writing of this thesis most of the bottles are incinerated and are not recycled.

2.4.2 Incompatible polymers

The presence of incompatible polymers in the main constituent polymer stream can cause structural defects and regions of high stress intensity within the molecular network. Incompatible polymers tend to have different thermal and chemical characteristics. Voids may occur from two materials shrinking at different rates or from the lack of any interfacial bonding between the materials. In these areas the ability of the material to carry any significant stress diminishes and the product will fail. The objective of a reclamation system is to minimize the presence of incompatible polymers. However, in some cases the lack of interfacial bonding can be overcome with the use of compatibilizers (Chen, 1989).

2.5 Reprocessing

After a plastic has been separated and cleaned it is reprocessed. There are 3 categories of reprocessing, primary, secondary and tertiary. Primary reprocessing can be defined as the reforming of polymer scrap (sprues, edge trim etc.) into its original product application. An HDPE blow moulded detergent bottle, blow moulded back into a fabric softener bottle or a PET pop bottle reprocessed into a tennis ball bottle are classified as primary processes. Secondary reprocessing involves reforming a polymer into a lower valued product such as HDPE blow moulded bottles compression moulded into stall liners for livestock or the shredding of PET pop bottles into fibres for use as clothing insulation. The distinction between primary and secondary lies in the type of process used and source of material. While primary reprocessing is restricted to the original forming process, using scrap, secondary reprocessing usually involves a different product, an alternative forming process and waste plastics which have to be cleaned. In plant primary or secondary recycling has existed virtually since the time plastics were first polymerized and this is referred to as post industrial recycling. It is usually done in conjunction with virgin polymers at relatively low percentages (>20%) of reclaimed material. While coextrusion is not a new technology, it is increasingly being used as a method for using recycled material in food approved (FDA) applications. A three layer, single resin system is used where the outer skin and inner food contact layer are virgin resins and the middle layer is recycled resin (Waters, 1989).

The third type, tertiary reprocessing, involves the breaking down of plastics, either thermally or chemically, back to feedstock material such as crude oil. The feedstock can be repolymerized back into plastics, used in other chemical products or used as an energy source. Tertiary recycling became prominent in the 1970's during the energy crisis when plastics were considered as an energy source. Within the last 5 years this form of recycling has been receiving more attention and in reaction to legislation such as the Dual System, tertiary recycling is expanding rapidly. It is expected that over 4 b lb. of capacity to convert plastics back to crude oil will come on stream in Europe by 1997. A schematic diagram of how the 3 types of reprocessing categories fit into the life of a polymer is shown in Figure 2.5.

2.5.1 Commingled reprocessing systems

Except for some processes, the current market for recycled polymers demands virtually 100% separation of the plastic waste into specific polymers, the exception is the commingled process (Renfree, 1989).

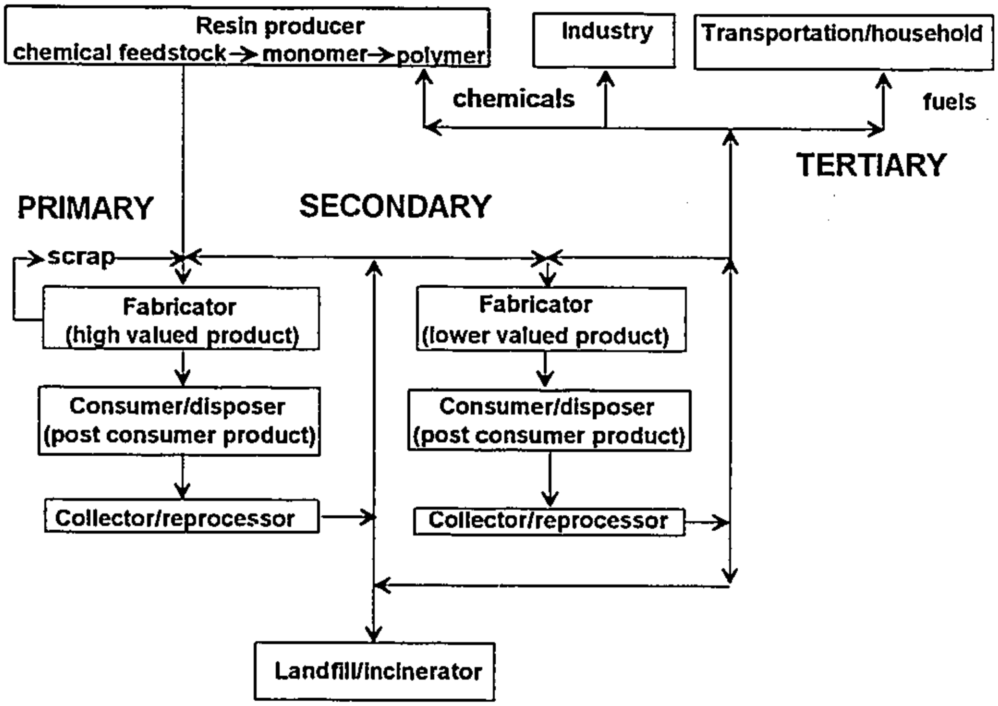


Figure 2.5: Reprocessing categories

Commingled systems were at first considered as a panacea for recycling plastics. The ability to combine a variety of polymers with other non-polymer materials seemed a viable approach to avoid costs associated with separation. However, the process used for commingled materials only produces large simple parts and which are intended to compete directly against wood. It has been demonstrated that they can be nailed and sawed in a manner similar to wood. Studies have been conducted to demonstrate that the minor component mingled with the thermoplastic actually acts as a reinforcing material in the "plastic wood" (Salas, 1990, Selke, 1989). Research was done to develop products with equivalent and even superior properties to wood but they were not cost effective in the short term. The main selling advantage for the commingled product is its long term life and low maintenance costs.

The ET-1, Welding Engineers and Superwood systems require a high thermoplastic content. Their process is based on melting through friction. A short adiabatic screw rotates at high speed softening the low melting point polymer which encapsulates the higher melting point polymers and metals. The short screw ensures short residence times and there are provisions for venting HCL if PVC is the primary thermoplastic (Maczko, 1990). The molten material is continuously extruded, which is cut after cooling or extruded into moulds which are rotated in a gattling gun type system. After extrusion the parts are cooled slowly to avoid internal stress concentrations. Today, with the high degree of separation now in place, many commingled systems use the "tailings", difficult to separate material from materials recovery facilities (MRF's) and separation facilities. There is one exception in the US, Eaglebrook Plastics Inc., which uses a highly separated HDPE source material obtained with the Bottle Sort system integrated into their process.

Other commingled processes under development include HDPE/ rubber and PP/wood flour products. In both cases the thermoplastic is used as a matrix for a fine ground non-thermoplastic material. The HDPE/rubber system is intended for use in sheet extrusion and compression moulded products (Engleman, 1992). The PP/wood flour system is intended for use in compression moulded sheet for sound deadening in automobiles (Meyers, 1991).

Chapter 3 - Polyethylene and Recycling

3.1 Polyolefins

Plastics fall into two categories, thermosets and thermoplastics. Thermosets are materials which undergo a chemical reaction during processing and harden after moulding. The chemical reaction, known as crosslinking, cannot be reversed and creates a three dimensional network from the highly branched polymers. They decompose during heating and cannot be reformed. Typical thermoset materials are phenolics, epoxy and urethanes.

Thermoplastics are materials that can be melted or softened at increased temperatures and repeatedly formed or moulded into a variety of shapes. Polyolefins are members of the thermoplastic family. The polymerization of small molecules, α-olefins, leads to molecular chains of repeated C-H groups called polyolefins. Characterized as unsaturated, aliphatic hydro-carbons, α-olefins have one double bond between the first and second carbon atoms. Polyolefins produced from α-olefins include polypropylene (PP) from propylene (CH_3-$CH=CH_2$) and polyethylene (PE) from ethylene ($CH_2=CH_2$) (Modern Plastics, 1991).

Polypropylene is manufactured in a polymerization reactor and can be in the form of a homopolymer, copolymer or impact modified type rubber. The characteristics of PP are similar to PE and both materials compete in similar markets such as films and rigid containers. The impact modified material tends to dominate the battery case market where over 200 million lb. (90 thousand MT) is used annually in North America, almost 80% of which is recycled. About 18 billion lb. (8 million MT) of PP is consumed in the world each year. This is the extent that PP and thermosets will be discussed in this thesis. The remainder of this work will focus on PE, specifically HDPE extruded into blow moulded bottles.

3.2 Polyethylene

Ethylene was first polymerized in the 1930's when Imperial Chemical Industries (ICI) produced low density polyethylene (LDPE). A 20 year period elapsed before linear LDPE (LLDPE) and high density polyethylene (HDPE) was produced using new technology. The advancement of PE polymerization and catalyst technology accelerated rapidly in the 1970's and 1980's as variations of copolymers and densities were added to the product list. Ultra or very low LDPE (ULDPE or VLDPE) and ultra high molecular weight PE (UHMWPE) were developed to provide unique properties for niche markets such as stretch wrap and high impact structures. The density of the PE is directly related to the amount of side branching along the length of the backbone molecule. The higher the density the more orderly the molecular chains are packed. This produces a more crystalline material that tends to be opaque. In contrast, the longer and greater the amount of side branching, the greater the amount of entanglement that will occur between chains. This opposes any opportunity for close packing and produces a less dense material. Lower density material tends to be more amorphous and has better optical properties. Typical applications of PE include film for bags and diapers, blow moulded milk and commercial fluid bottles, injection moulded rigid containers and rotational moulded large parts.

Two methods of polymerization are used to manufacture PE. A high pressure reactor, with a free radical initiator is used to produce the highly branched low density PE (LDPE, 0.910-0.925 g/cm^3). A low pressure, transition metal catalyzed process is used to produce minimal branched high density PE (HDPE, >0.940 g/cm3) or slightly branched linear LDPE (LLDPE, 0.900-0.940 g/cm^3). In figure 3.1 the differences in molecular structures for the 3 different PE's are shown.

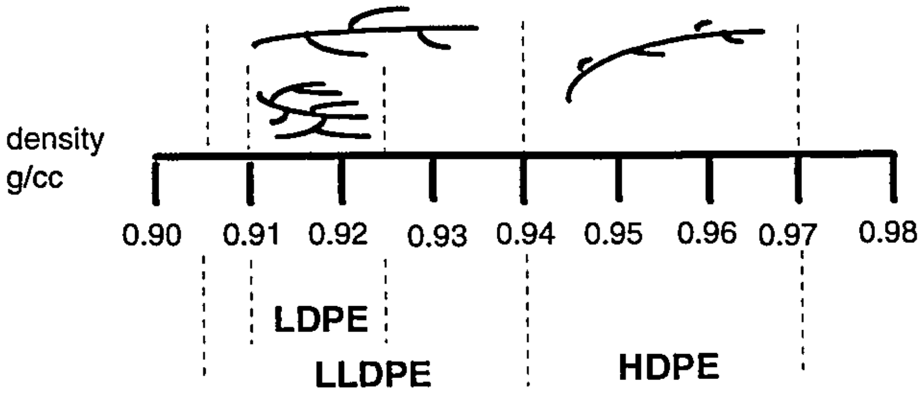


Figure 3.1: Molecular structures of polyethylene

Linear LDPE is considered to be a copolymer material in that other α-olefins are copolymerized with ethylene. HDPE can also be a copolymer, though a significant volume of homopolymer HDPE is also produced. Globally, approximately 77 billion lb. (35 million MT) of PE is produced at a ratio of 40/60 HDPE/LDPE(LLDPE) (Modern Plastics, 1994)

3.2.1 Production of low density polyethylene

The ICI technology for producing LDPE uses a very long tubular or autoclave reactor (Fawcett, 1938). At pressures of between 100 and 300 MPa and temperatures between 150 and 250°C the process initiates branches of differing length along the backbone molecule using an oxygen or peroxide free radical initiator. The long residence time in the reactor and higher degree of branching produces a broad MWD material. The branching frequency can vary from 7-17 branches per 1000 carbon backbone atoms for short chain branches and up to 2 per 1000 carbon backbone atoms for longer chain branches (Beasley, 1989).

3.2.2 The production of high density polyethylene

The low pressure polymerization of ethylene using heterogeneous catalysts was developed in the 1950's. The Standard Oil, Phillips and Ziegler were the most predominant processes. They were characterized by their catalyst systems (Allen, 1983). The Standard Oil catalyst was molybdenum based, the Phillips chromium based and the Ziegler-Natta titanium based. Two types of reactors are used to produce a polymer with very little side chain branching. Liquid phase reactors can be either solution or slurry. Gas phase reactors, such as used in the UNIPOL process developed by Union Carbide in the 1960's, have a fluidized bed.

The Ziegler liquid phase process operates at temperatures of 50-75°C and pressures of 1 MPa. Batch or continuous systems are used where the HDPE is in a slurry with a hydrocarbon diluent. After polymerization the diluent and catalyst are stripped and the powdery polymer is extruded and pelletized.

The Phillips process uses higher temperatures and pressures than the Ziegler. Typical conditions are 125-175°C and 2-3 MPa. The reaction may involve a solution or a slurry with the latter having a high catalyst efficiency. This point is important because it often allows the elimination of the catalyst removal step. A Phillips slurry process was used to produce the homopolymer, QUANTUM HDPE LM6007, which was studied in this work.

The gas phase process operates at a temperature less than 100 °C and between 0.6 and 2.0 MPa pressure. The catalyst originally was chromium based and was used to produce HDPE. As catalyst technology evolved, a Ziegler, Ti type catalyst, was developed and the process became capable of producing LLDPE. The bulk of PE production from this process is LLDPE.

3.2.3 High density polyethylene copolymers

Variants in the processes described above can use a higher molecular weight α-olefin comonomer to produce a copolymer. Either butene-1, hexene-1 or octene-1 are used to produce copolymer resins. The addition of a comonomer promotes some short chain branching along the backbone. More importantly, the copolymer is used to increase the amount of the high molecular weight fraction in the resin. The DOW HDPE 32060C, used in this research study was manufactured using a Ziegler process and is a butene-1 HDPE copolymer.

3.3 Molecular weight and molecular weight distribution

The length and weight of each PE molecule varies and the frequency of molecular weights is measured in terms of a molecular weight distribution (MWD). The MWD is typically a skewed Guassian distribution and is established by dividing the molecular weights into a series of classes or fractions (McCrum, 1988). Each fraction is described by molar mass ($\mathbf{M}_i$), the number of moles ($\mathbf{n}_i$) and the total mass ($\mathbf{w}_i$). The relationship between the three parameters is

$$w_i = n_i M_i \tag{1}$$

The two most common central measures of the MWD are the number average $\mathbf{M}_n$ and the weight average $\mathbf{M}_w$. They are defined as

$$M_n = \frac{\sum n_i M_i}{\sum n_i} \tag{2}$$

and

$$M_w = \frac{\sum w_i M}{\sum w_i} \tag{3}$$

or by substituting for w_i

$$M_w = \frac{\sum n_i M_i^2}{\sum n_i} \tag{4}$$

The number average is the mass of the polymer divided by the total number of moles and is sensitive to the lower molecular mass fraction. With M^2_i the weight average tends to be biased towards the higher molecular mass fractions. In all plastics M_w is always greater than M_n.

Independently the two central measures provide some description of the MWD. However, the two can be combined to create a polydispersity index, **PI** where

$$PI = \frac{M_w}{M_n} \tag{5}$$

As PI increases the breadth of the MWD increases. Typically for HDPE the PI falls in the range of 2-30.

Molecular weight and the MWD are usually determined by gel permeation chromatography (GPC). In this method, a sample of the polymer is put into solution which is introduced into a column containing porous beads. The molecules either pass through the pores or pass over the beads. The longer the molecule or higher the molecular weight the greater the probability the molecule will pass over the beads and the faster they will proceed to the bottom of the column. Sophisticated optical or spectrotography techniques are used to count the molecules as they pass to the bottom. Computer software transforms the counts into a distribution which is fractionated and M_w and M_n are determined. The required equipment, sample preparation, length of time and the high level skill of the operator, tend to make this method viable only for resin producers and large production facilities. In this work an alternative method for studying the MWD is used and will be discussed later.

3.4 Additives and high density polyethylene recycling

The processing system and the base resin system are well understood, their effects on degradation are documented and it could be demonstrated that they have the most significant effect on degradation. However, the effects of additives cannot be underestimated, especially their cumulative effect. Initially, they are incorporated into a resin system but as they are blended into a reclaimed batch of material, the amounts and different types of additives could increase to significant levels. It may be impractical to attempt to list the types and levels of additives in a batch of material, let alone predict the impact the additives would have on the final product. However, their presence should not preclude the use of other additives such as compatibilizers or lubricants to aid in the production of a product which incorporates reclaimed materials.

The incorporation of additives into a resin system is a well established technology and a widely accepted method of imparting stability, enhancing physical properties, minimizing static effects, preventing or initiating cross-linking, improving processability and tinting/colouring a thermoplastic polymer (Lutz, 1989, Morton, 1987). The basic categories that additives fall under are: anti-oxidants, light (UV) stabilizers, plasticizers lubricants/processing aids, impact modifiers, flame retardants, anti-static agents, cross linkers, bio/photo degradation initiators, pigments and fillers. Within each basic grouping there is a large number of types and suppliers of compounds which will achieve the desired results. Most additives are added in at the 100 - 10,000 parts per million (ppm) level.

Antioxidants are probably the most essential additive in a resin system. They prolong the life and minimize the effects of processing by retarding the rate of free radical propagation initiated by heat, mechanical shearing or incomplete termination of the polymerization process. There are 2 types of stabilizers. Hindered phenolics and amines are used as primary stabilizers to promote chain termination and phosphites and metal deactivators are used as secondary antioxidants to destroy hydroperoxides and prevent the proliferation of free radicals.

Light stabilizers are used to slow the rate of degradation due to ultra-violet light and are "ultra-violet absorbers." Traditionally these absorbers are phenolic or hindered amine (HALS) compounds which absorb the energy generated by UV light and prevent the generation of heat necessary to initiate degradation. Pigments and some fillers are also good absorbers with carbon black the most effective.

Impact modifiers, flame retardants and anti-static agents are used to alter the mechanical, ignition and electrical properties of thermoplastic polymers. The introduction of rubber such as polybutadiene into polystyrene greatly improves the energy absorption of the material and thus increase the impact strength. Flame retardants serve 2 purposes, first they increase the resistance to ignition and second, once a material is ignited, they are used to reduce the rate of flame spread. Aromatic halogen compounds with chlorine or bromine tend to be the most stable and most widely used flame retardants. Since plastics are very good insulators they accumulate static electricity and are unable to discharge the energy due to their low surface conductivity. Internal anti-static agents are incorporated as surfactant additives which migrate to mould surfaces whereas external agents are applied to the mould surface.

Cross linkers are generally peroxide based products which are used to improve dimensional stability at high temperatures or to improve chemical resistance properties. In contrast, degradation initiators are used to decrease physical properties. Biodegradation initiators fall into 2 categories. One type, starch, is introduced as a filler which is attacked by microbes. This physically introduces air gaps between polymer chains and reduces the integrity of the material to a dust. The incorporation of IGEPAL, a chemical soap which attacks polymer chains is the other type and it chemically dissolves the actual molecules. Photodegradation initiators are similar to UV stabilizers in the sense that they absorb energy. However, the energy is used to initiate degradation by providing a free radical site. Carbon monoxide incorporated into polyethylene is an example of this type of additive.

The extrusion and moulding of thermoplastics involves the melting and pumping of a high molecular weight, high viscosity material through very narrow passages. The resultant product tends to have a smooth, glossy finish. There is a need to minimize wear of the passages and energy consumed during extrusion. As well, it may be necessary to maintain a smooth glossy surface, for cosmetic purposes, while at the same time minimizing surface to surface adherence. In order to achieve the above effects, lubricants are incorporated into the resin system or during the forming process. The types of lubricants or processing aids (PA) can be categorized by their point of application and their operative mechanism The use and effect of each type varies with the thermoplastic and they rarely act completely internally or externally. The implications of using these additives in recycling is important because they can contribute to and be a source for degradation but they could also be used to minimize degradation from repeated heating and shearing. Internal lubricants are compatible with the polymer and are used to decrease the melt viscosity of a resin and reduce heat generation due to internal friction from polymer chains sliding over each other. These lubricants tend to stay within the polymer, are at low concentrations and have little impact on the final physical properties. Waxes are generally used as internal lubricants in polyolefins, depending on the type of wax and type of polyolefin. For example, polyethylene (PE) based waxes are compatible with PE, therefore they remain in the PE but when they are used with polypropylene (PP), they are incompatible and migrate out of the PP. Waxes tend to have lower melting points and could be subject to severe oxidation (burning) at temperatures lower than those for the base polymer (Gachter, 1987). On the other hand, these waxes would tend to benefit from the same stabilizers used for the base resins. This has very positive implications for recycling because they can continue to be incorporated into blends to achieve the same results when they are used in virgin resin products.

In comparison to internal lubricants which are compatible with the base resin, external lubricants are highly incompatible and tend to migrate out of the resin at the first opportunity. This has profound effects during blending and during processing, assuming the lubricants is directly incorporated into the resin prior to processing. Some external lubricants are applied to mould and extrusion surfaces prior to processing and are classified as mould release agents. In general, a highly polar lubricant such as stearates and esters will tend to act as an external lubricant for the non-polar polyolefins such as polyethylene. In contrast polyethylene waxes and paraffins which have limited compatibility with PVC act as external lubricants for PVC (Whelan, 1977).

External lubricants are directly formulated into the resin blend and perform at different times based mostly on their melting point. As a polymer is melted the lubricant will also soften and flow out of or away to an external surface. When it reaches the surface it will adhere for a limited time, and provide a low flow resistance interface for the polymer to slide across. Therefore, these lubricants are really only effective in the molten state, though some effect may be achieved at the throat of the extruder.

External lubricants such as silicones, soaps and some amides are post extrusion type materials which assist in releasing products from moulds and aid in high speed cutting or trimming operations. Silicones and soaps are usually mould release agents which can be applied directly to external surfaces or in some cases are a part of the lubricant system incorporated into the resin. They are usually quite incompatible with the resin, provide a layer of material between the resin and mould surface, and perform during cooling of the part.

All additives could have a significant effect during recycling. Additive level and particle size are critical to their performance. Each formulator and processor has their own system and reasons for using additives. However, once the product is discarded and enters the recycling system, those reasons can no longer be associated with one particular batch. What would be consistent is that there is a high probability that the batch of reclaimed material is based on a single thermo-plastic i.e. PE only. Problems could arise around the amount and particle size of any residual additive that remained with the polymer during processing and cooling. If it is assumed that none, or a negligible amount remains in all products which are reclaimed, then any additional amount of an additive blended into the reclaimed resin system should perform as it always did. However, if this assumption is not correct then build up and agglomeration could occur. This could have significant implications for recycling. The unknown factors are the types and levels of residual additives which are present in a batch of reclaimed resin.

3.5 Life cycle of a high density polyethylene blow moulding resin

The life cycle of a HDPE blow moulding resin begins with polymerization in a reactor. When the reaction is terminated molten or powdered product is passed through a melt blending extruder where anti-oxidants, processing stabilizers and processing aids are added. Thermal exposure and extrusion shear rates (< 500 s^{-1}) at this stage generally are kept low to minimize the onset of degradation. The polymer melt is then passed through a pelletizer and batches of the pellets are shipped to the manufacturer of the primary product application. In most applications the material is either dry or melt blended with other materials such as pigments, anti-static, flame retardant or UV light stabilizing additives. The material is then extruded and/or moulded into the primary product. Extrusion shear rates tend to be around 500 s^{-1} though in some final moulding stages shear rates >1000s^{-1} can be experienced by the polymer. Thermal exposure can be quite severe depending on the type of process and the desire for optimizing throughput. Since the viscosity varies inversely with temperature, a higher temperature will allow for a greater throughput.

Once the product is used the polyolefin will take one of 2 paths. It will either be discarded in the form of the primary product (likely into a landfill, possibly in a waste to energy system) or it will be diverted from the waste stream. If it is discarded and left exposed to the atmospheric environment, the product will degrade due to UV exposure, wear, and thermal-oxidative ageing. Arguably, complete degradation will not occur until the carbon or hydrogen atoms are liberated from each other. If the material is collected and landfilled the speed of the degradation process will be severely reduced as the material is virtually entombed and not exposed to the degrading elements. It is worth noting that degradation for virtually all landfilled material, and not polyolefins alone, is also stagnant under these conditions (Rathje, 1989). If the material is collected and used in a waste to energy system, the energy stored in the molecule, in terms of its calorific value, is transformed into heat where it can be used in a district heating system.

If the polyolefin is collected and diverted from the waste stream it will be reclaimed through a separation, cleaning and pelletizing system. The material is separated using near infra-red analysis (NIR) and/or a flotation system, shredded into flakes, passed through a blending extruder and pelletized (Ehrig, 1992, Paudich, 1993). Anti-oxidants and processing stabilizers are added at the blending extruder, similar to those added when the resin is first manufactured. Again shear rates and thermal exposure are minimized such that the shear rates are $< 500\ s^{-1}$ and melt temperatures are kept as low as possible. Prior to the pelletizer, the molten polymer passes through a screen pack. All extruders use screen packs to filter out particulates and breakdown gels. In reclamation processes this stage takes on a greater importance because the frequency of the particulates is substantially higher and the composition is less predictable. As discussed previously, particulates are generally considered contaminants which could adversely affect the performance of a primary product.

Depending on the quality of the reclaimed material, the polyolefin will then be re-extruded into another primary product application or into a durable good. In a primary product, the reclaimed polyolefin could be blended with virgin material at ratios as high as 50/50 and in some cases, tests are being done using 100% reclaimed material. The heating and shearing exposures experienced at this stage are similar to those in the initial product extrusion. If the material is incorporated into a durable good, it is temporarily diverted from both the recycling and the waste streams. A durable good is characterized as large part products which have longer term use/reuse in an application. Garbage cans, injection moulded beer crates and compression moulded sheet for truck liners are considered durable goods in contrast to single use blow moulded bottles or stretch wrap for pallets. The manufacture of a durable good will expose the polyolefin to another thermal and shear deformation process. It has been shown by Vink (1985) that the life of a reusable durable good such as a beer crate can be described by a Weibull distribution. In this study the life of crates was tracked and the number of crates still in use at any time from the original batch was determined. The end of the useful life of the crate was based on a controlled assessment of its state in terms of physical damage and UV degradation. In contrast, single use, post consumer products do not undergo the same scrutiny. The life of the resin in a value added application, such as a blow moulded detergent bottle or milk bottle, tends to be limited to the first use before it enters the solid waste/recycling stream.

The random nature of the recycling system can lead to extreme lot to lot variation in batches of reclaimed material. If the life cycle described earlier is repeated a number of times, it can be shown that the variability in the source material for recycling will increase dramatically. This puts tremendous pressure on the recycler to maintain consistency. In one comparative study it was shown that while lots of reclaimed material could have average physical and rheological characteristics similar to virgin material, the consistency was very unpredictable (Gibbs, 1990). The presence of contaminants produced numerous extrusion, odour and smoke problems.

In general, the path the resin follows will determine its heat, shear and contamination history. The life cycle process as a flow chart is shown in figure 3.2. For illustrative purposes, to demonstrate the state of polyolefin recycling in 1992, the life of 200 kg of virgin HDPE bottle resin is studied. The assumptions are that 10% of the resin is used in milk bottles, which is a homopolymer product, 8% is in motor oil bottles, a difficult to clean product and the remainder is used in other consumer bottles.

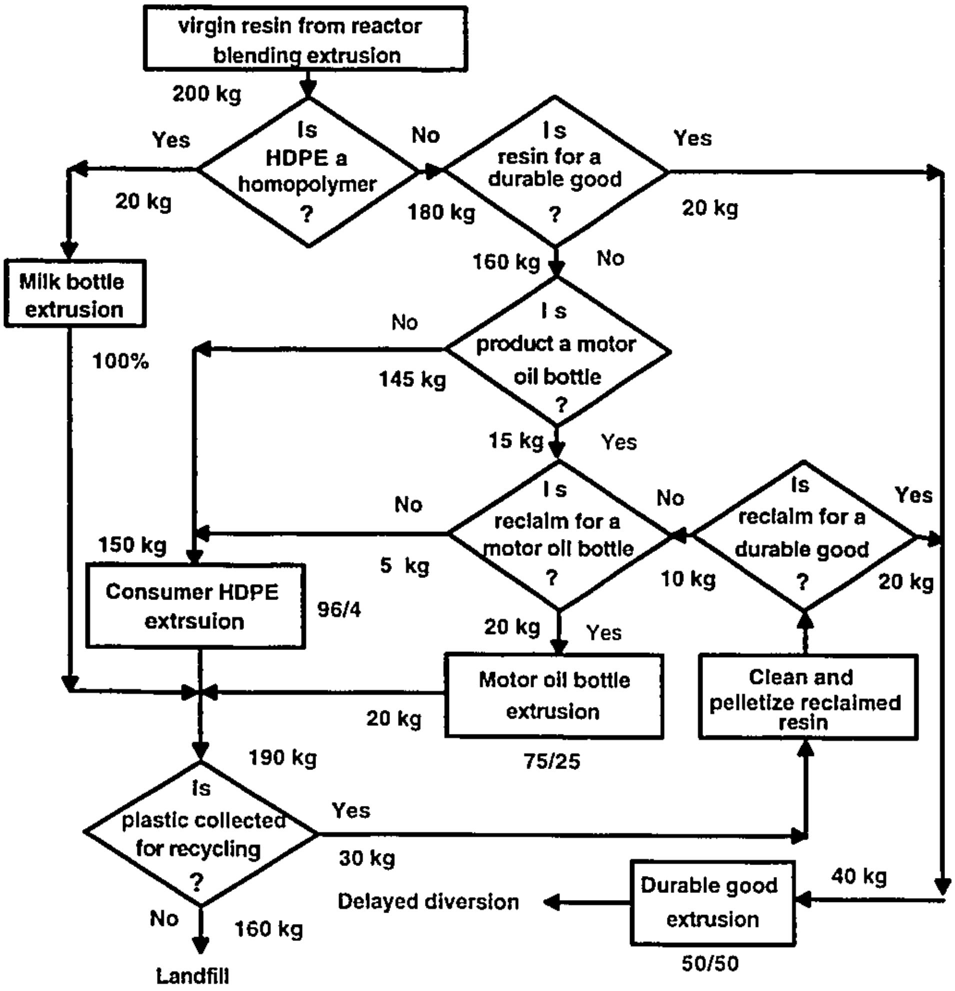


Figure 3.2: Life cycle of HDPE

A macroscopic perspective suggests that consumer products use about 5% post consumer recycled material and motor oil bottles about 25%. Some products would use more and some none at all. This does not take post industrial or internal scrap levels into consideration in terms of reclaimed content. It can be concluded that at the current levels of recycling, a large fraction of the polyolefin molecules will be exposed to at most 4 thermal and shearing cycles. Based on these blending percentages and assumptions, the following theoretical scenario could be presented to describe the composition life of a product in terms of processing cycles:

Table 3.1 Theoretical composition scenario

Product	**Composition**				
	% virgin	**% 1 cycle**	**% 2 cycles**	**% 3 cycles**	**% 4 cycles**
first	100.00	-	-	-	-
second	75.00	25.00	-	-	-
third	75.00	18.75	6.25	-	-
fourth	75.00	18.75	4.69	1.56	-
fifth	75.00	18.75	4.69	1.17	0.39

From Table 3.1, it can be seen that at a 75/25 virgin/PCR blending ratio, < 1% of the composition would see 4 heat histories. As the percentage of PCR increases the proportions of material with longer reprocessing lives increases and their impact on the overall product properties would become more significant.

Chapter 4 - Properties of High Density Polyethylene

4.1 Properties of high density polyethylene

Polyethylene, like all polyolefins, is described by its density, strength, MW, crystallinity and melt flow or rheological characteristics. Other properties such as environmental stress crack resistance (ESCR) and optics tend to be application specific measures. This work studies changes in rheological, strength and ESCR properties and their relationship to changes in MW and crystallinity. The molecular weight and molecular weight distribution characteristics were described in chapter 3. This chapter will focus on the rheological and strength properties of HDPE. The mechanisms of degradation and the effects of multiple extrusion cycles on the rheological and strength properties is discussed. The following is not intended as a detailed investigation of these specific properties, rather it provides a foundation for the discussion of the experimental results.

4.2 Rheological properties of high density polyethylene

Rheological characterization of HDPE involves measuring the viscosity and viscoelasticity of the molten polymer. Unlike simple fluids, these properties for HDPE have a strong dependence on temperature, shear rate, molecular weight and MWD. Optimizing the processing of reclaimed HDPE must take into account these relationships.

There are 2 primary flow mechanisms for HDPE, shear and elongational flow. Shear flow describes the response of the polymer to an imposed shearing force. Elongational flow is the response of the polymer to an imposed stretching or pulling force. Though not independent of each other, they both have their own viscosity measures.

4.2.1 Shear flow viscosity

Shear flow properties of HDPE are used to determine extrusion parameters such as screw design and temperature profiles. For Newtonian fluids the shear flow viscosity μ is a constant and is defined as

$$\mu = \frac{\tau}{\dot{\gamma}} \qquad (6)$$

for a given shear stress, τ, and shear rate, $\dot{\gamma}$.

At very low shear rates ($\dot{\gamma} < 10^{-2}\ s^{-1}$) a molten polymer behaves roughly as a Newtonian fluid. Beyond this point the shear stress of molten HDPE has a non-linear relationship with shear rate. As the shear rate increases the rate of increase in shear stress decreases and this is described as shear thinning. Within the range of typical manufacturing shear rates ($5 < \dot{\gamma} < 5000\ s^{-1}$) this relationship can be described by a power law expression

$$\tau = m\dot{\gamma}^n, (n < 1) \tag{7}$$

Substituting (7) into (6) gives

$$\eta = m\dot{\gamma}^{n-1} \tag{8}$$

The coefficient **m** is a measure of the viscous nature of the polymer. The power law index, **n**, is a measure of the effect of shear thinning. As n approaches 1, $m \cong \mu$ and the fluid tends to be Newtonian.

The shape of the MWD and the average molecular weight are directly related to the melt flow properties and processing performance, in terms of extrusion output rate and pressure (Christensen, 1991). As the length of the molecule increases the resistance to flow increases. As the breadth of the distribution increases there is a greater tendency to shear thinning (Figure 4.1) (Schott, 1961). A capillary rheometer and rotational plate on plate rheometer were used to measure shear flow viscosity in this study. The details of the equipment, test method and applied correction factors will be explained later.

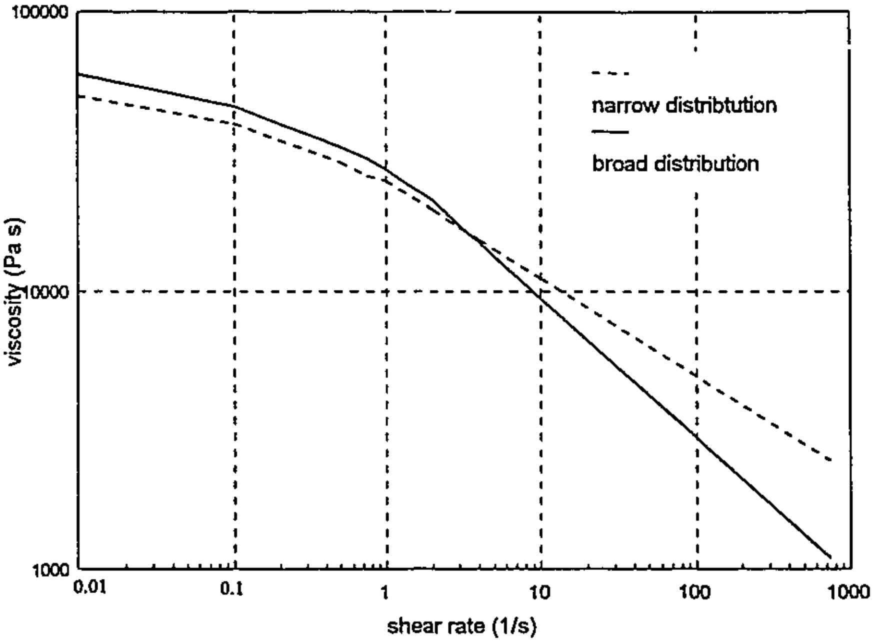


Figure 4.1: Viscous shear thinning of polyethylene

4.2.2 Elongational viscosity

In a blow moulding process HDPE is extruded into a molten tube called a parison. After the bottle moulds are clamped around the parison air is blown into the parison which expands it to conform to the mould. Minimal stretching of the parison prior to clamping and the ability of the parison to expand during blow moulding is critical. The elongational flow characteristics described by the elongational viscosity, η_e, is a measure of how well the parison will resist stretching and conform to the mould during blowing. By definition

$$\eta_e = \frac{F_e/A}{\dot{\varepsilon}} \qquad (9)$$

where F_e is the elongational force applied over the cross sectional area **A** normal to the flow and $\dot{\varepsilon}$ is the rate of elongation or stretch rate (Tadmor, 1979). The measurement of η_e is difficult but it has been shown by Laun and Munstedt (1978) that at very low shear rates, where the shear flow is near Newtonian, the Trouton relationship holds for LDPE where

$$\eta_e = 3\eta(\hat{\gamma}) \qquad (10)$$

At higher shear rates Cogswell (1972) proposed that η_e is related to the shear rate, shear viscosity and entrance pressure loss, ΔP_e,

$$\eta_e = \frac{9(n+1)^2(\Delta P_e)^2}{32\eta\dot{\gamma}^2} \qquad (11)$$

and

$$\dot{\varepsilon} = \frac{4\eta\dot{\gamma}^2}{3(n+1)\Delta P_e} \qquad (12)$$

4.2.3 Viscoelasticity

The term viscoelasticity refers to the elastic recovery of a polymer after a load is applied to cause viscous creep. This phenomenon is time and temperature dependent. As a load is applied the molecules tend to disentangle and align themselves in the direction of the load. When the load is removed the molecules relax.

The time dependent stress relaxation modulus, **G(t)** is defined as the ratio of an applied shear stress, τ, to the shear strain, γ,

$$G(t) = \frac{\tau}{\gamma} \tag{13}$$

When a sinusoidal rotational shear strain is applied, as done in dynamic measurements, G is a function of the rotational speed ω and as a complex function can be decomposed

$$G(\omega) = G'(\omega) + iG''(\omega) \tag{14}$$

which results in the following complex function for the shear stress

$$\tau = \gamma\,[G'\sin(\omega t) + G''\cos(\omega t)] \tag{15}$$

The elastic or storage modulus **G'(ω)** is in phase with the applied strain and measures the mechanical energy stored during each rotation. The loss modulus **G"(ω)** is out of phase with the applied strain and measures the amount of mechanical energy dissipated per cycle. For analytical purposes both are plotted against ω as shown in Figure 4.2. Similar to the importance of elongational viscosity, viscoelasticity manifests itself in the

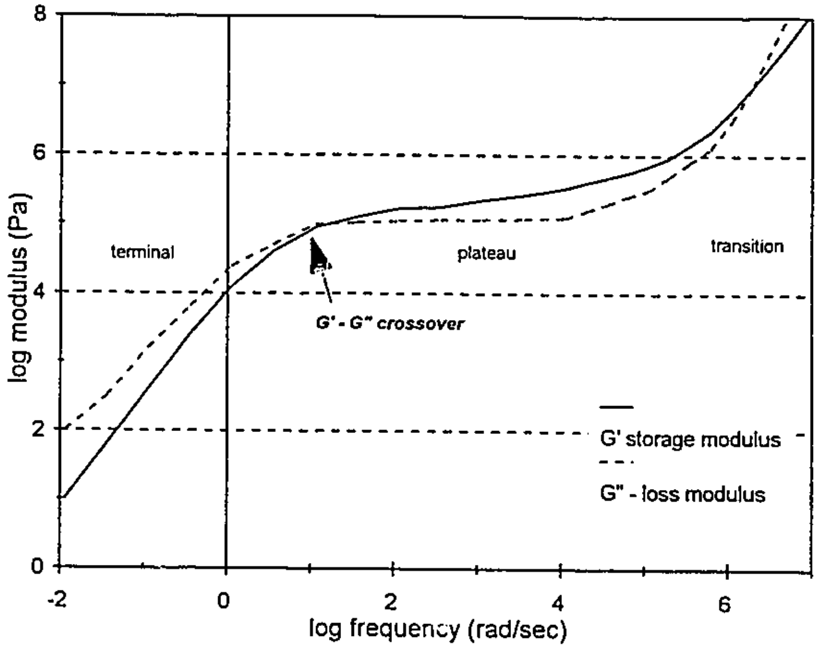


Figure 4.2: Typical viscoelastic modulus curves

behaviour of the molten polymer in the parison. Changes in swelling, due to the elastic relaxation of the polymer, can cause problems during clamping and blowing of bottles (McCrum, 1988).

The relationship between viscoelastic properties and MW characterization has been reported widely (Han, 1976). However, it has usually been in the direction of MW predicting visco-elasticity. Within the last 15 years Tuminello (1986, 1991), Yu (1992) and others have successfully used dynamic measurements to describe MW and MWD properties. More specifically, Zeichner (1982) and Shang (1993) have used the terminal zone crossover point, $G_c(\omega)$, of $G'(\omega)$ and $G''(\omega)$ to predict the polydispersity, (**PI** = $\frac{M_w}{M_n}$) of polypropylene, where

$$PI = \frac{10^6(Pa)}{G_{c(\omega)}} \tag{17}$$

at

$$G_c(\omega) = G'(\omega) = G''(\omega) \tag{18}$$

Although this technique is not widely applied to PE, similar to the work by Hinsken (1991) and Moss (1989), it was used in this study for comparison purposes. For post consumer resins this technique allows for MWD comparisons independent of the purity of the material, where pigments and residual contaminants may be present. Accuracy of measuring MW with GPC decreases with the presence of contaminants, often it cannot even be done because impurities can foul the apparatus.

4.3 Physical properties

As the molecular weight, crystalline structure and density change, strength properties and environmental stress crack resistance (ESCR) change. These physical properties are particularly important to HDPE blow moulding resins. Tensile and yield strength and elongation are used to establish design parameters such as wall thickness and any variation due to recycling could lead to costly design changes or increased material requirements. Changes in ESCR could have an effect on the shelf life of a bottle and on the type of fluids it can contain. A description of crystallinity, strength properties and ESCR follows.

4.3.1 Crystallinity

The importance of the morphological structure in terms of crystallinity cannot be overlooked in recycling. Changes in morphology incurred as a result of multiple extrusions may modify molecular movement. The ability of the molecular chains to bend and move within a polymeric structure has a direct effect on the strength and toughness of the material.

The HDPE structure is described as semi-crystalline with a combination of amorphous and thin lamellae crystals (Allen, 1983). A material with a high degree of crystallinity tends to be brittle because of the weak crystal-crystal interface. In contrast, a highly amorphous material will behave as a rubbery or glassy material depending upon its glass transition temperature. The combination of these two structures in HDPE gives it high toughness at room temperature which tends to decrease at low temperatures as it behaves more like brittle, glassy material.

The growth and size of crystals is greatly dependent on the cooling rate of the final product. Quick quenching can lead to a material with only 50% crystallinity while controlled long cooling can produce 100% crystalline material. In blow moulding the moulds are often cooled to control the amount of crystallinity. Molecular weight, in particular low molecular weight ($M_i < 5000$), also affects crystallinity. As the chains get shorter they tend to conform easier to the crystalline structure and crystallinity rises (Allen, 1983).

4.3.2 Tensile strength and elongation

The tensile strength properties of HDPE, like most materials are described by the yield tensile strength (YTS), ultimate tensile strength (UTS) and elongation. The YTS is the maximum strength HDPE will reach before plastic deformation takes place under slow loading conditions. The stress - strain relationship up to the yield point tends to be linear. Immediately after the YTS is reached and during plastic deformation strain softening and localized necking occurs. During plastic deformation as the strain increases the stress remains relatively constant and extensive elongation occurs before complete fracture occurs. The mechanism contributing to the large elongation can be attributed to the ability of the molecular chains to slip through crystalline regions and the relative easy movement of the lamellae crystals along their interface.

4.3.3 Environmental stress crack resistance (ESCR)

The definition of ESCR is given as the promotion of cracking in the presence of an environment and a stress (Williams, 1984). While the mechanism of environmental stress cracking (ESC) is not clearly understood, it is agreed that an aggressive medium tends to accelerate stress cracking. One possible explanation given by Williams suggests that under stress a microvoided zone develops at the tip of a crack. This porous region tends to have a large surface area to material volume ratio which allows for rapid diffusion of the media into the thin ligaments. It is theorized that the media plasticizes the ligaments which reduces the critical energy release rate, $\mathbf{G}_{crit}$, or stress intensity factor, $\mathbf{K}_{crit}$, necessary for fracture.

In general, for a tensile load around a crack the stress intensity

$$K = f(\sigma, a^{1/2}) \tag{19}$$

where σ is the plane stress and **a** is a crack length parameter. A critical plane-stress for failure of the polymer around the crack can be described in terms of Young's Modulus, **E**, and G_{crit}

$$\sigma_f = f(E^{1/2}, G_{crit}^{1/2}, a^{1/2}) \tag{20}$$

and

$$K_{crit} = f(\sigma_f, a^{1/2}) \tag{21}$$

or

$$K_{crit} = f(E^{1/2}, G_{crit}^{1/2}) \tag{22}$$

Under a constant load, once K_{crit} or G_{crit} is reached and a crack is initiated the crack front will propagate and K and a become time dependent,

$$K(t) = f(\sigma, a(t)^{1/2}) \tag{23}$$

or

$$\dot{a} = a(t) = f(\sigma, K(t)^2) \tag{24}$$

The fracture surface of PE appears to be microscopically ductile with small cusps. The cusps appear to nucleate from microvoids. The semi-crystalline morphology and presence of particulates, in terms of catalyst residues and additives, in PE are thought to contribute to the presence of microvoids.

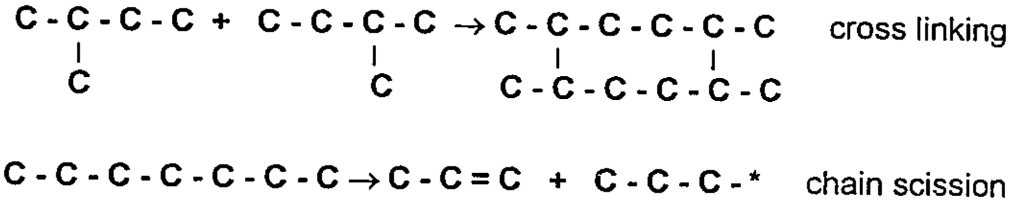
When aggressive media is introduced the relationships are modified to account for the diffusion of the media. Darcy's law for diffusion in a porous material is used to describe the rate of flow, $\dot{u}$, of the media in the crack zone in terms of the pore area, $\mathbf{A}_p$, fluid viscosity, η_f, and pressure gradient, dp/dx, of the fluid

$$\dot{u} = f(A_p, 1/\eta_f, dp/dx) \tag{25}$$

The pore area, determined by the amount of material that is exposed during fracture, is relatively small and will not vary with time. However, it will vary with the presence of microvoids. As the crack propagates the media will continue to difuse through the microvoids and into the ligaments. This leads to a complementary relationship of diffusion to crack propagation. Increasing MW and some short chain branching enhance ESCR properties (Mctigue, 1959). The longer molecules and short chains tend to create a more rigid structure with some entanglement which resists cracking. They also tend to resist attack from the aggressive medium by reducing the opportunity for porous regions. This would explain the differences between the ESCR properties of a copolymer with some short chain branching and higher MW and a homopolymer with little or no branching.

4.4 Degradation of high density polyethylene

The presence of degradation is detected on a macroscopic level through changes in processability, such as back pressure or physical characteristics, such as colour and tensile properties. In general, degradation represents a modification of the molecular structure of the entire polymer due to exposure to heat, oxygen, UV light, chemical attack or mechanical forces. During processing, linear polymers such as PE, degradation can manifest itself by altering the chain length and branching along the backbone structure. Shear and temperature induced changes, in the presence of oxygen, during multiple extrusions can cause thermal/ oxidative or thermal/mechanical degradation which can lead to cross-linking or chain scission (Kelen, 1983, LaMantia, 1989).



$$\mathrm{C-\underset{\underset{C}{|}}{C}-C-C + C-C-\underset{\underset{C}{|}}{C}-C \rightarrow \begin{array}{ccccccccccc} C&-&C&-&C&-&C&-&C&-&C\\ &&|&&&&&&|&&\\ C&-&C&-&C&-&C&-&C&-&C\end{array}} \quad \text{cross linking}$$

$$\mathrm{C-C-C-C-C-C-C \rightarrow C-C=C + C-C-C-{}^{*}} \quad \text{chain scission}$$

Figure 4.3: Degradation mechanisms

Both events depicted in Figure 4.3 are competitive and occur simultaneously, to varying degrees. Cross linking is best described as a recombination of radicals which leads to an increase in chain length or branching.

Chain scission occurs from thermally induced oxidative reactions or from the combined thermal/mechanical separation of carbon-carbon bonds causing a reduction in molecular length or branching. Chain scission can change the tendency for failure from ductile yielding to brittle fracture and crack propagation. This results from higher crystallinity at lower molecular weights.

The degree of branching can have an effect on processing. In a study of LDPE, it has been shown by Hamielec and Vlachopoulos(1983) that increasing long chain branches can change the melt flow characteristics. When considering the mechanisms and possible outcomes of degradation, their work could provide some insight into the rheological changes observed during recycling particularly if significant changes in branching occur.

Degradation from UV exposure results from photo-oxidation reactions occuring as a result of absorption of UV radiation initiating the production of radicals. Degradation due to chemical attack is a complex process in terms of opportunity for chemical reaction, diffusion and concentration. In most cases it involves a catalytic reaction which results in either chain scission or cross linking.

4.4.1 Changes in properties with multiple extrusions

The effects of degradation can be highly interactive on the melt flow and physical characteristics of a polyolefin. In terms of molecular structure and depending on the catalyst system, the average molecular weight (MW) may increase or decrease and the distribution (MWD) may narrow or broaden with multiple extrusions. It has been shown that a Phillips based HDPE (Cr catalyst) increases in MW and decreases in melt flow index (MFI) with multiple passes through an extruder at elevated temperatures. In contrast a Ziegler based HDPE (Ti catalyst) produces the opposite effect (Moss, 1989). It has also been shown that changes in MWD and branching affect elastic properties and would appear as a change in swell characteristics (Fleissner, 1973).

The efficiency of the original polymerization process also contributes to molecular changes during extrusion (Dole, 1958). The level of unsaturation in the virgin polymer will have a direct relationship with the change in branching along the polymer chain. Vinyl groups which are present after polymerization is terminated will react with unsaturated groups along the backbone chain and form branches. With each extrusion pass the number of vinyl groups should decrease as they become absorbed into the chains. This type of modification tends to occur within a very few number of extrusion passes. The combined effects of multiple extrusions and in service use, in terms of ageing, on LDPE has also been investigated and it has been shown that the combination appears to have a greater effect than extrusion alone (Boldizar, 1993).

In general, the direction of research into multiple extrusions at the time of the start of this study, and which still prevails today, involved the investigation of specific properties of HDPE. The foregoing discussion demonstrates the complexities of the recycling system and the highly interdependent nature of the process and the change in polymer properties. This research is the first of its kind that attempts to examine the resin property system as a single entity and the technique used in this study, principal component analysis (PCA), is described in the next chapter.

Chapter 5 - Design and Analysis of Experiment

5.1 Planning the experiment

In order to take advantage of the properties recycled polymeric materials can offer, a systematic research approach, incorporating multivariate analysis, is necessary to demonstrate the effects reprocessing may have on the materials. In the development of a research strategy to study changes in a polymer, the interaction of experimental parameters and the correlation of the response variables can not be overlooked. If some statistically based methodology is used, a level of confidence can be established for the performance characteristics of a product which uses reclaimed material and proper statistical process control (SPC) can be applied to the manufacturing process.

An objective of this thesis was to develop and test an experimental and analytical methodology that is appropriate to the broad study of plastics recycling. In this chapter a complete description of the experimental methodology, including the planning, assumptions, use of equipment and data analysis techniques is given.

5.2 The application of quality improvement tools

The phrase "quality improvement" used by Phillip Crosby was an outcome of the explosion of the quality industry in the late 1970's (Goetsch, 1994). Experts in the field such as the late Edwards Deming, Joseph Juran and others are associated with their own versions of managing and improving quality. Regardless of the slogans, all focus on process improvement to minimize waste by minimizing defects and this has a direct application to recycling HDPE. As confidence grows with quality improvements in HDPE PCR, waste will be minimized.

Within the quality improvement process there exists an arsenal of tools to aid in problem solving. The list of tools include: process flow diagrams; cause and effect diagrams; control chart; checksheets; pareto diagrams; histograms; scatter plots; design of experiments (DOE) (Montgomery, 1991). A flowchart for the application of these tools is shown in Figure 5.1. Each tool has a specific purpose and they are used as needed. Process flow diagrams, cause and effect diagram, scatter plots and DOE have been incorporated into this study.

5.3 Designed experiments and statistical analysis

Statistically designed experiments are a series of strategically designed runs where systematic changes are made to controllable variables

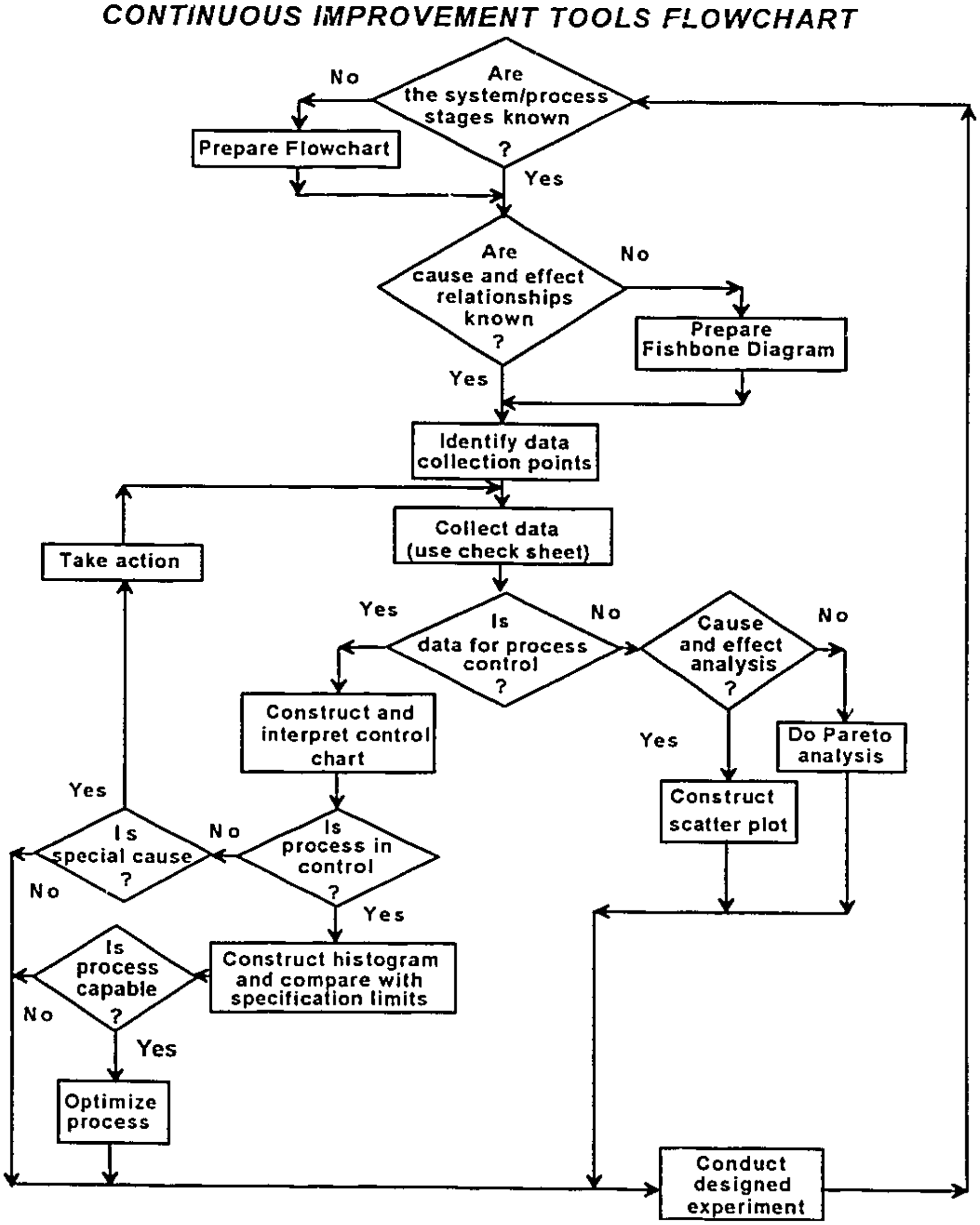


Figure 5.1: Flowchart for problem solving tools

to observe changes in output variables. The statistical tool hypothesis testing is used in these experiments as a means of determining the significance of the observed changes. This type of analysis accounts for the natural variability of the system relative to the variability associated with the observed changes (Box, 1978). Controllable variables are called factors and output variables are referred to as responses. The resulting change on a response from a change in a factor or combination of factors is called an effect.

5.3.1 Factorial Experiments

One of the best tools available to develop the largest experimental database possible is the factorial designed experiment. Variations such as fractional factorials, Taguchi designs, Latin Squares or Plackett-Burman designs, like full factorials, are based on some form of analysis of variance (ANOVA). The efficiency of these designs has been exhaustively presented in all fields of scientific research. In comparison to one-at-a-time experimentation, using ANOVA in a designed experiment is effective in studying scientifically based interactions between factors (Montgomery, 1991). The contribution of interactions to the response of a system often are neglected. The nature of the factorial design allows interactions to be analyzed and statistically based decisions to be made on their level of contribution to changes in a response. Factorial experiments integrated into a response surface analysis also provide a systematic and efficient means of optimization, especially with systems described by higher order mathematical models.(Adewole, 1994) The extrusion and recycling systems with their inherently high number of factors and responses are ideal for factorial experiments.

5.3.2 Principal component analysis

Where factorial experiments allow for the analysis of relationships between controllable factors alone, some form of multivariate analysis must be used to study the nature of the relationships between all factors and responses. This is particularly significant with systems that have a large number of response variables. Consider the relationship between the number of response variables and the risk associated with rejecting a null hypothesis of no significant difference between treatment means (type I error). If the predetermined level of significance for a one factor study is,

$$\begin{aligned}\alpha &= 1 - 0.95^1 \\ &= 0.05\end{aligned}$$

5% of the time a decision of no significant difference is rejected. It has been suggested by Stahle (1988) that, as more responses are added to the analysis the level of the risk increases with the power of the number of responses. Then, for a 2 factor study,

$$\begin{aligned}\alpha &= 1 - 0.95^2 \\ &= 0.0975\end{aligned}$$

With 10 responses the true level of significance becomes 40%. The risk of missing any significant differences, due to correlation, increases dramatically. In contrast, multivariate analysis, considers all variables together and takes advantage of the covariance or correlation in the analysis.

Principal component analysis (PCA) is one form of multivariate analysis where a set of related variables is reduced to a potentially smaller set of uncorrelated variables (Jackson, 1991). The development of PCA can be traced to earlier 1900 but the first real applications appeared in the 1930's and 1940's. The large number of mathematical transformations associated with the procedure precluded any application to problems with a large number of variables. As computers evolved a greater number of applications used PCA and the algorithms and techniques were refined. There is no evidence to date that PCA has been applied to the recycling of plastics.

The essence of PCA is that if 2 variables are correlated one predictive equation can be developed such that prediction of one variable with another can be accomplished in either direction. The equations are obtained by transforming the factors and associated observed responses. Transformation is achieved through a series of manipulations of the covariance **[S]** or correlation **[R]** matrix,

$$S = \begin{bmatrix} s_1^2 & s_{12} & \cdots & s_{1p} \\ s_{12} & s_2^2 & \cdots & s_{2p} \\ & & & \\ s_{1p} & s_{2p} & \cdots & s_p^2 \end{bmatrix} \tag{26}$$

$$R = \begin{bmatrix} 1 & \rho_{12} & \cdots & \rho_{1p} \\ \rho_{12} & 1 & \cdots & \rho_{2p} \\ & & & \\ \rho_{1p} & \rho_{2p} & \cdots & 1 \end{bmatrix} \tag{27}$$

where s^2_i is the variance and of the ith variable and s_{ij} and ρ_{ij} are the covariance and correlation between the ith and jth variables and

$$\rho_{ij} = \frac{s_{ij}}{s_i s_j} \tag{28}$$

With this technique, a principal axis transformation takes the p correlated variables and transforms them into p uncorrelated variables. This is achieved by using an orthonormal matrix **U** to reduce **S** to a diagonal matrix **L**, where

$$U'SU = L \tag{29}$$

The diagonal elements of **L** are the Eigenvalues or characteristic roots of **S** and the columns of **U** are the Eigenvectors or characteristic vectors of **S**. The characteristic vectors represent the direction cosines used to rotate the original principal co-ordinate axis about the means of the 2 correlated variables. The variables are transformed to a new set of principal axes and are referred to as principal components (PC). The actual observed values are also transformed and are referred to as t or z scores. A property of the characteristic roots is that they are the variances of the principal components and when summed together they equal the sum of the variances of the original variables.

Once the process is completed, the resultant transformed variables are analyzed in terms of cluster analysis. A plot of the PC's identifies which variables, in terms of their magnitude, contribute most to the transformed variables and a plot of the scores identifies any trends or tendencies exclusive of any correlation which have been taken into account by the transformation process.

5.4 Selection of variables

Referring back to Chapter 4, in particular the discussion on the effect of multiple extrusion in section 4.4.1, some research on almost all aspects of virgin HDPE has been done including studies on molecular synthesis and catalyst systems, reactor kinetics and modelling, reactor control systems and optimization, modelling of extrusion, degradation and polymer modification. In terms of recycled HDPE research has been limited to polymer modification with additives (compatibilizers), separation systems and commingled systems.

5.4.1 Application of the cause and effect diagram

In order to gain information on the scope of the possible causes contributing to the effect of changes in HDPE during recycling, a cause and effect diagram or fishbone chart was developed and is shown in Figure 5.2 (Ishikawa, 1980).

The number of possible factors that could be barriers to the acceptance of recycled HDPE in primary applications is quite large and the C&E diagram illustrates the complexity of the problem. However, the diagram was quite useful in narrowing down the selection of the control variables or factors to be studied.

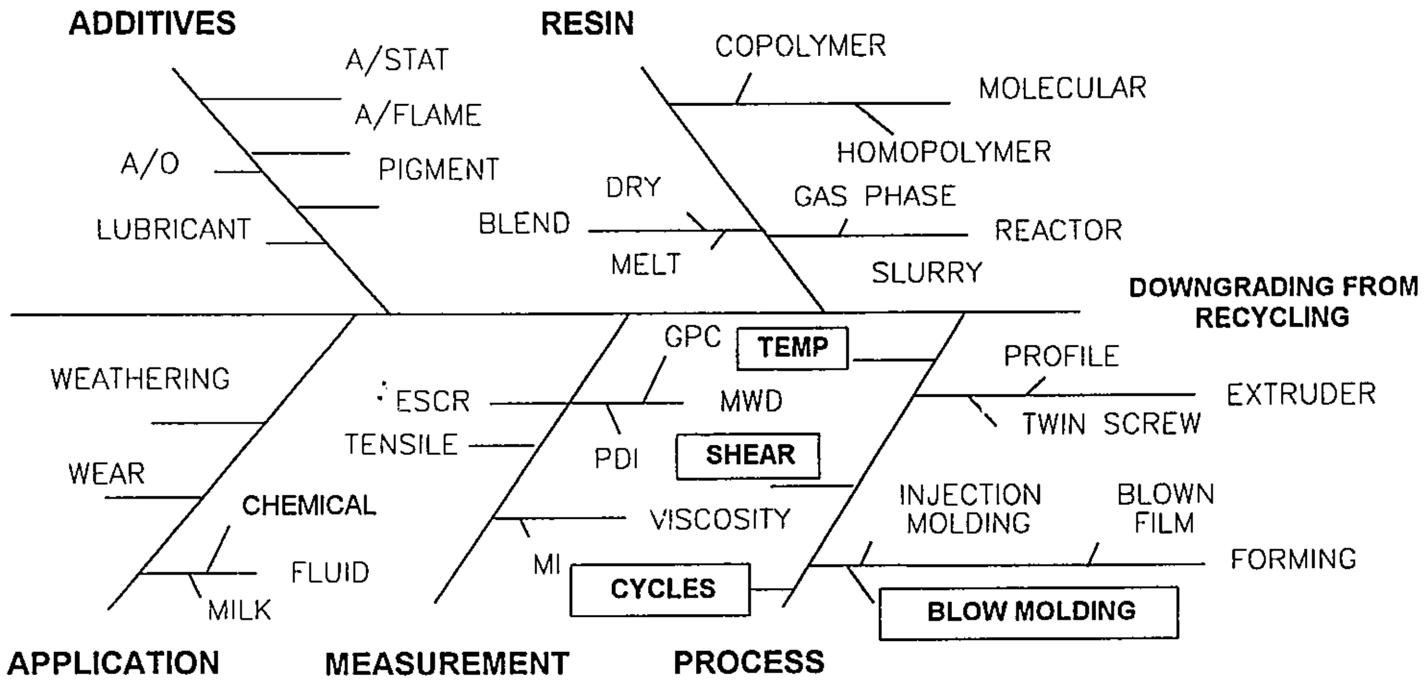


Figure 5.2: Downgrading from recycling cause and effect diagram

5.4.2 Selection of factors and levels

The factors chosen for study fell into 3 categories: time, process and material. The time factor was studied in terms of the number of extrusion cycles/passes and was different for 2 sets of experiments. In the first set 8 passes were studied and after those results were analysed it was decided to reduce the number of passes to 4 for the second set. A practical justification in the reduction of the number of passes for the second set in relation to the current state of HDPE recycling was described in section 3.5.

The process factors selected for study were extrusion shear rate and melt temperature. These were varied only for the first set. The levels of shear rate were controlled entirely by changing the screw speed on the extruder, and the level of the barrel temperature was controlled with the temperature controllers on the extruder.

The broad category of HDPE blow moulded bottle resin was broken down into the matrix of attributes described in Table 5.1:

Table 5.1 Categories of resins studied

		polymer type	
		homopolymer	copolymer
source	virgin (from reactor)	x	x
	post consumer	x (natural)	x (mixed colour)

The virgin homopolymer was a 0.7 MI, 0.960 g/cc resin, LM6007 from QUANTUM Chemical and the virgin copolymer was a 0.32 MI, 0.960 g/cc resin, 32060C from DOW Chemical Canada. The post consumer resins were from Resource Plastics, Brantford, Ontario, Canada. The categories of the PCR material were natural PCR and mixed colour PCR. The natural PCR came from the unpigmented bottle post consumer stream and is marketed has having similar properties to a homopolymer HPDE blow moulding resin. The mixed colour bottle resin came from a pigmented bottle stream and was marketed as having copolymer material as its primary constituent. The first set of experiments used only the virgin homopolymer, while the second set of experiments examined the effects of multiple extrusions on all 4 combinations of resins.

Neither a compatibility study of the PCR material with the virgin material nor a comparative field trial performance evaluation between the resins was done. That type of analysis has been reported by other researchers (Gibbs, 1990). This work focused specifically on the effects of multiple extrusions and was primarily a screening experiment done to identify those properties which were sensitive to the effects of multiple extrusions. This is significant to recycling because the properties most sensitive to the effects of multiple extrusions can be used to guide the design of useful products which incorporate some recycled resin. The materials were drawn from a single lot of production, from each supplier. While lot to lot variation is expected during the production of all materials, this was not considered in this study. It was assumed that while specific properties vary within a product specification range, the general characteristics for a specific resin will change very little.

5.4.3 Selection of measurable responses

The following criteria was used in the selection of the response variables. First, the responses either are already used in or could be easily incorporated into an SPC system. Second, the collective group of responses should in some way describe any changes to all of the fundamental characteristics of an HDPE resin including molecular, processability, physical and extrusion. In table 5.2 the general group of

Table 5.2 Categories of properties studied

Response type	Analytical Tool
molecular	DSC, polydispersity index
processability	viscosity, swell, viscoelasticity
extrusion	extruder output, back pressure, sag
strength	yield and ultimate strength, elongation, ESCR

responses are given. Finally, waste reduction was a priority and a minimal amount of the material used was to be disposed as solid waste. When scrap was generated it was set aside as purge material for other research projects or returned to a recycling facility.

5.5 Experimental procedure

The experimental work reported on in this thesis was broken down into 2 sets of factorial experiments. The first set studied the effect of shear, temperature, polymer type and extrusion passes on viscosity, swell and physical properties. The second set examined the effect of polymer types, resin sources and extrusion passes on viscosity, viscoelasticity, molecular weight, crystallinity and ESCR.

In both sets, continuous extrusion was done, without any form of blending or addition of stabilizers, through a 25 mm, 24:1 L/D, Brampton Engineering single screw extruder. The melt was drawn through a low pressure 12.5 mm die and was air cooled into a strand using a twin roller take-off system (Figure 5.3). After each pass through the extruder the strands were chopped in a knife mill to an average particle size of < 9 mm (Figure 5.4). Roughly 600 g of polymer was retained after each pass for analysis. The material was loosely stored and the extrusion runs were

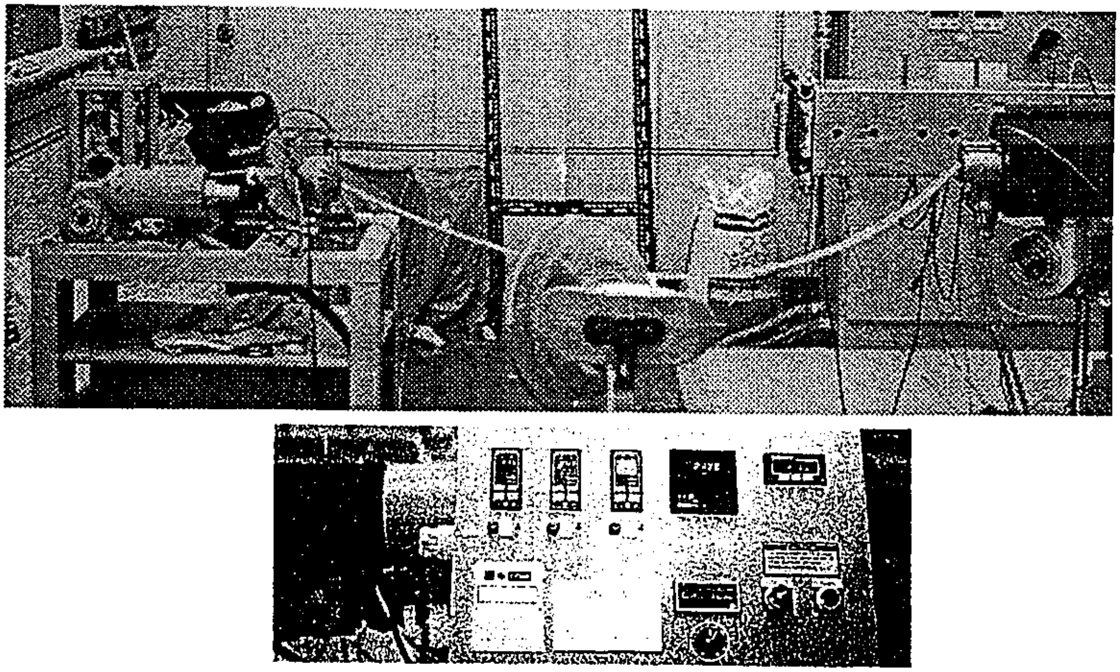
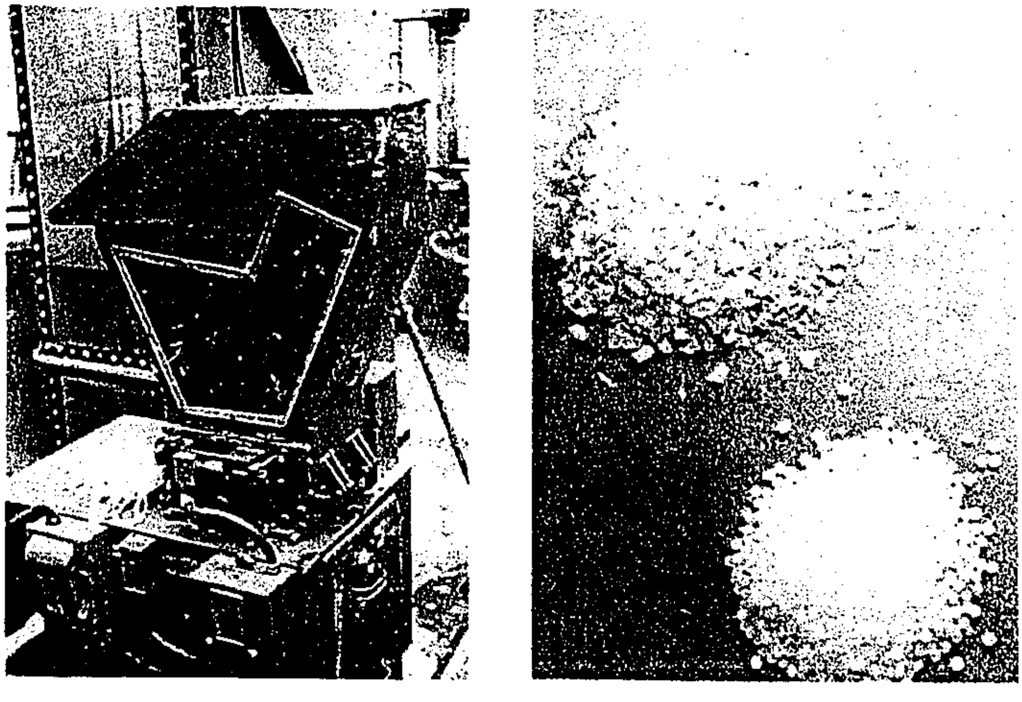


Figure 5.3: Extrusion and take off system



a) knife mill b) pellets and shredded strands

Figure 5.4: Shredding system

done within a one week period. The only attempt to randomize the experiment was to vary the order of the resins that were extruded on any given day.

5.5.1 Studying the effects of shear, temperature and polymer type

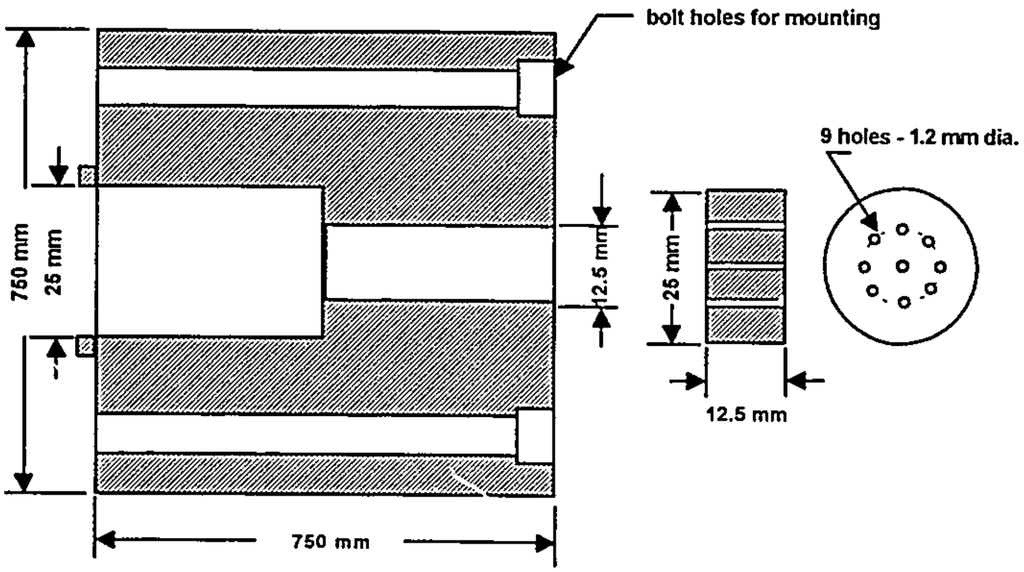
A 2x2x4 factorial experiment was planned for this study with the factors and operating levels described in Table 5.3.

Table 5.3 Operating levels set 1

Factor	Levels	Units
extrusion shear rate	8 470	s^{-1}
melt temperature	190 240	° C
extrusion cycles analyzed	0 1 4 8	

To achieve the extrusion shear rates in Table 5.3, extruder speeds of 60 and 70 rpm, were used with and without a breaker plate (Figure 5.5). The calculations for the shear rates are given in Table A-1 and they ranged from 8 s^{-1} to 460 s^{-1}.

It was assumed that a completely randomized experiment for all factors would not be practical. Therefore, the runs were randomized only within each set of extrusion passes so as to minimize storage problems.



a) die design b) breaker plate design

Figure 5.5: Die and breaker plate design

Essentially the experiment was blocked by the extrusion cycles.

Processing conditions, including extruder pressure and melt temperature at the die wall, were monitored throughout each run. After each run a purge was done using scrap HDPE for at least 5 minutes. The five minute time period was arrived at through previous work on the residence time for HDPE in the Brampton extruder. During the purge the temperature, speed and die configuration were changed for the next run. After the purge the next material to be studied was introduced and was run until the die wall temperature and extruder pressure stabilized. The Brampton extruder was considered stable when the temperature variance was less than 2°C and the pressure range was less than 5% of the mean.

Output measurements for each run were made by weighing a sample of resin melt collected over a 2 minute period. As the quantity of resin decreased after each pass because of retention for analysis, the number of output measurements for each run also decreased. At least 2 output measurements were made for each experimental run.

Material related responses were analyzed on the virgin resin (0 passes) and after 1,4 and 8 extrusion passes. Swell and viscosity measurements, at 4 shear rates, were done using a constant rate Instron Capillary Rheometer, following ASTM D3835-79, D = 31 mm, L/D = 24:1. The shear rate measurements were corrected with the Rabinowitsch correction factor, equation (30), to obtain the shear rate at the wall (Rabinowitsch, 1929).

$$\dot{\gamma}_{true} = \frac{4Q}{\pi R^3}\frac{(3n+1)}{4n} \tag{30}$$

The power law model (equation 8) was fit to the viscosity data for each combination of the factors and levels. The viscosity at each shear rate and the parameters m and n derived from the viscosity curves were all considered as response variables.

The swell measurements were done by taking the ratio of the extrudate diameter to the capillary diameter. At least 3 samples, 30 - 50 mm in length, were cut from the capillary strand at the die exit. The short strands were kept vertical and rapidly quenched in water at room temperature. They were checked for roundness before the diameter was measured approximately 15 mm from the leading end of the strand.

Tensile properties were measured in accordance with ASTM D638-90. Dog bone specimens were injection moulded. A Lloyd Instruments Materials Testing Machine was used to pull the specimens.

5.5.2 Studying the effects of polymer type and resin source

A 2^3 factorial experiment was planned for the second set of experiments with the factors and operating levels described in Table 5.4.

Table 5.4 Operating levels experimental set 2

Factor	Levels	
extrusion cycles analyzed	0	4
polymer type	copolymer	homopolymer
polymer source	virgin	PCR

With knowledge from the first set of experiments, the processing conditions for the second set were fixed at 80 rpm and 215 °C. Using the breaker plate described in section 5.5.1, shear rates were anticipated to be approximately 560 s^{-1}. Of course it is also known that a small amount of leakage will occur over the screw flight and the small amount of polymer that does pass in the gap between the barrel and screw flight is sheared at even higher shear rates. However, it is virtually impossible to assess the exact level of the maximum shear rate. The shear rate estimated through the breaker plate was higher than the value for first set because at the higher temperature the speed could be increased until the pressure limitation on the extruder was reached. The combination of 190°C and 70 rpm, with the breaker plate, used during the first set reached the same pressure limitation. The temperature chosen for this set was based on recommendations from the suppliers and was also the average of the high and low levels from the first set of runs.

Since there was little evidence from the first set of experiments to show any significant changes in tensile strength properties, they were not studied for the second set. The properties studied were the viscosity, swell, viscoelasticity, elongational viscosity, crystallinity and ESCR. As in set 1, melt temperature, extruder pressure and output were also measured.

The viscosity and swell measurements were done as in section 5.5.1. The Rabinowitsch correction factor was again applied. The Bagley correction factor, n_B, was also used in this set to obtain the true shear stress, τ_w (Bagley, 1957).

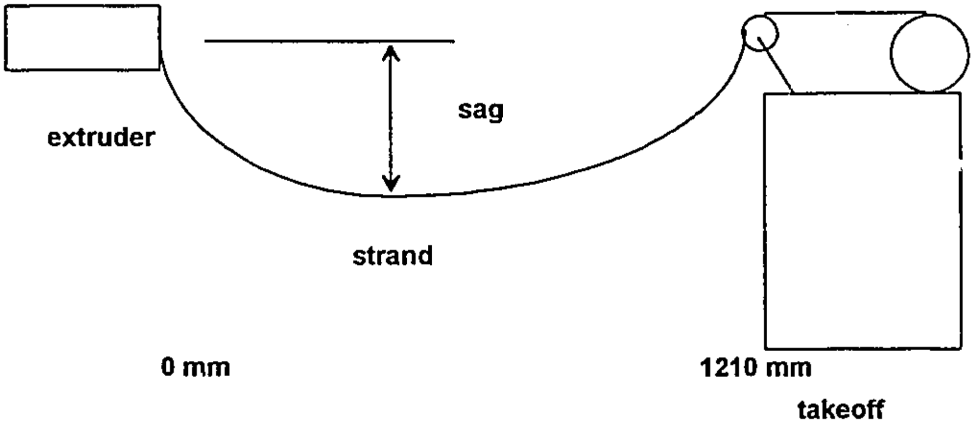
$$\tau_W = \frac{\Delta P}{2(\frac{L}{R} + n_B)} \tag{31}$$

In addition to studying the shear viscosity properties, a study of the elongational viscosity was also done in the second set of experiments. In section 4.2.4 the relationship between elongational viscosity and the capillary entrance pressure drop was shown (equations 11,12). The pressure drop at the capillary entrance, ΔP_e, can be determined by using τ_w, where

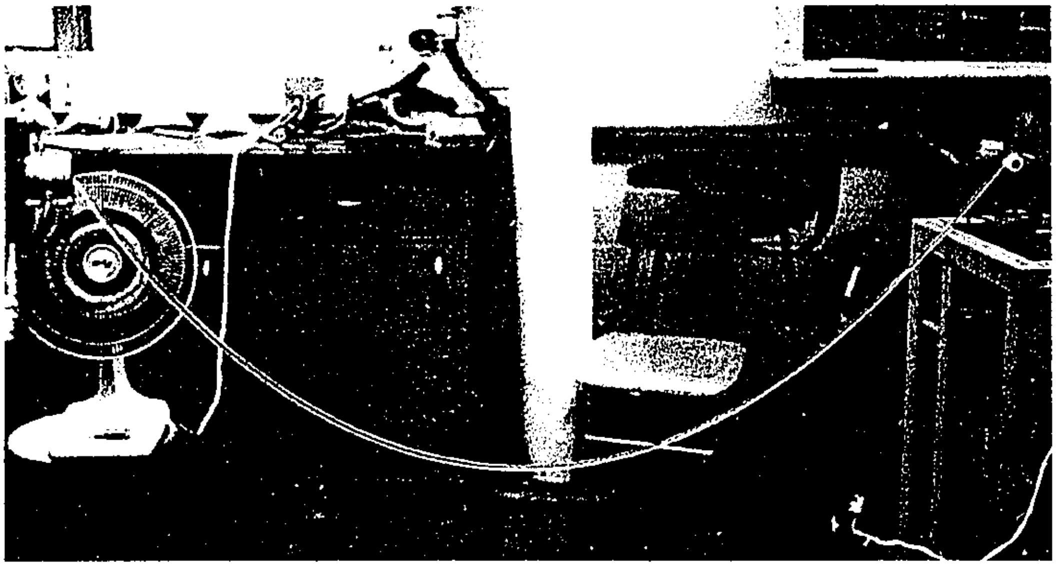
$$\Delta P_e = 2\tau_W n_B \tag{32}$$

During preliminary testing, from the extruder die exit to the take off rollers there was a significant difference in the extrudate sag characteristics between the different polymer types and sources. A crude sag measurement was designed to quantify these differences. The amount of sag was determined by measuring the height from the level floor to the extrudate strand at 410, 610, 810, 1010 and 1210 mm from the die exit to the take off rollers (Figure 5.6).

The dynamic viscosity measurements were done using a plate on plate configuration on a BOHLIN VOR Rheometer System. The plates



a) schematic of sag measurement



b) actual observation

Figure 5.6: Description of sag measurement

were 25.4 mm in diameter and were set at a gap of 1 mm. All samples were measured at 190°C over a frequency sweep of 0.6 rad/s to 126 rad/s. Storage and loss modulus curves, polydispersity indices (equation 17) and an estimate of the zero shear viscosity were analyzed.

Crystallinity was measured with a DuPont 2000 differential scanning calorimeter. Each sample was subjected to a 2 stage heating process. The first stage heated the sample to 190 °C at a rate of 10 °C /min. This was done to remove any inconsistencies between samples in terms of cooling histories. The samples were then cooled at a rate of 5 °C /min to room temperature. The second stage was a repeat of the first stage heat up cycle. The melt temperature, maximum peak temperature, maximum endothermic heat flow and percent crystallinity are determined with the aid of software directly integrated with the DSC.

The ESCR properties were determined in accordance with ASTM D1693-80 using condition B. Plaques 75x125 mm and 1.75 - 2.00 mm thick were compression moulded at 190°C. Approximately 5 specimens were punched from each plaque and notched. Ten specimens for each retained sample were mounted as bent strips and placed in a 100% IGEPAL CO-630 solution in individual test tubes and held at 50°C in a 2 l beaker of water (Figure 5.7). The specimens were monitored for failure which was determined to be the time where crack initiation was first observed. The observation interval varied from every 10 minutes for the first 100 min to every hour thereafter. The F50 point or 50% failure point, was determined to be the median failure value for the 10 specimens.

For both sets of experiments all responses measured had between 2 and 5 replicates to obtain a measure of the variance in the data. Any unusual observations which could be explained by a special cause were noted and the data excluded from further analysis. Further transformations or manipulations of data specific to particular responses will be discussed in the next chapter.

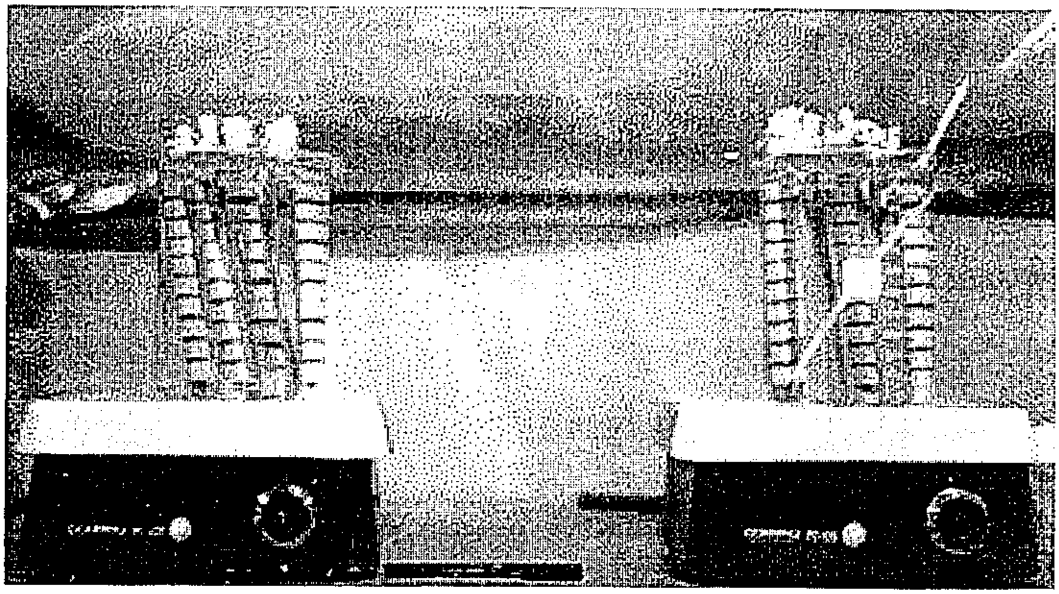


Figure 5.7: ESCR setup

Chapter 6 - Experimental Results

Consistent with the separation of this work into 2 separate sets of experiments, the following presentation of the results is also divided into 2 parts. A summary of the detailed calculations not referenced to equations previously defined or not described in ASTM standards are presented in Appendix-A. The raw and transformed data is summarized in Appendix-B. Graphs summarizing the data are presented directly in this chapter. There were no replicates of experimental runs but the measurement for each response was repeated at least twice and in most cases 5 times. This was done to obtain a measure of the measurement system variance. In the following presentation of the results only average values for each response are considered and responses with large within measurement variances are noted.

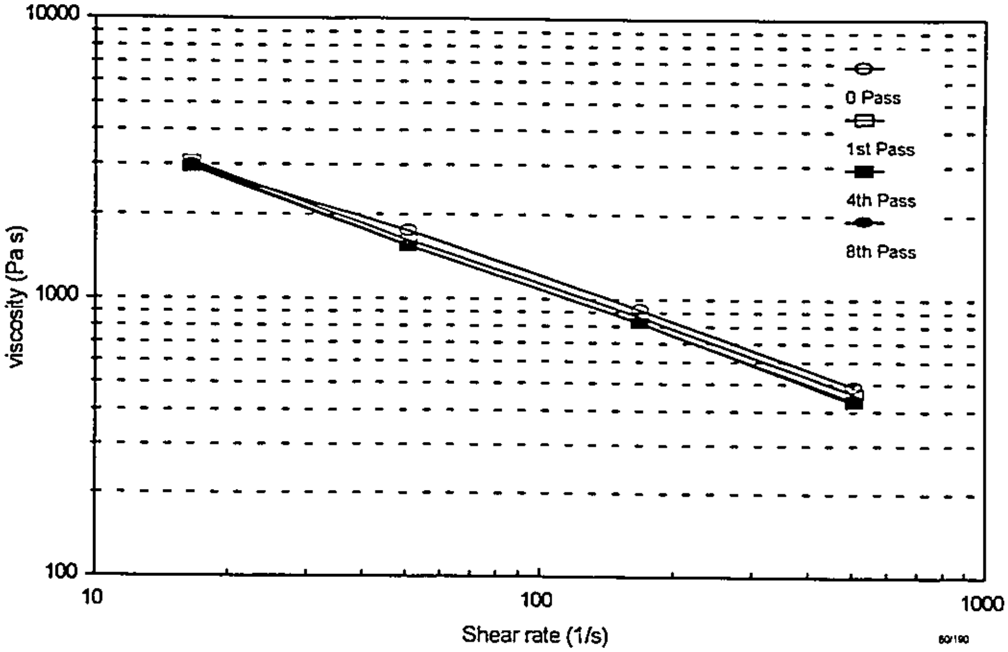
6.1 Results of experimental set 1

The extrusion runs were done over a 2 week period. The responses fall into 4 general material property categories: viscosity, swell, tensile strength and extrusion. Within the categories, general trends or observed changes in specific parameters are described. Any special observations or detailed information about a specific test procedure are also presented.

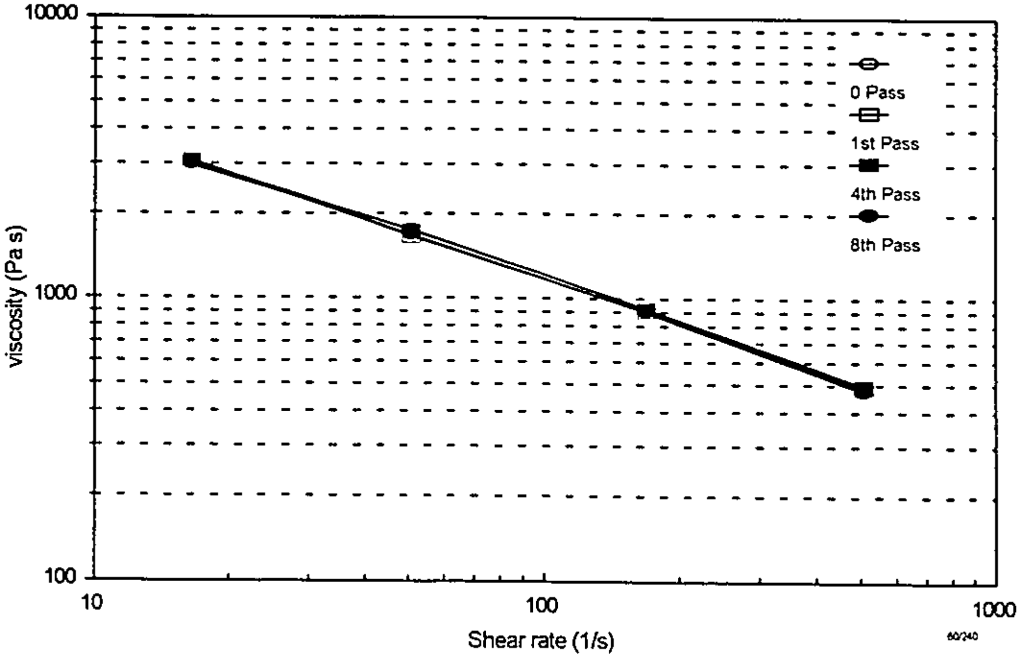
6.1.1 Changes in viscosity

The viscosity curves for the 4 extruder temperature/speed combinations are shown in Figure 6.1. The data used to develop the curves are presented in Table B-1. All of the measurements were made using a capillary rheometer, as described in section 5.5.1, with a capillary die L/D ratio of 24:1 and incorporating the Rabinowitsch correction factor (eq. 30). From the curves, at all combinations of extrusion temperature and shear rate there is no discernible difference from 0 to 8 passes.

The viscosity curves shown in Figure 6.1 allow for the analysis of macroscopic viscosity characteristics such as the non-Newtonian behaviour of polymers. At specific shear rates, a viscosity curve may not provide sufficient resolution to identify subtle differences in viscosity, especially from the effect of multiple passes. A possible remedy for this weakness is the development of a time based plot. In Figure 6.2, a plot of the viscosity versus extrusion passes, at 4 shear rates, is shown. From this graph there is some variation in the viscosity at the low shear rates (Rabinowitsch corrected from 10 to 17 s^{-1}).

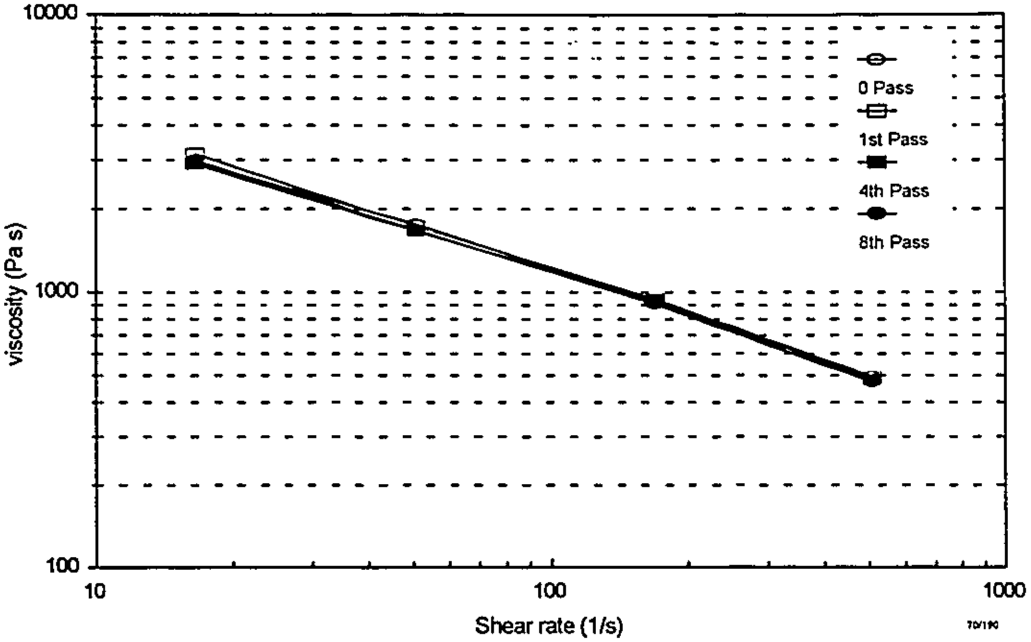


a) 60 rpm, 190 °C

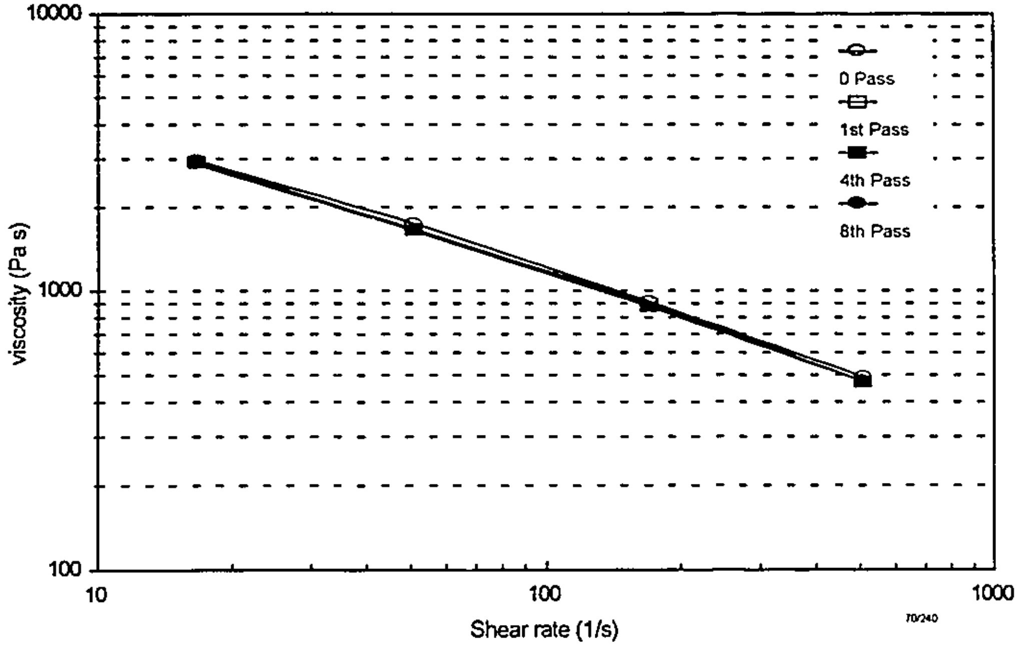


b) 60 rpm, 240 °C

Figure 6.1: Viscosity curves experiment set 1



c) 70 rpm, 190 °C



d) 70 rpm, 240 °C

Figure 6.1 (cont.): Viscosity curves experiment set 1

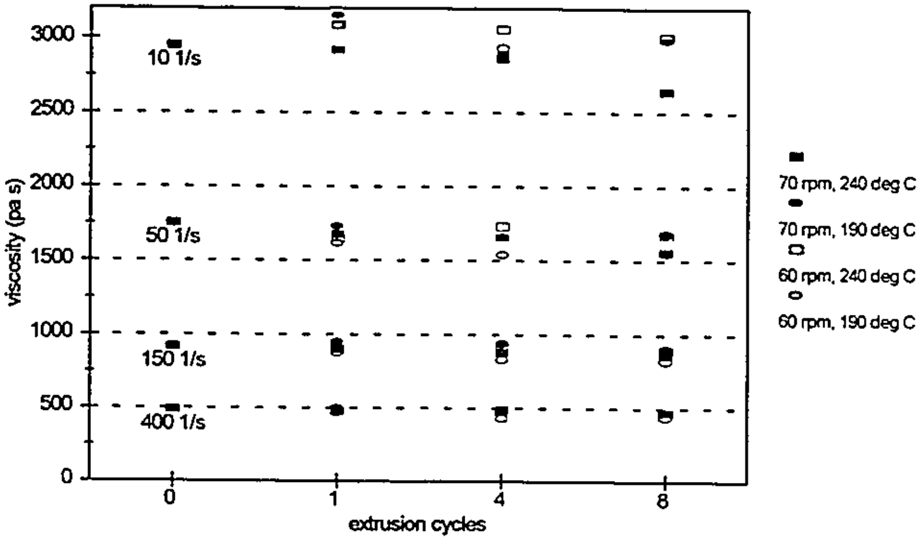
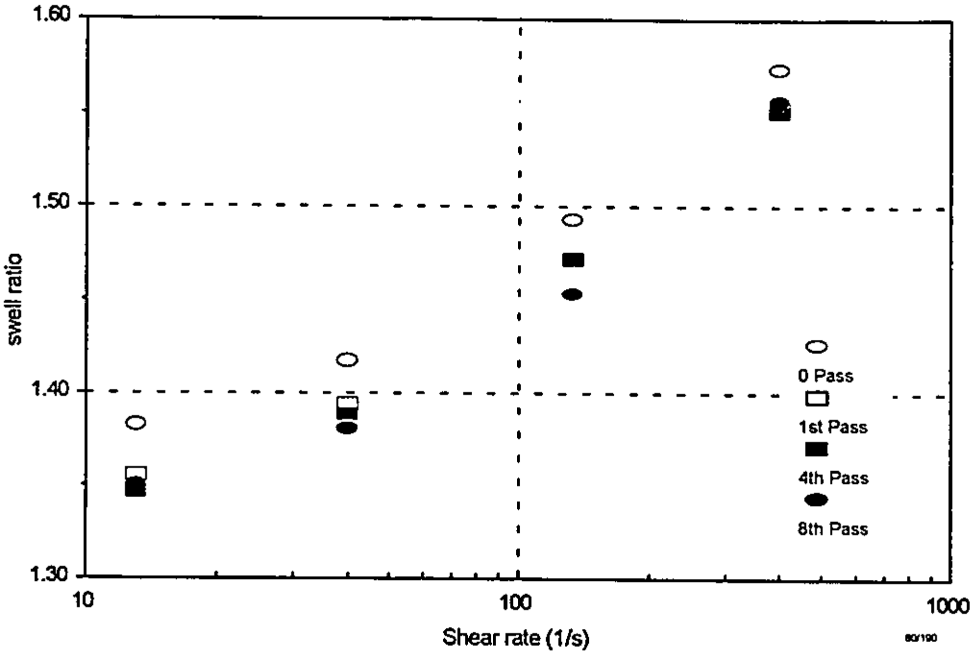


Figure 6.2: Plot of viscosity versus cycles at 10, 50, 150, 400 s^{-1} (uncorrected)

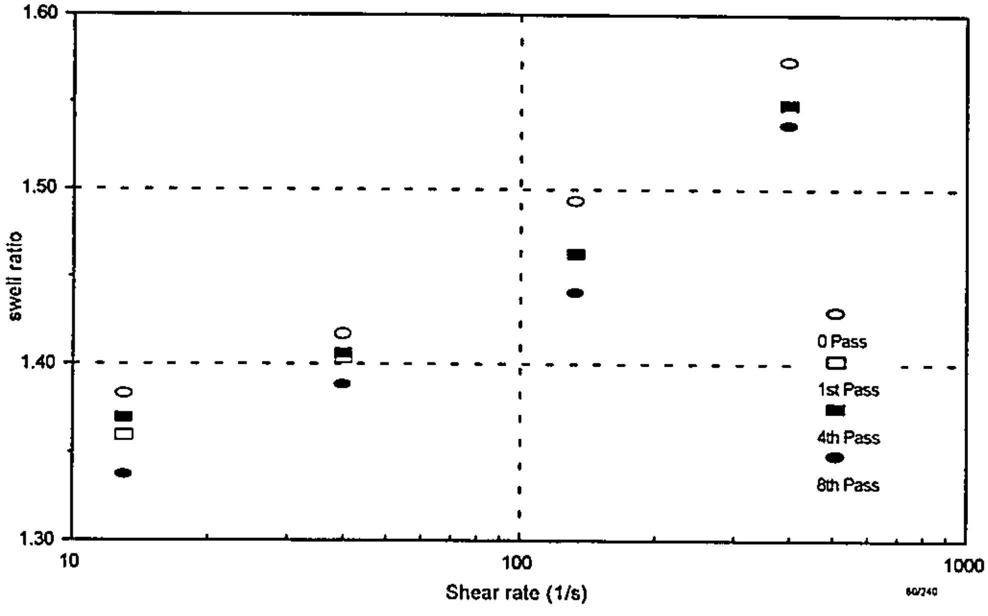
The viscosity at the lower shear rate and under severe extrusion conditions (70 rpm, 240 °C) is slightly lower than the viscosity for the other combinations especially at 8 passes.

6.1.2 Changes in swell characteristics

Swell measurements were made using the technique described in section 5.5.1, with a capillary die L/D = 24:1. The raw data are summarized in Table B-2 and shown graphically in Figures 6.3 a) to d) where the swell ratio is plotted against the corrected capillary shear rate. For all combinations of extrusion speed and temperature the swell ratio increases with shear rate and decreases from the 0 to the 8 pass state.

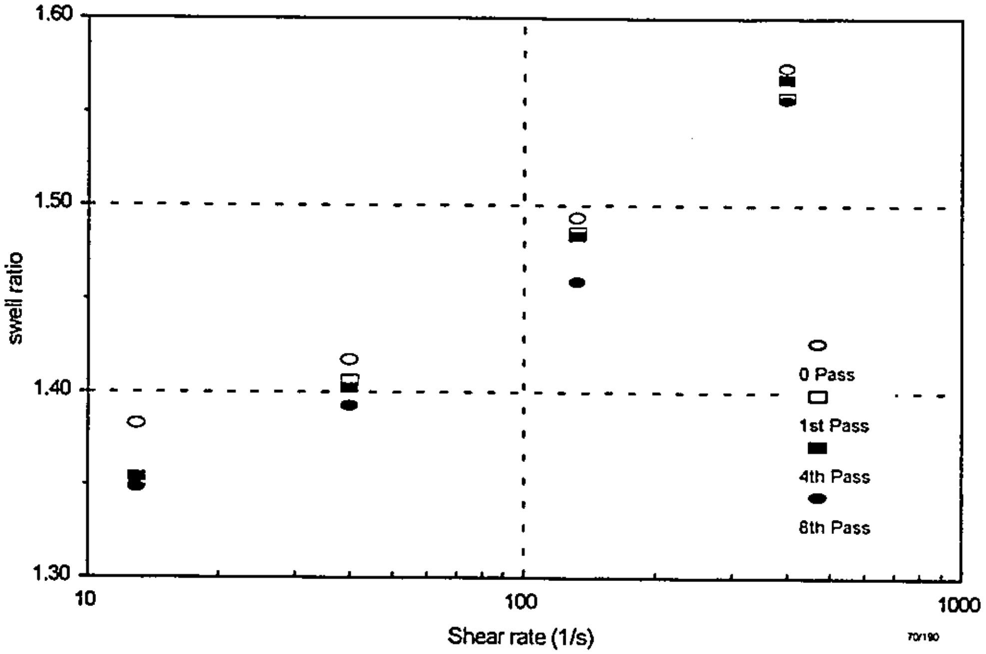


a) 60 rpm, 190 °C

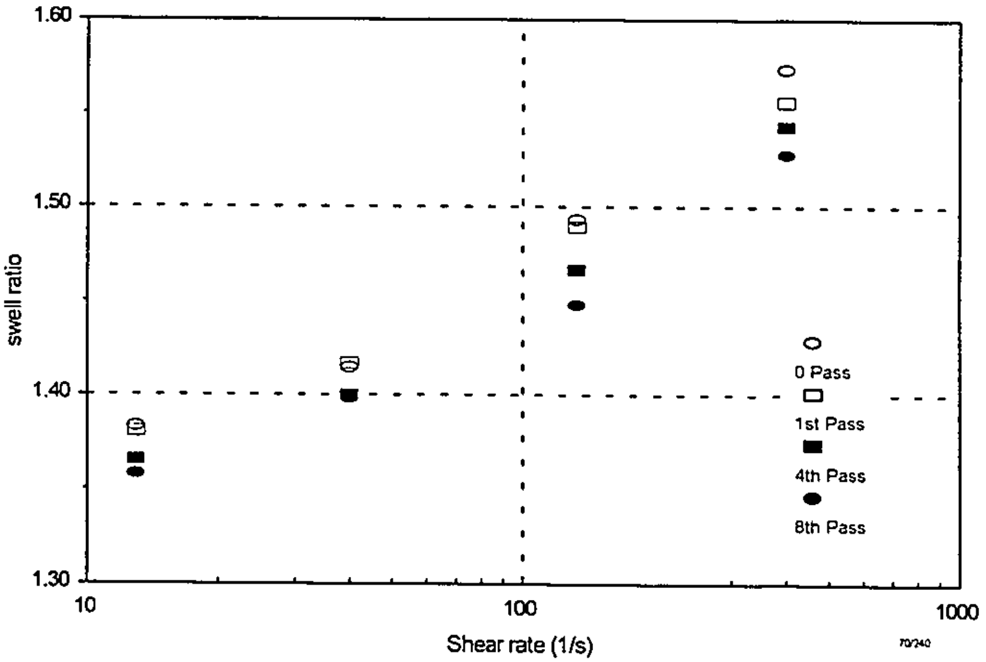


b) 60 rpm, 240 °C

Figure 6.3: Swell ratio curves experiment set 1



c) 70 rpm, 190 °C



d) 70 rpm, 240 °C

Figure 6.3 (cont.): Swell ratio curves experiment set 1

There is no strong evidence showing that one shear rate is any more sensitive than the other at distinguishing the change in swell ratio. The relative magnitude of the change in swell is not very large, roughly 5%, but the variance of the actual measurements was quite low (> 3% of the average). Similar to the change in the low shear viscosity, examination of the effect of the extrusion speed / temperature combinations, shows the most severe condition (70 rpm, 240 °C) as having the greatest effect on reducing the swell ratio, though the high temperature low shear combination (60 rpm, 240 °C) also exhibited a similar behaviour. In both cases the drop in swell from 0 to 8 passes appears to be more distinct than at the other 2 combinations.

6.1.3 Changes in tensile properties

The tensile strength properties were measured as described in section 5.5.1. The complete raw data set for the tensile strength properties is given in Table B-3. In Figures 6.4 to 6.7 the relationships of the tensile strength at yield (YTS), elongation at YTS, tensile strength at break or ultimate tensile strength (UTS) and elongation at UTS, to extrusion passes are shown. The observed raw data values had a large amount of within measurement variance. This was especially the case for

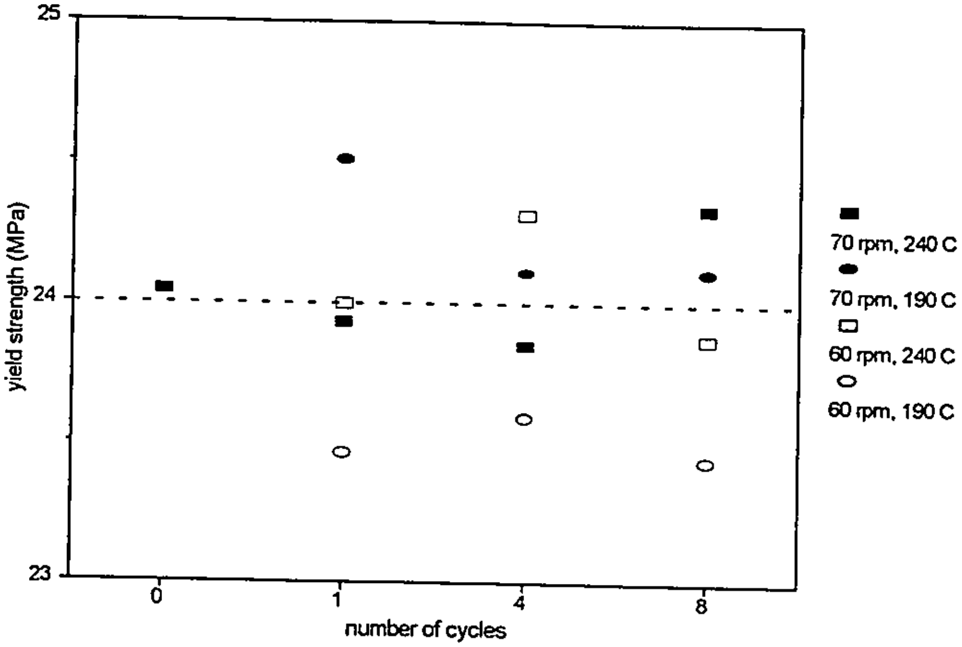


Figure 6.4: Change in yield strength with extrusion passes

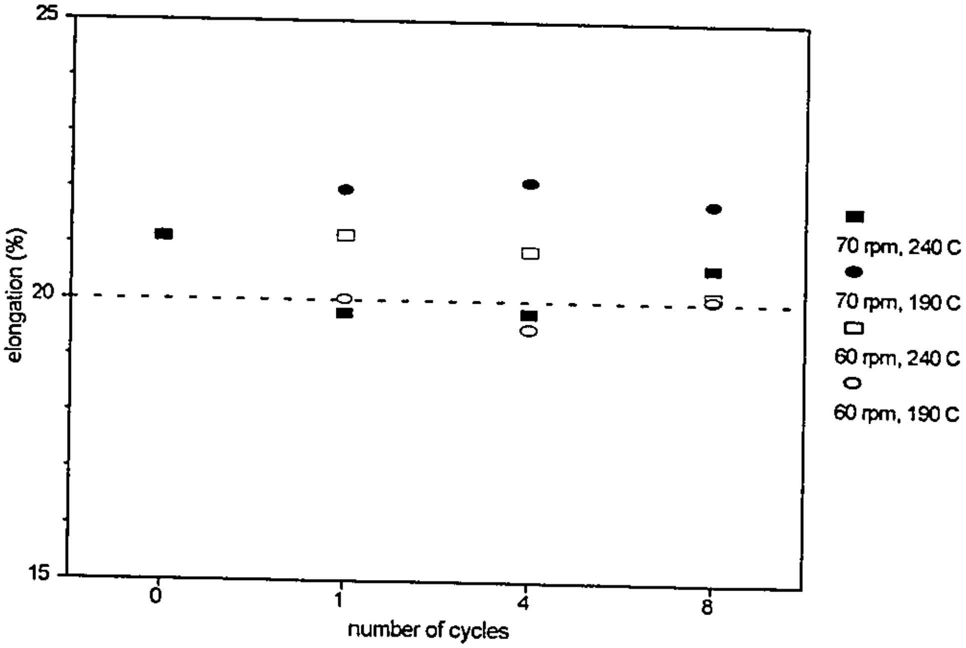


Figure 6.5: Change in elongation at yield with extrusion passes

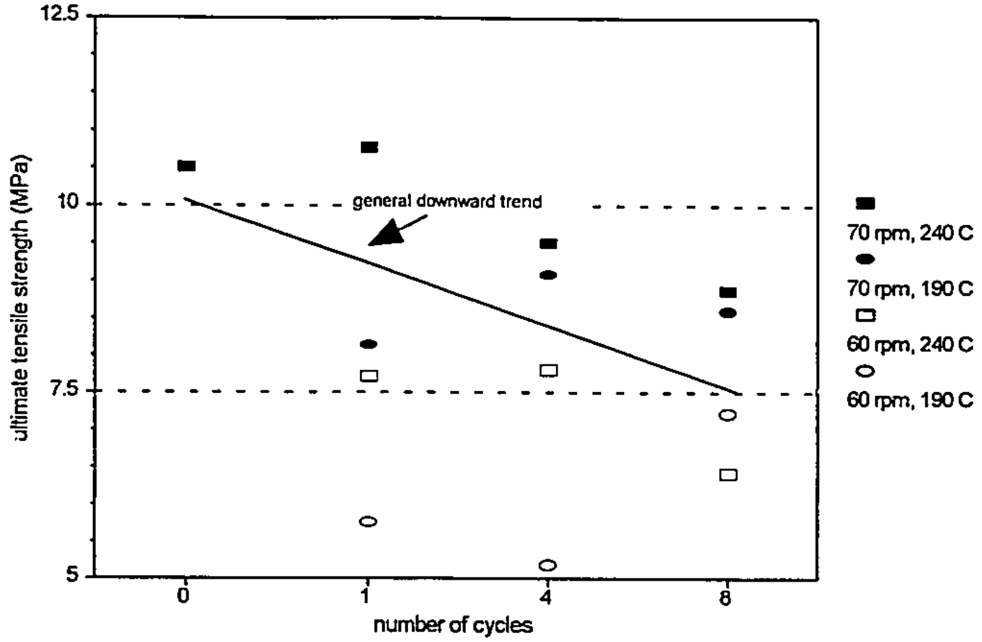


Figure 6.6: Change in ultimate tensile strength with passes

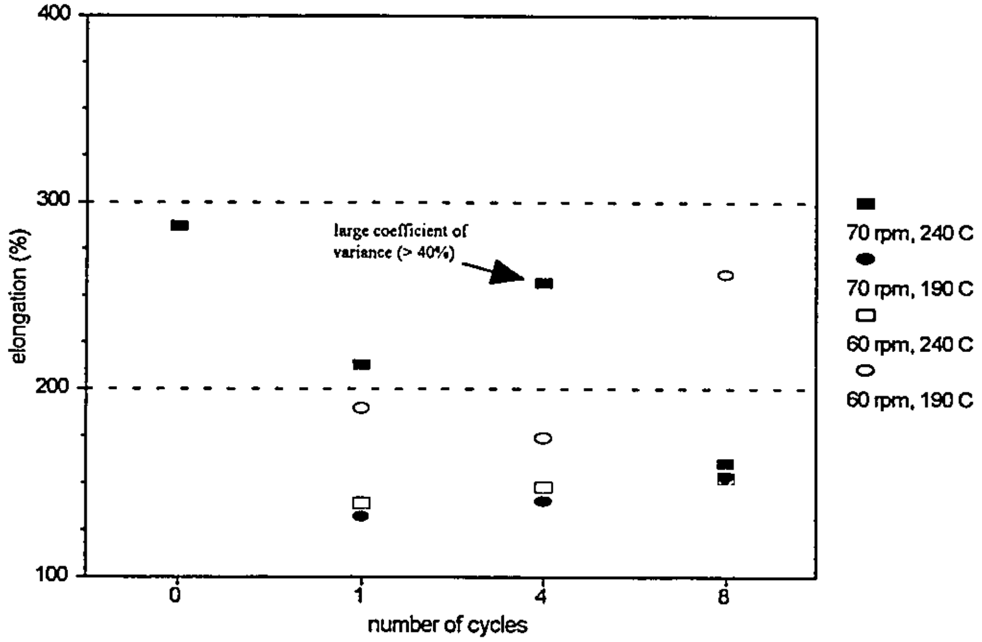


Figure 6.7: Change in elongation at break with extrusion passes

the UTS and elongation at UTS where many of the samples did not fail before they extended beyond the limit of the test equipment.

From the 4 graphs, only the UTS (Figure 6.6) showed any sign of a relationship with extrusion passes. In the YTS plot (Figure 6.4) the low shear/low temperature (60 rpm, 190 °C) condition appears to cause a significant drop in YTS compared to the other combinations but the differences are quite small (< 5%). The UTS results produced a general downward trend with an increase in extrusion passes. With the large amount of variance in the UTS data, as described above, this observed trend is not highly correlated with extrusion passes and it would be highly speculative to suggest any molecular mechanism for the decline in UTS. A direct outcome of these observations and the difficulty in obtaining repeatable results, was the decision to move to a different measure of the strength characteristics, more specifically the ESCR test.

6.1.4 Changes in extrusion responses

There was no significant effect of extrusion passes on the extrusion output, output efficiency and pressure. The output or throughput was a simple measure of the mass of polymer extruded per hour and the efficiency was the output per screw revolution. The second measure is a useful indicator of the effort required to extrude a polymer under a given set of conditions. The extrusion pressure is measured at the screw tip and actually measures the pressure drop through the die system. The plots of these responses versus extrusion passes are shown in Figures 6.8 to 6.10, with the raw data given in Table B-4. Regardless of the number of passes this resin had experienced, the best extrusion efficiency was achieved at the lower extrusion speed (Figure 6.9).

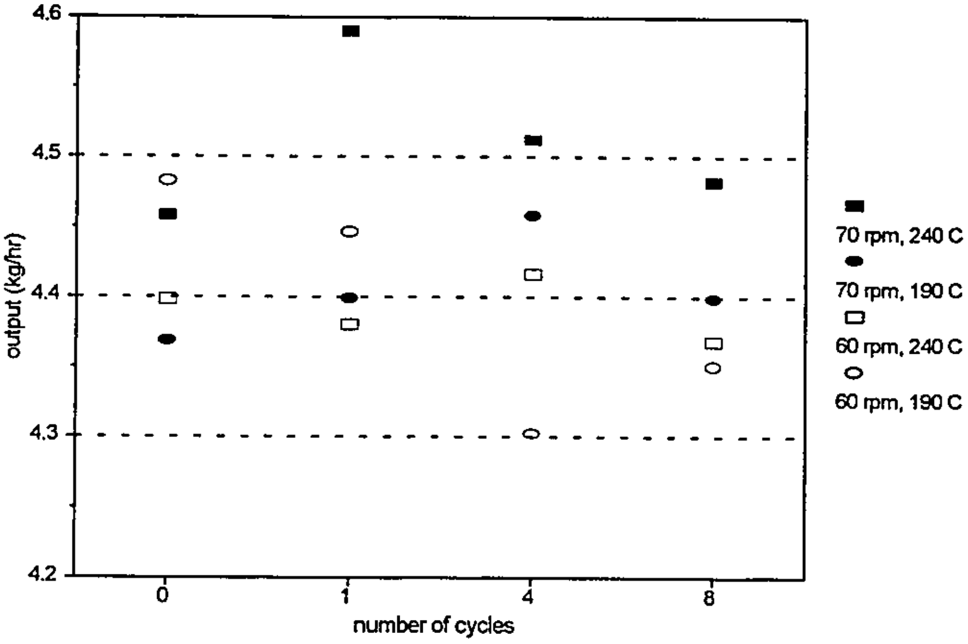


Figure 6.8: Change in output with extrusion passes

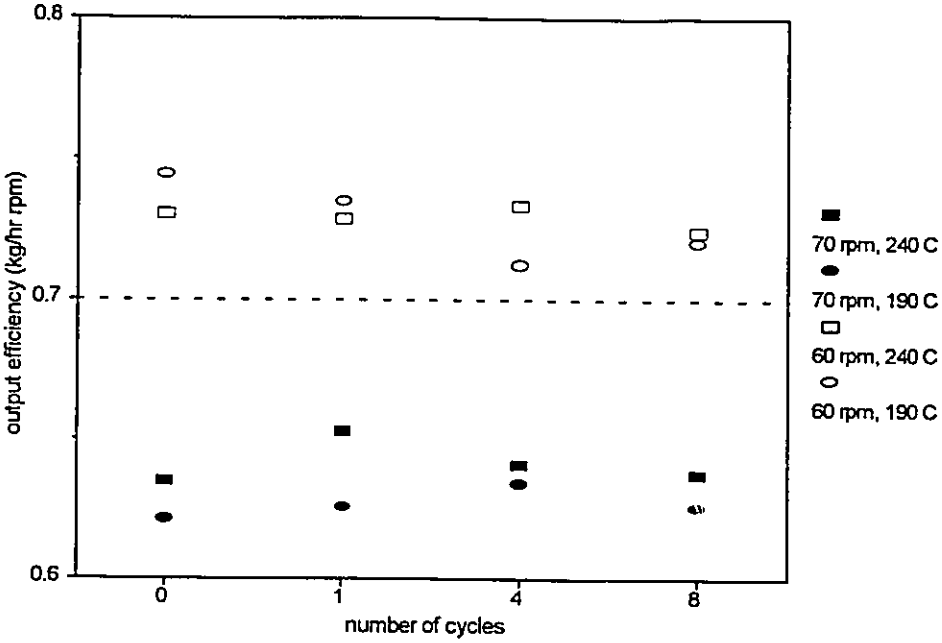


Figure 6.9: Change in output efficiency with extrusion passes

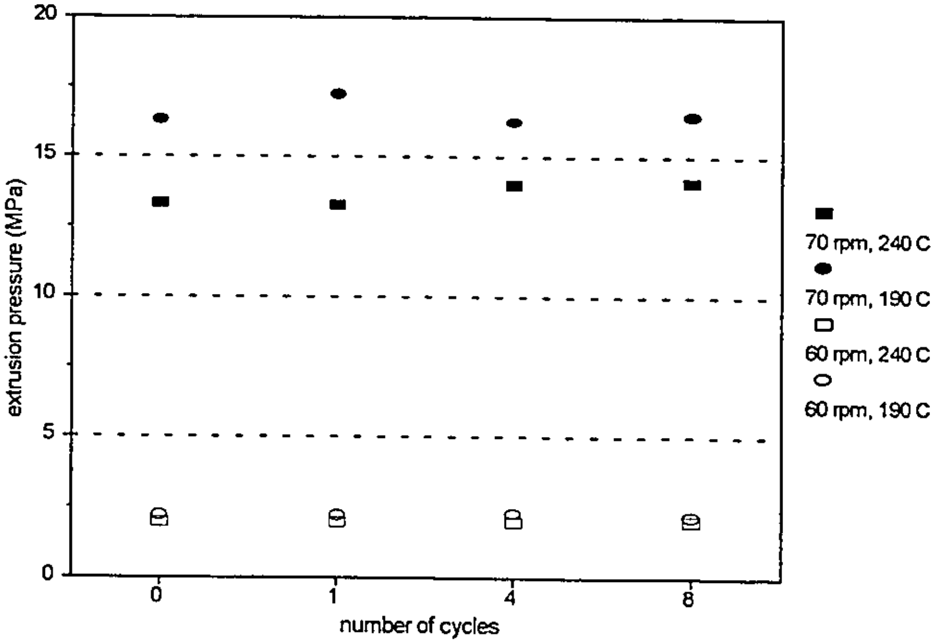


Figure 6.10: Change in extrusion pressure with passes

6.2 Results of experiment set 2

Changes were made in the response system for the second set of experiments. Using the knowledge gained from the first set, greater attention was given to the study of the low shear viscosity properties, elongational viscosity and dynamic viscosity properties. The study of the swell ratio was expanded from a single die to a range of capillary dies. Measures of extrudate sag and thermal characteristics, in the form of DSC observations, were introduced. The ESCR test replaced the tensile strength tests as a response within the physical properties category.

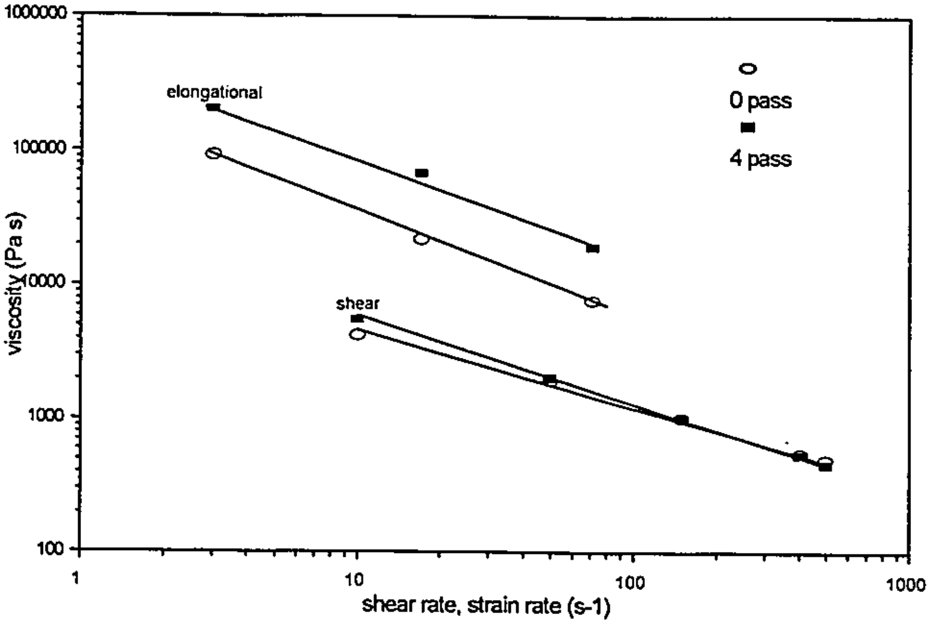
6.2.1 Changes in viscosity and viscoelastic properties

The data is broken down into viscosity and viscoelastic properties. The viscosity data is divided into the elongational viscosity, shear viscosity and complex viscosity. The steady state shear viscosity was determined with a capillary rheometer using the procedure described in sections 5.5.1 and 6.1.1 with additional measurements made to incorporate the Bagley factor into the shear stress calculations (eq. 31). The elongational viscosity was determined from the pressure loss at the entrance to the capillary die using the Bagley correction factor and equations 11, 12 and 32. Dynamic viscosity and shear modulus measurements were recorded using a plate on plate geometry in a forced air heating chamber following the procedure described in section 5.5.2. The capillary rheometer data are summarized in Tables B-5 and B-6.

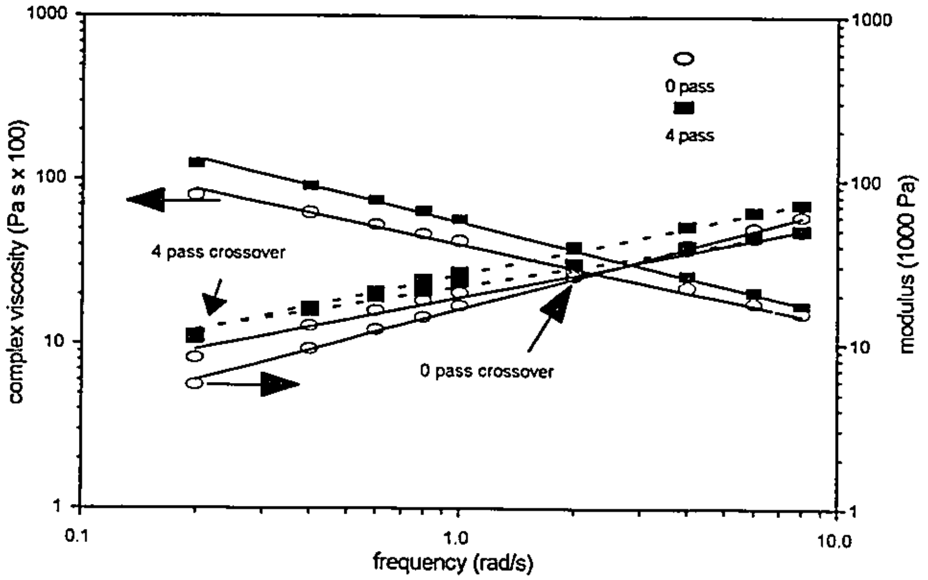
The following diagrams (Figures 6.11 a to h) summarize the data for each of the 4 resin systems. In general, all 4 resins showed a small difference in the shear viscosity, as determined by the capillary rheometer, from the "as is" or 0 pass state and the 4 pass state. In terms of the complex viscosity, the virgin copolymer showed little difference from 0 to 4 passes whereas the other 3 showed a more significant difference especially at the lower frequencies. The viscosity curves for the virgin copolymer appeared to shift down, while the viscosity curves for the other 3 resins appeared to shift upward.

The behaviour of the elongational viscosity changed for all 4 materials but the differences for the PCR materials were less defined. The nature of the change was different for the virgin copolymer, with a change in the slope of the curve, to a greater dependency on shear rate (Figure 6.11 e). The other resins had an upward shift in the elongational viscosity curve, with virtually the same slope.

The storage and loss modulus curves followed the opposite pattern as described by the elongational viscosity. The virgin copolymer G'-G" curves shifted down, with essentially the same slopes, from 0 to 4 passes

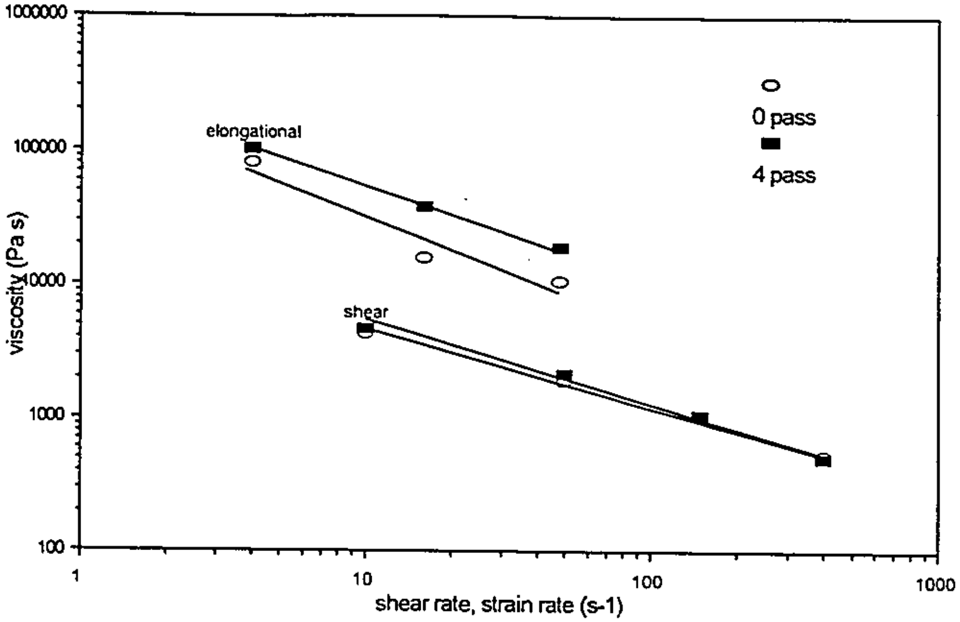


a) virgin homopolymer, shear and elongational viscosity

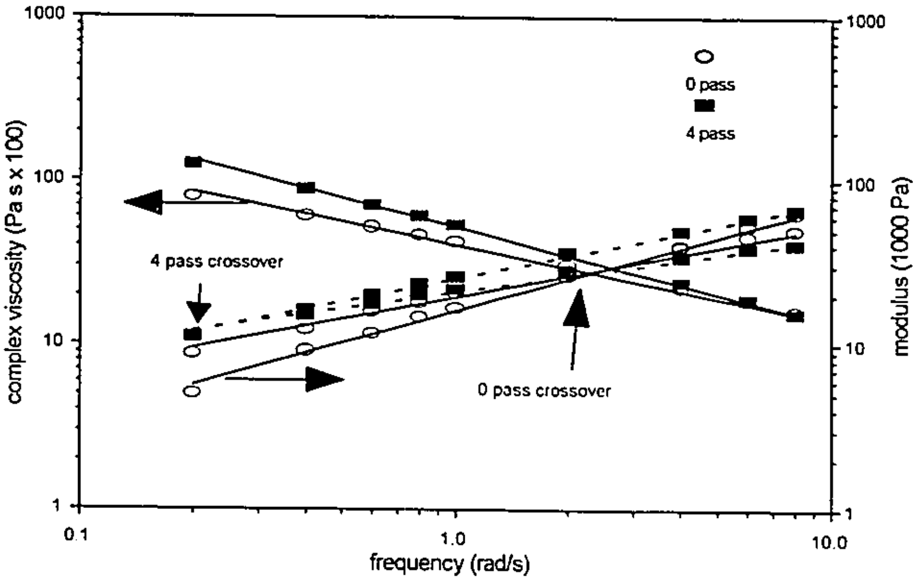


b) virgin homopolymer, complex viscosity, storage and loss modulus

Figure 6.11: Rheology curves for experiment set 2

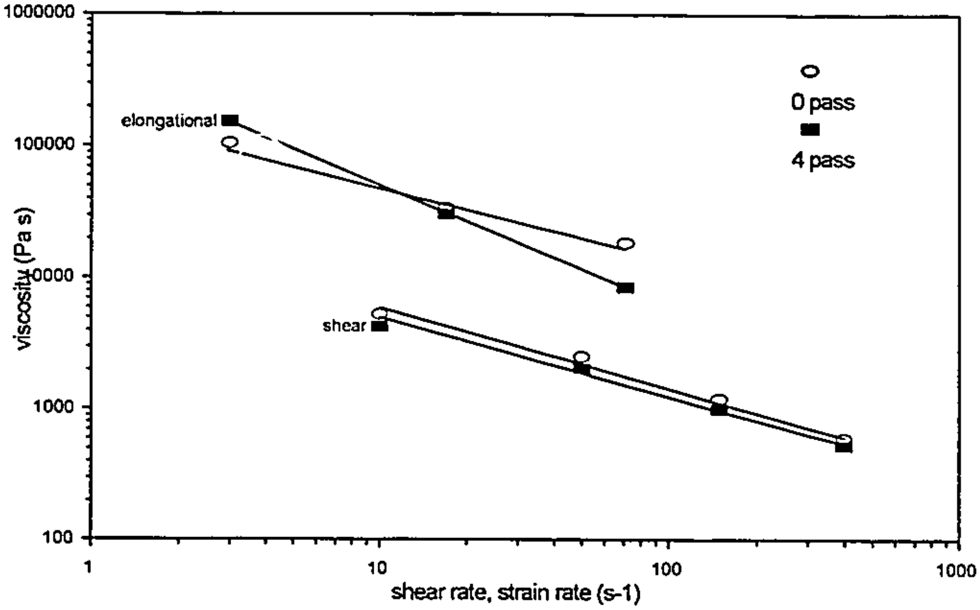


c) natural PCR, shear and elongational viscosity

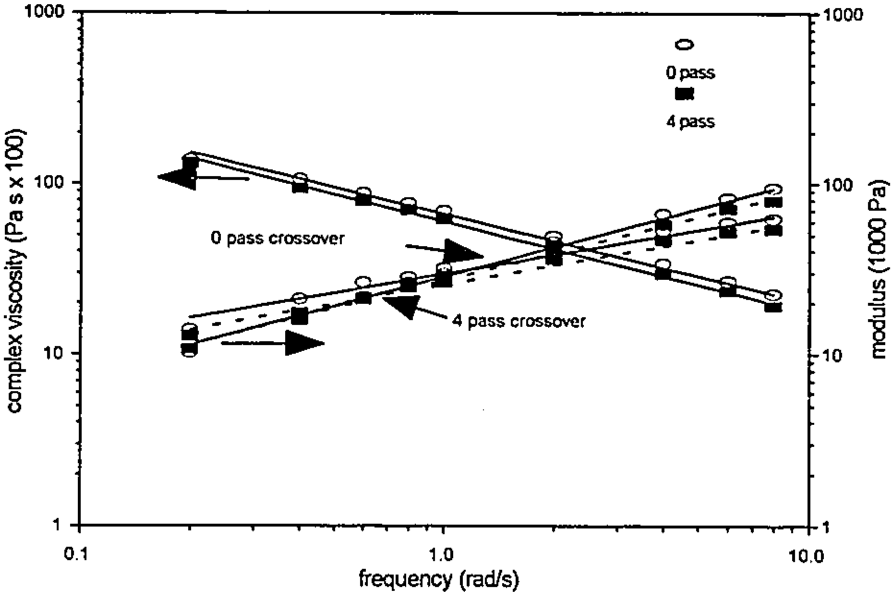


d) natural PCR, complex viscosity, storage and loss modulus

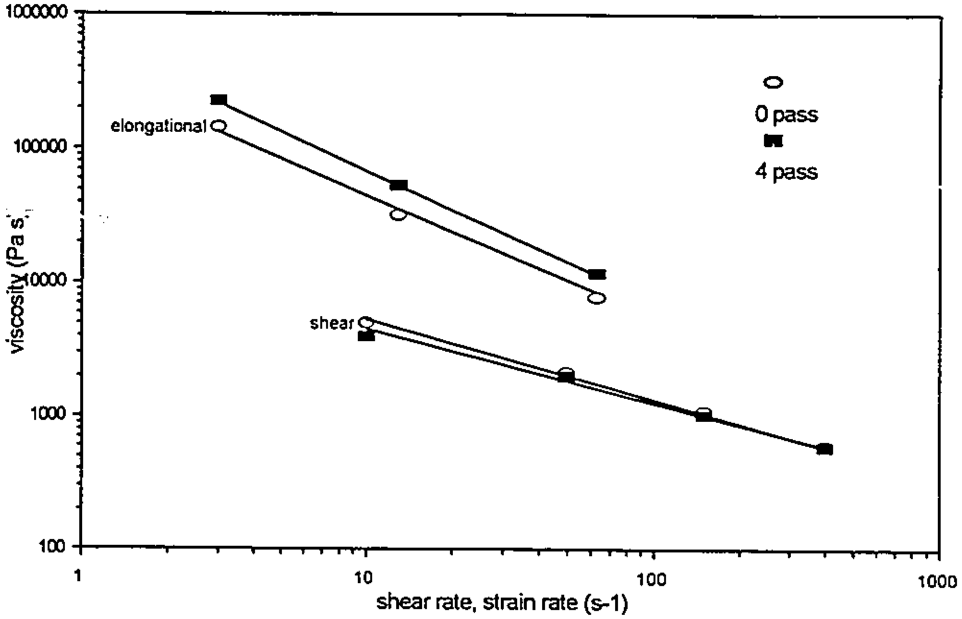
Figure 6.11 (cont.): Rheology curves for experiment set 2



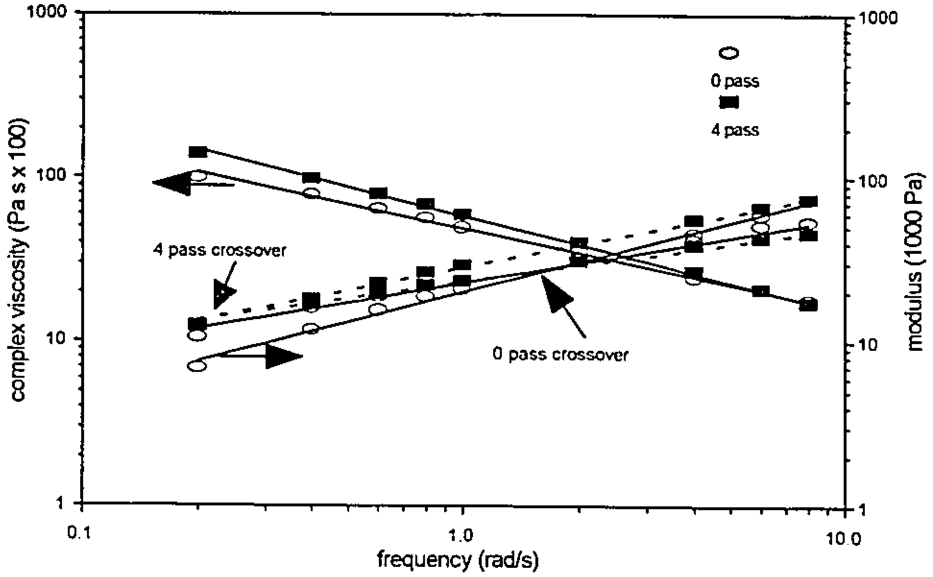
e) virgin copolymer, shear and elongational viscosity



f) virgin copolymer, complex viscosity, storage and loss modulus
Figure 6.11 (cont.): Rheology curves for experiment set 2



g) mixed colour PCR, shear and elongational viscosity



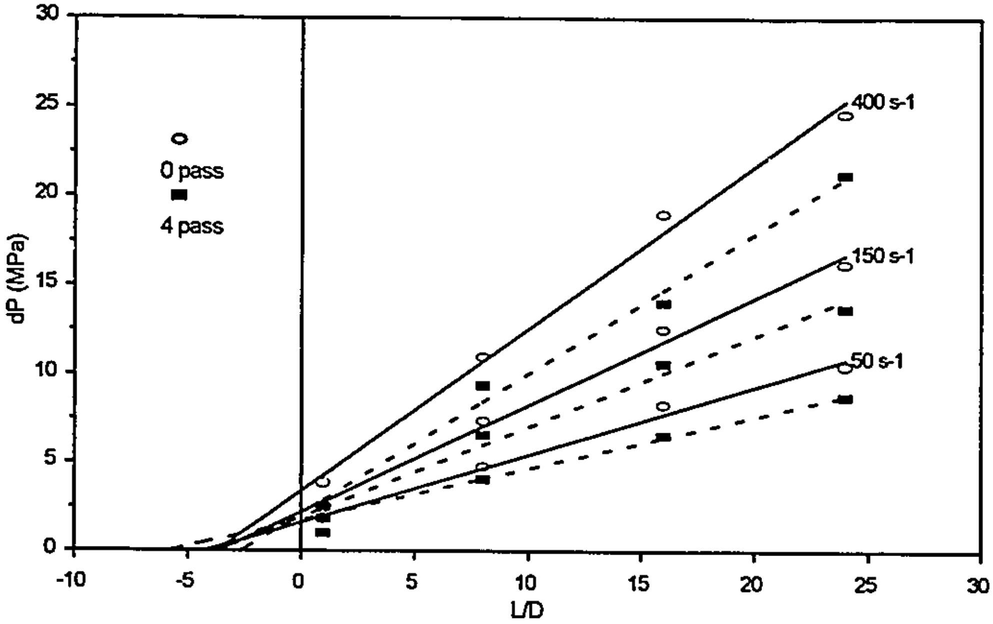
h) mixed colour PCR, complex viscosity, storage and loss modulus
Figure 6.11 (cont.): Rheology curves for experiment set 2

(Figure 6.11 f), while the other 3 materials shifted up slightly but had a significant decrease in slope from 0 to 4 passes (Figures 6.11 b,d and h).

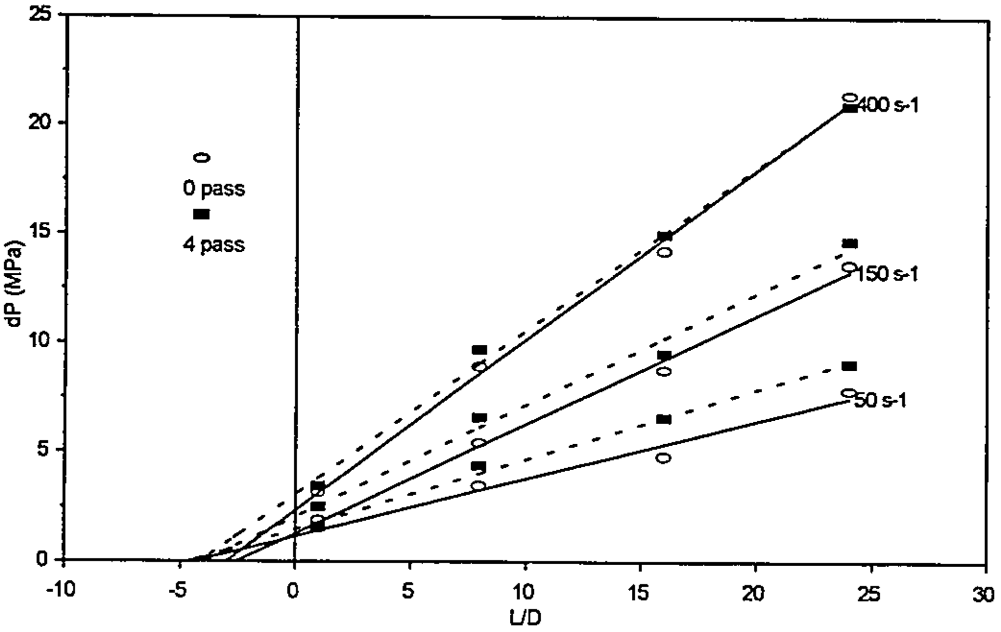
There is clearly a distinction in the viscosity and viscoelastic properties between the virgin copolymer and the other 3 materials. The natural PCR material behaves in a similar fashion to the virgin homopolymer but with less definition in the changes from 0 to 4 passes. The mixed colour PCR behaves more like the virgin homopolymer than the virgin copolymer but the changes are not even as defined as the natural PCR.

In Figure 6.12 the Bagley plots for the 4 resins are shown. The correction factors for the 50, 150 and 400 s-1 shear rates were determined mathematically using a simple least squares linear regression fit to the capillary pressure drop versus capillary L/D data. An average of the correction factors at the 3 shear rates, for each resin, at the 2 levels of passes, was used for the statistical analysis. Similar to the previous discussion, the virgin copolymer showed the opposite effect from the 4 passes. At the low shear rate (50 s^{-1}) the Bagley factor for all resins at 0 passes was lower than the factor at 4 passes. While this relationship prevailed at the 150 and 400 s^{-1} shear rates for the homopolymer and PCR resins, the opposite result occurred at 400 s^{-1} for the copolymer. Since the correction factors for each shear rate were used for the individual elongational viscosity calculations then the tendencies in the Bagley factors are similar to the tendencies of the elongational viscosity.

The Bagley correction factor is also useful in extrusion modelling. It can be used as an estimate of the pressure loss due to entrance effects in a die system. In Table 6.1 a comparison of the observed pressure drop versus a theoretical pressure drop, incorporating the Bagley correction factor, through the die / breaker plate system, is summarized. A supporting sample calculation is shown in Table A-2. Using the average Bagley factor, the theoretical pressure is within 15% of the actual for all of the resins at 0 and 4 passes, except for the virgin copolymer at 4 passes where the theoretical pressure drop is 20% greater than the observed pressure drop. This result demonstrates that the "as received" PCR resins used in this study and all of the resins exposed to multiple passes behave as a typical HDPE resin in this simple application of the Bagley correction factor.

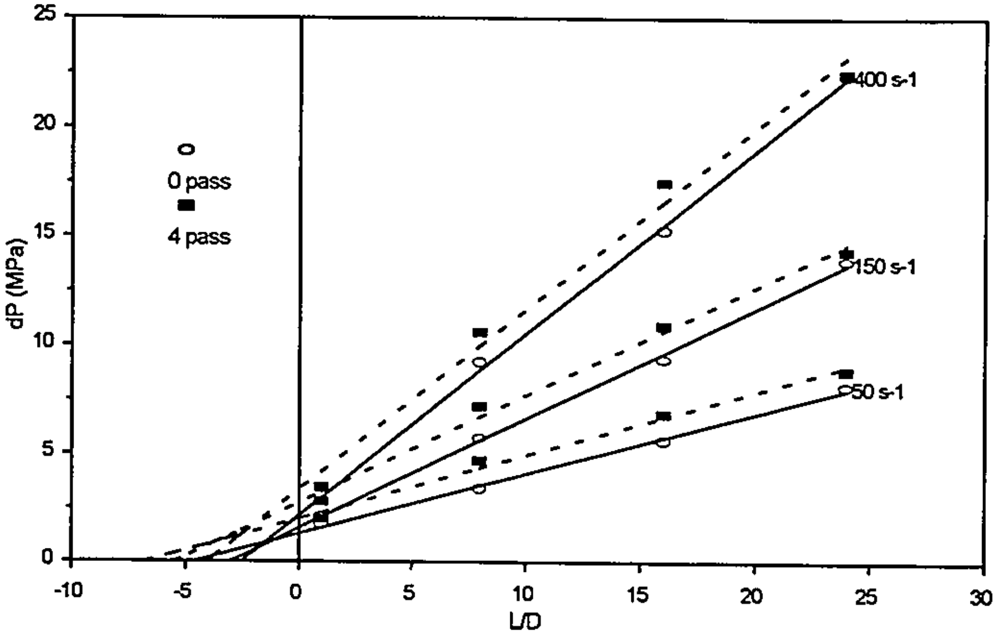


a) virgin homopolymer

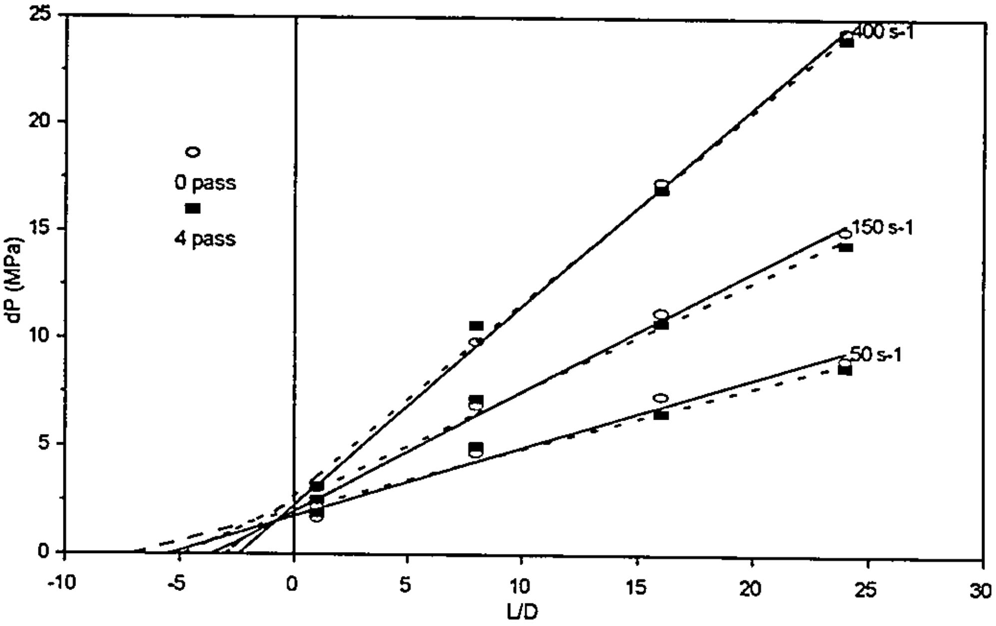


b) natural PCR

Figure 6.12: Bagley correction factor plots



c) virgin copolymer



d) mixed colour PCR

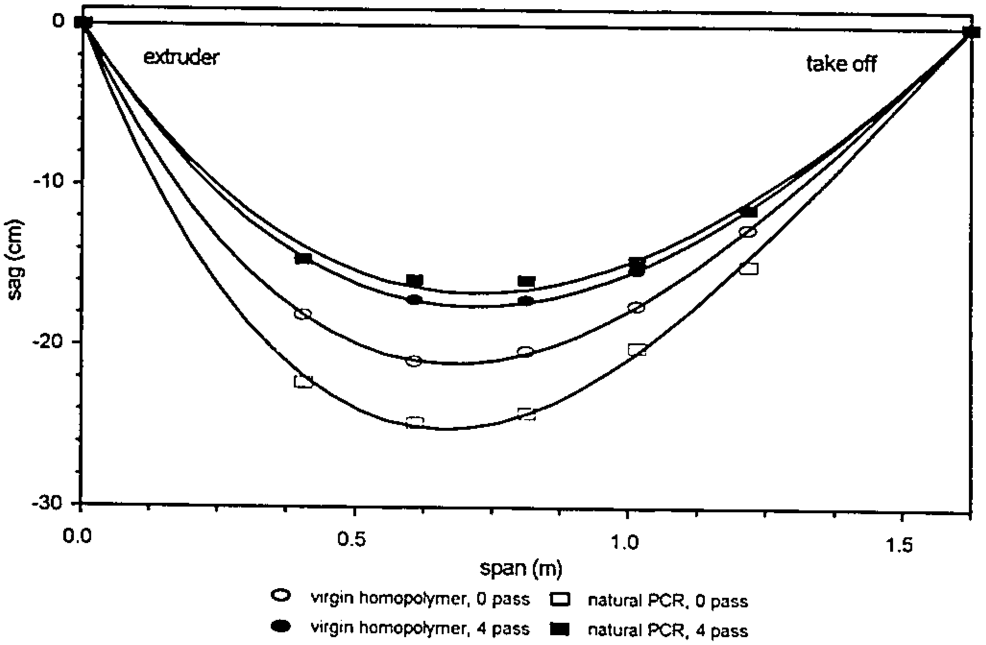
Figure 6.12 (cont.): Bagley correction factor plots

Table 6.1 Experiment set 2 observed extrusion pressure drop versus theoretical pressure drop
(using the average Bagley correction factor)

Observed extrusion responses								
polymer	virgin copolymer		mixed colour pcr		virgin homopolymer		natural pcr	
pass	0	4	0	4	0	4	0	4
extruder output (kg/h)	5.2	5.3	5.4	5.6	5.3	5.3	5.4	5.5
observed extruder dP (MPa)	**12.4**	**11.9**	**11.1**	**11.2**	**10.9**	**11.4**	**10.6**	**11.1**
V cc/s @ 0.725 g/cc	1.99	2.03	2.07	2.15	2.03	2.03	2.07	2.11
THEORETICAL PRESSURE DROP THROUGH DIE SYSTEM								
n	0.38	0.40	0.40	0.45	0.42	0.34	0.41	0.37
m	25493	19732	21824	15928	17993	27315	18603	23529
average Bagley factor	**3.9**	**4.1**	**3.8**	**5**	**3.4**	**5.4**	**3.3**	**4.2**
Breaker Plate (9 holes)	R = (1/32") 0.07938 cm				length =1 cm			
pressure drop (MPa)	8.1	7.2	8.0	8.1	7.4	6.8	7.2	7.2
entrance loss	1.3	1.2	1.2	1.6	1.0	1.5	0.9	1.2
Reservoir	R = (1/2") 1.252 cm				length = 2.81 cm			
pressure drop (MPa)	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1
entrance loss	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1
Die	R = (1/4") 0.635 cm				length = 3.81 cm			
pressure drop (MPa)	0.8	0.7	0.8	0.6	0.7	0.8	0.7	0.8
entrance loss	0.3	0.2	0.2	0.3	0.2	0.4	0.2	0.3
Theoretical dP	**9.0**	**8.0**	**8.9**	**8.8**	**8.2**	**7.8**	**8.0**	**8.1**
Bagley corrected dP	**1.7**	**1.5**	**1.6**	**2.0**	**1.3**	**2.0**	**1.2**	**1.6**
Total Corrected Theoretical	**10.7**	**9.5**	**10.5**	**10.8**	**9.5**	**9.8**	**9.2**	**9.7**
difference from observed	1.7	2.4	0.6	0.4	1.4	1.6	1.4	1.4
% difference from observed	**13%**	**20%**	**6%**	**4%**	**14%**	**14%**	**13%**	**13%**

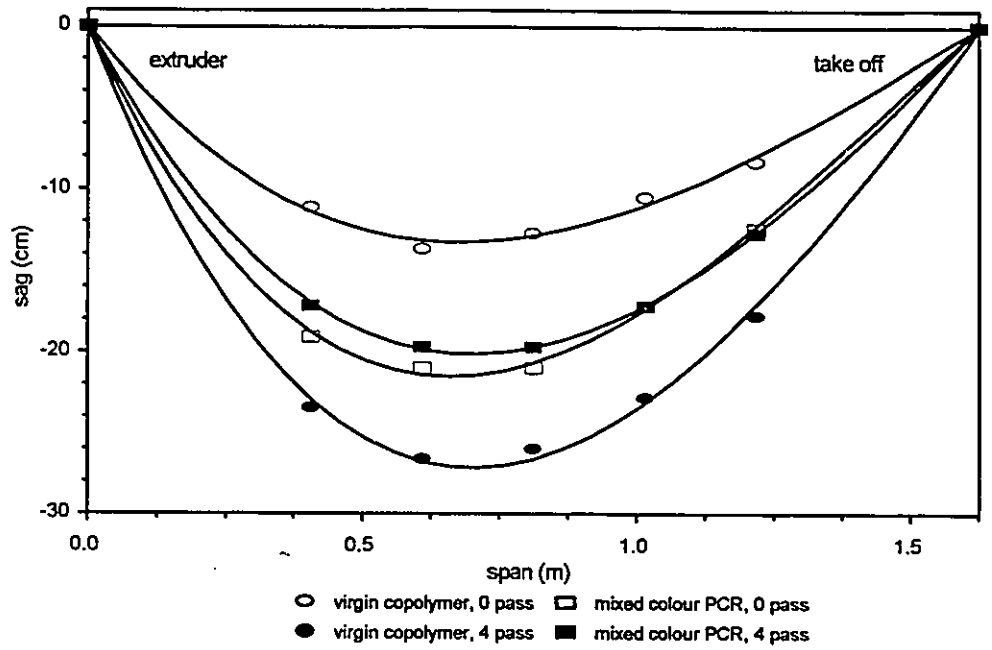
6.2.2 Observed differences in extrudate sag

In section 5.5.2 the description of a crude measure of sag was given. The data from this measurement is presented in Table B-7 and is described graphically in Figure 6.13. The points on the curve represent the average of 2 observed values, while the lines represent a cubic function fitted to the observed values. Since the extrudate was air cooled, the ambient temperature was monitored closely throughout the procedure. There was less than a ± 1°C difference in the ambient temperature during all measurements of the sag.



a) virgin homopolymer, natural PCR

Figure 6.13: Sag plots for experiment set 2



b) virgin copolymer and mixed colour PCR

Figure 6.13 (cont.): Sag plots for experiment set 2

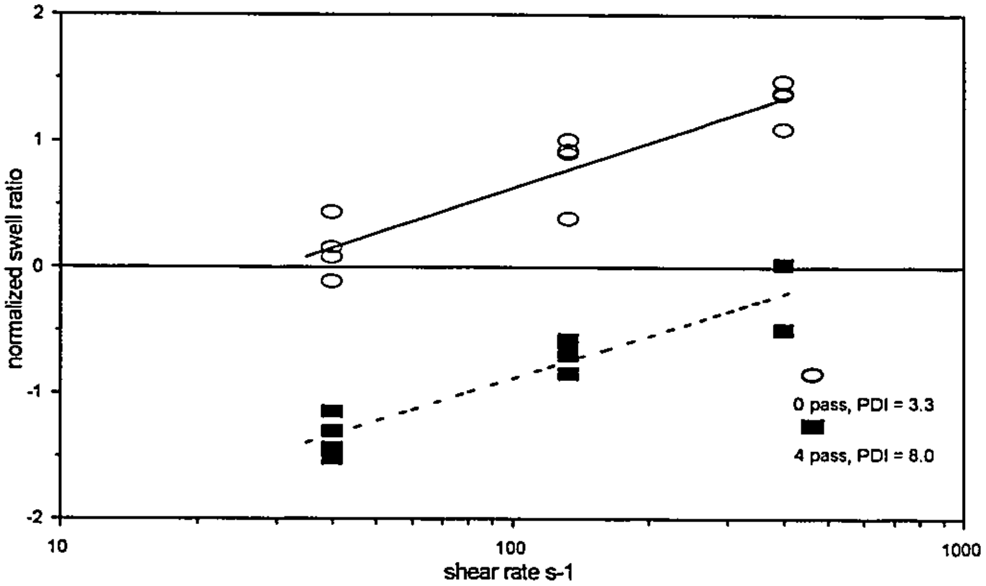
At 0 passes the virgin copolymer exhibits superior sag resistance compared to the other 3 resins, in particular the natural PCR. However, at 4 passes the reverse is true. The virgin copolymer sag resistance drops dramatically and the natural PCR sag resistance increases significantly. The virgin homopolymer also demonstrates an increase in sag resistance while the mixed colour PCR maintains the same characteristics from 0 to 4 passes.

6.2.3 Change in swell ratio

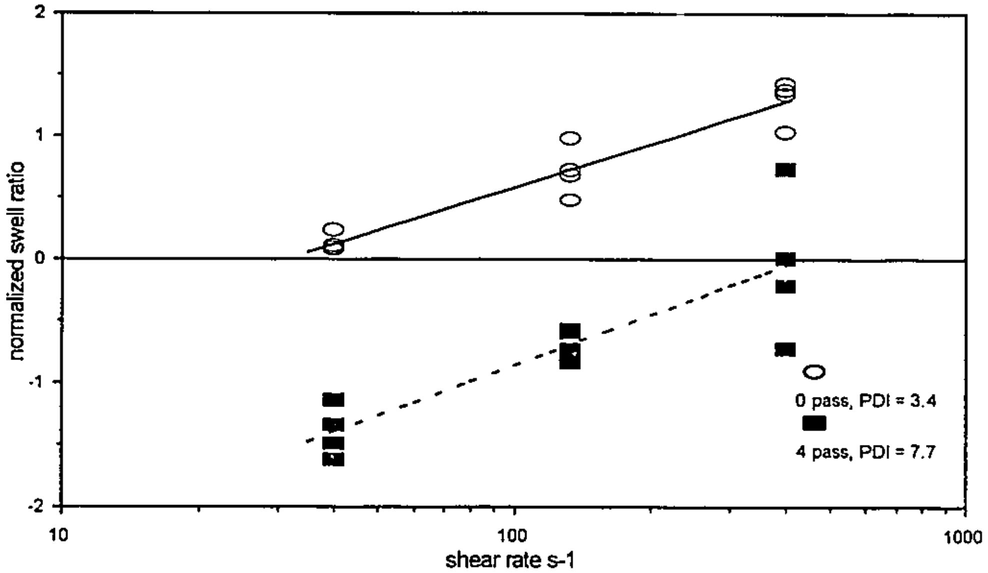
The swell measurements were obtained by using the same technique used in the first set of experiments and the data is summarized in Table B-8. The swell ratio was measured using strands from the extrudate of the Bagley correction factor and viscosity measurements. In Figure 6.14 plots of the swell ratio versus 3 shear rates (50, 150 and 400 s^{-1}) for 4 L/D ratios (1, 8, 16 and 24) for the 4 resins are shown. The swell ratio data was normalized to remove the effect of the variance in swell due to the different capillary L/D ratios used in the viscosity and Bagley correction factor measurements, where

$$t_{@L/D,\text{shear rate}} = \frac{\text{swell ratio}_{@L/D,\text{shear rate}} - \text{avg. swell ratio}_{@\,L/D}}{\text{st. dev.}_{@\,L/D}} \qquad (33)$$

In general, for all resins the swell ratio increased with an increase in shear rate and decreased with an increase in L/D. In term of the relationship with multiple passes, the same overall trend as described in 6.1.3 for the first set of experiments was observed for this set. The swell ratio decreased with an increase in passes for all resins. The decline in swell from 0 to 4 passes was greatest with the virgin homopolymer and natural PCR while the mixed colour PCR had the lowest drop in the swell ratio.

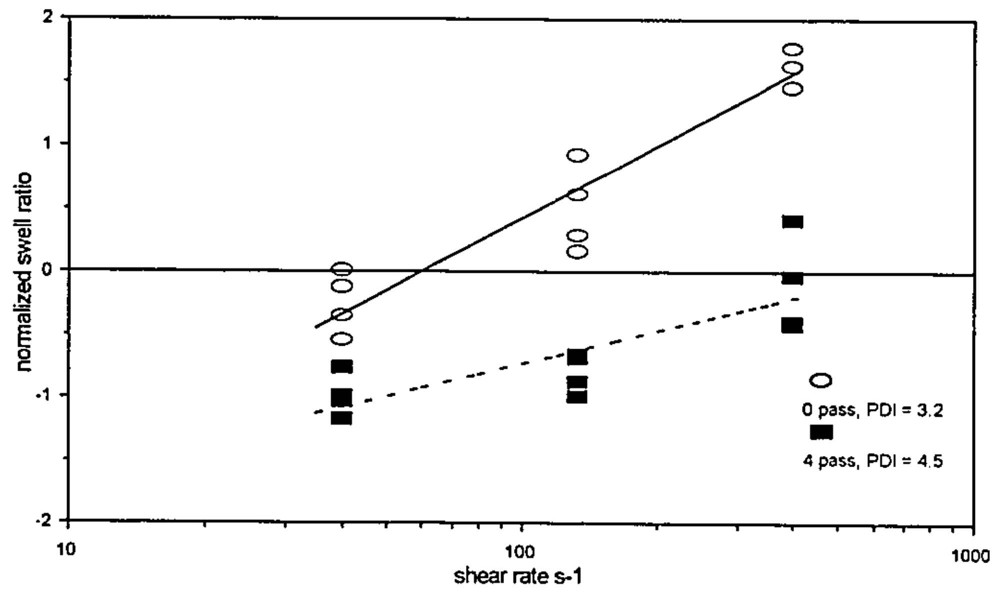


a) homopolymer

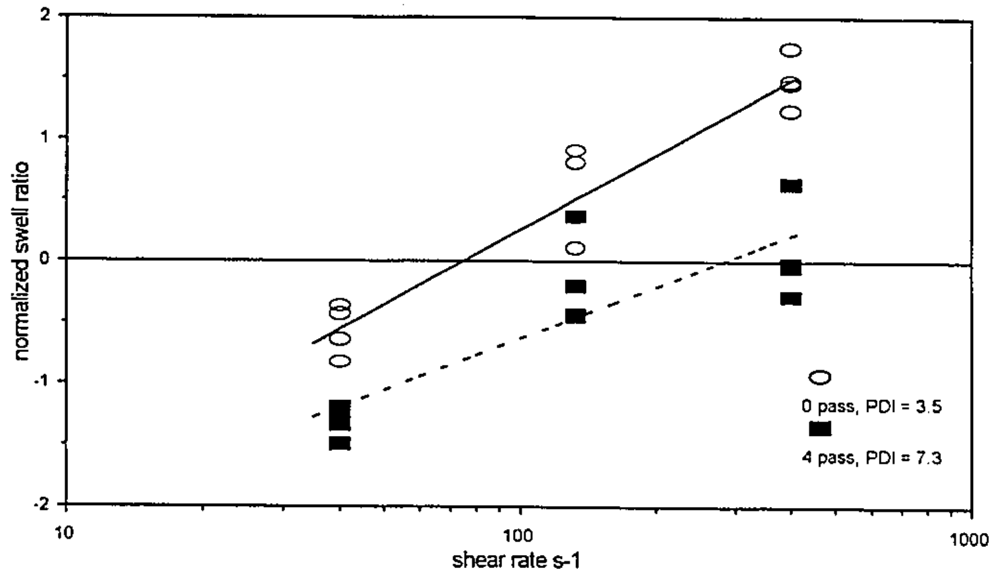


b) natural PCR

Figure 6.14: Normalized swell ratio for experiment set 2 (L/D = 1:1, 8:1, 16:1 and 24:1)



c) virgin copolymer



d) mixed colour PCR

Figure 6.14 (cont.): Normalized swell ratio for experiment set 2 (L/D = 1:1, 8:1, 16:1 and 24:1)

6.2.4 Changes in polydispersity index and molecular weight

In section 6.2.1 the changes in the loss and storage modulus curves were briefly described. The primary intent of studying the modulus data was to use the information to examine changes in the molecular weight distribution. As described in section 4.2.3, it has been reported that the G' - G" crossover, G_c, point in the terminal zone can be used to measure the poly-dispersity index (PI), (eq. 17). The breadth of the MWD has a direct relationship with PI and an inverse relationship with G_c. Consequently, as G_c shifts down it indicates a broadening of the MWD. Prior to using it in this experimental set, the PI was measured for the virgin homopolymer with a Waters 150 C gel permeation chromatograph (GPC) using trichlorobenzene as the solvent and a BHT anti-oxidant to stabilize the samples during analysis, following ASTM 3536-76. The PI as measured with the GPC was 6.02 compared with 3.3 using G_c. It was concluded that using the modulus crossover point was useful but only for studying relative changes in MWD. A more comprehensive comparative study done by Moss (1989) reached similar conclusions.

A summary of the G_c and PI for this experimental data set is given in Table 6.2. In all cases the PI increased with an increase in extrusion passes. The magnitude of the increase was significantly larger for both the virgin hompolymer and natural PCR. The virgin copolymer had the least amount of change.

Table 6.2 Summary of modulus crossover, polydispersity and viscosity index

Experiment design			Modulus crossover, polydispesity and viscosity ratio	
resin	**source**	**pass**	**G' - G" crossover Pa**	**Polydispersity Index (PI)**
hopolymer	virgin	0	30083	3.3
hopolymer	virgin	4	12503	8.0
natural	pcr	0	29307	3.4
natural	pcr	4	12920	7.7
copolymer	virgin	0	31638	3.2
copolymer	virgin	4	22437	4.5
mixed colour	pcr	0	28463	3.5
mixed colour	pcr	4	13665	7.3

Along with the G_c value, the G" curve can also provide more information into the MW properties. Referring back to Figure 6.11, the G" curve shifts to the right, after 4 passes, for the virgin copolymer and the opposite occurs for the homopolymer and natural PCR, and to a lesser extent, the mixed colour PCR. The slope of G" decreases for all materials except the copolymer resin.

6.2.5 Changes in thermal analysis characteristics

The addition of DSC data to the response system was done to study the thermal and crystallinity characteristics of PCR and to examine the effect of multiple passes on these properties. They were also used to provide a supporting morphological analysis for the ESCR response. As discussed in section 4.3.4, the ESCR relationship to crystallinity has been extensively studied.

Each sample was heated twice with the first cycle used to remove any inconsistencies in the crystalline structure due to variances in solidification from the air cooling during the multiple extrusion runs. There were 4 measurements taken from the DSC trace including the melt temperature, % crystallinity, maximum peak endothermic temperature and maximum heat flow at the endothermic peak. The data is summarized in Table 6.3.

The melt temperature decreased slightly for all materials from 0 to 4 passes though the drop was less than 1.5 °C. The percentage crystallinity also drops for all materials with the virgin polymers decreasing less than the post consumer resins. The crystallinity for the mixed colour bottle dropped by almost 10%. Similar to the melt temperature, the maximum peak endothermic temperature changed by less than 1 °C for all materials. The heat flow at the endothermic peak did not change for the natural PCR, but fell by 0.3 to 0.5 W/g for the other 3 materials.

Table 6.3 Summary of DSC data for experiment set 2

Experiment design			DSC responses			
resin	source	pass	melt temp. °C	% cryst.	max. peak temp. °C	max. heat flow W/g
hopolymer	virgin	0	128.0	59.1	135.9	-2.6
hopolymer	virgin	4	127.6	58.3	137.6	-2.1
natural	pcr	0	126.8	60.8	135.5	-2.4
natural	pcr	4	125.5	56.7	135.9	-2.4
copolymer	virgin	0	125.2	65.6	134.7	-2.6
copolymer	virgin	4	124.8	62.8	135.6	-2.2
mixed colour	pcr	0	124.8	65.2	135.0	-2.3
mixed colour	pcr	4	123.7	55.3	134.5	-2.0

Other than the changes in crystallinity, there were no real differences between the virgin and post consumer resins or the homopolymer and copolymer materials.

6.2.6 Changes in extrusion performance

A summary of the extrusion performance data is given in Table 6.4. The output for all resins does not differ significantly. This observation is consistent with results from the first set of experiments. The number of extrusion cycles does not appear to have an effect on the pumping capacity of the material which implies that the resin/extrusion screw interface is not adversely affected.

While the output did not change, the extrusion pressure drop showed some effect from the multiple passes. The homopolymer and natural PCR resins had an increase in pressure and the mixed colour PCR showed no change. Again the virgin copolymer behaved opposite to the other materials as the pressure drop decreased with an increase in extrusion passes. The variance in the measurement was less than 2% and the magnitude of the changes in pressure drop was less than 5%.

Table 6.4 Extrusion performance for experimental set 2

Experiment design			**Extrusion performance**	
resin	**source**	**pass**	**output kg/h**	**extr. press. MPa**
hopolymer	virgin	0	5.3	10.9
hopolymer	virgin	4	5.3	11.4
natural	pcr	0	5.4	10.6
natural	pcr	4	5.5	11.1
copolymer	virgin	0	5.2	12.4
copolymer	virgin	4	5.3	11.9
mixed colour	pcr	0	5.4	11.1
mixed colour	pcr	4	5.6	11.2

6.2.7 Changes in ESCR

The ESCR F50 values were determined from the diagrams given in Figure B-1, following the procedure described in section 5.5.2. The results for the designed experiment are summarized in Table 6.5. In direct contrast to the tensile strength results of the first set of experiments, this response provided the most dramatic effect from multiple extrusion passes. The virgin homopolymer, mixed colour PCR and virgin copolymer decreased in ESCR and the natural PCR showed little no change. The magnitude of the decrease for the homopolymer and mixed colour PCR was about 20%, with the virgin copolymer dropping by over 60%.

Table 6.5 ESCR response for experiment set 2

Experiment design			ESCR F50
resin	source	pass	
hopoly	virgin	0	7.25
hopoly	virgin	4	5.75
natural	pcr	0	6.00
natural	pcr	4	6.75
copoly	virgin	0	90.0
copoly	virgin	4	19.0
mixed colour	pcr	0	10.0
mixed colour	pcr	4	8.0

Examination of the plots shown in Figure B-1 shows that the variance in the data was between 10 to 15% for all samples except the natural PCR at 4 passes. Two of the 10 samples for this material lasted over 19 hours, triple the median value. This result may seem unusual, and decrease the reliability of the test . However, provisions are made within the ASTM standard to exclude abnormally long failure times. If the 2 observations are excluded the median value drops to 6.75 hours.

Chapter 7 - Analysis and Discussion

7.1 Anaiysis of experimental set 1

In the system of responses for the first experimental set the swell ratio showed the most significant effect from the number of extrusion passes and the viscosity comparisons showed the least. The swell ratio appears to be sensitive to small molecular changes resulting from multiple passes. In contrast, the viscosity and corresponding extrusion performance, which changed very little, are less sensitive indicators and the measures of tensile properties produced inconclusive results.

Swell is a viscoelastic phenomenon, which is related to the relaxation of the polymer molecules, and any change in molecular structure, in terms of chain scission, cross-linking or branching will have a direct effect on the ability of the polymer to relax. It was previously noted that a Phillips based catalyst polymer, as used in this set of experiments, has a tendency to cross-link. During multiple extrusions cross-linking leads to a more rigid molecular structure and this rigidity tends to resist the relaxation process, which results in a decrease in swell.

In the blow moulding process some consideration is given to the swell characteristics of the resin and its effect on the behaviour of the extruded parison. When a blow moulding die is cylindrical, swell characteristics, determined from a capillary rheometer, are a reasonable predictor for determining the parison thickness. However, the same cannot be said for conical blow moulding dies, where there is no apparent correlation with the swell as measured with a capillary rheometer. This is explained by flow in the conical die, which is not viscometric, i.e. where there is more than one velocity which varies in one direction (Tadmor, 1979). While the predictive relationships may not be consistent, regardless of the die configuration, changes in molecular structure which affect swelling will be observed.

The results of the tensile properties analysis indicate a possible effect from the number of extrusion passes. Changes in UTS end elongation are directly related to the strain hardening characteristics of a polymer as molecular chains are unfolded and lamellae slip during the tensile pulling process, essentially a form of cold drawing. A decrease in UTS and elongation is often associated with an increase in the rigidity of the molecular structure. In light of the previous discussion on the changes in swell properties and crosslinking, a more rigid structure, as a result of crosslinking, would tend to lead to a greater resistance to the unfolding of molecular chains and slippage between lamellae resulting in a lower UTS and ultimate elongation.

Though lot to lot variation exists in production, for a given lot, the relative changes that were observed in this set of experiments are expected to be reproducible. These results are applicable to this particular homopolymer blow moulding resin and caution must be used when attempting to generalize these results to other HDPE blow moulding resins. The following analysis of the results of the second set of experiments provides more evidence to support this conclusion.

7.2 Analysis of experimental set 2

The primary objective of the second set of experiments was to expand the study of multiple extrusion passes to include a copolymer resin and post consumer resins. In general, the results from this set supports the findings of Moss (1989) and Hinsken (1991) and adds PCR materials and more application specific responses, such as swell and ESCR, to the analysis. The natural PCR material behaves much like the virgin homopolymer, confirming that the source of the natural resin is primarily homopolymer based bottles. The 0 pass characteristics of the natural resin are very similar to the virgin homopolymer, in particular the viscoelastic modulus, which may suggest the presence of some virgin homopolymer resin material blended into the natural resin. The mixed colour PCR has similar tendencies as the virgin homopolymer and natural PCR. However, the distinctions between the 0 and 4 pass curves for the mixed colour PCR are not as clear as they are for the other 2 materials. This indicates that this PCR stream is more of a composite of copolymer and homopolymer bottles, though mixed colour PCR is often marketed as a copolymer based material.

Aside from the change in polydispersity, which was also observed by Moss, the greatest effect of multiple passes was observed in the swell, Bagley correction factor and ESCR properties. Similar to the first set, the change in viscosity, as measured with the capillary rheometer, showed little effect regardless of the material. However, the complex viscosity at the lower frequencies and the elongational viscosity, as determined from the Bagley correction factor, did show some effect from multiple passes.

As discussed in section 7.1, swell represents a recovery of stored elastic energy. The results of the second set show that the normalized swell ratio index decreases with extrusion passes and the polydispersity index increases with extrusion passes for all resins. The molecular structure, in particular molecular weight and long chain branching have a profound effect on the swell characteristics but to date there is no consistent theory to explain the relationships.

Early investigations into the phenomenon of swell showed that HDPE appeared to behave in a similar fashion to polystyrene (PS) where an increase in the breadth of the MWD of PS produced an increase in swell. However, work by Mendelson (1975) showed that there was some doubt as to the strength of the relationship in the case of HDPE. This study led to an investigation by Shroff and Shida (1977) which attempted to explain the anomalous work of Mendelson. The conclusions of this work are best described by a direct quote from the final sentence:

> " ... Thus the effect of increasing MW is opposite of broadening MWD such that when polymers vary in both MW and MWD, die swell and compliance may decrease or increase depending on whether increase in MW is predominating or whether effect due to broadening of MWD is predominating."

Shida's earlier work with Nakajima (1966) did not study the relationship between MWD and swell rather they examined the mechanism of swell in terms of elastic recovery. In their study, they used 2 resins. The first was a Phillips based HDPE and the other was the same resin passed through an extruder 3 times at 240 °C, not unlike the first set of experiments done in this work. The technology at the time suggested that for this Phillips catalyst resin the re-extrusion process caused preferential chain scission. This was thought to reduce the higher molecular weight fractions without increasing low molecular weight components and it was also suspected that a small amount of long branches were created. This statement is in direct contrast to the conclusions of Moss and Zweifel (1989). The conflicting evidence in these papers show that a generalized link between swell, MWD and MW and the degradation of HDPE would probably not be a useful exercise. Taking into consideration these past studies, an analysis on swell mechanisms relative to changes in molecular structure resulting from multiple passes, should be done for a specific resin and take into account the primary polymerization process, the predominant degradation mechanism, and the effect of residual components in the resin i.e. pigments, dirt etc.

The results of the sag study provided a unique opportunity to study the changes in melt strength. Sag in blow moulding is best described as the extension of the molten parison due to gravitational force. Any variance in the sag properties of a resin will have a direct effect on the shape and physical characteristics of the bottle.

However crude the sag measurement was, the observed changes with multiple passes is evidence that some higher MW material in the copolymer is lost while some chain lengthening occurs in the homopolymer and natural PCR. Previously reported work on polyethylene used in blown film has shown an exponential relationship between melt strength and the zero shear viscosity, η_0 (Ghijsels, 1990). As η_0 increased the melt strength increased and it was found that

$$\text{melt strength} = k\,\eta_0^{1/3.4} \tag{34}$$

A link was made between the melt strength and average molecular weight because of the known relationship between η_0 and $\overline{MW}$ where

$$\eta_o \sim \overline{MW}^{3.4} \tag{35}$$

From this link it was concluded that the melt strength was directly proportional to $\overline{MW}$. In a later study on the melt strength of polypropylene, another polyolefin, the same relationship was reported (Ghijsels, 1994).

The findings in these 2 studies are consistent with results of the sag study and changes in the low frequency complex viscosity observed in this work. It has been established that chain scission is the dominant degradation mechanism in the copolymer resin and crosslinking dominates the modification of the homopolymer. The drop in low frequency complex viscosity and sag for the copolymer and increase for the homopolymer, after 4 extrusion passes, could then be attributed to a reduction in the $\overline{MW}$ of the copolymer and an increase in $\overline{MW}$ for the homopolymer. The natural PCR behaves much like the homopolymer and this provides more evidence that this material is primarily composed of homopolymer resin. On the other hand, as discussed earlier, the mixed colour bottle appears to behave more as a composite of copolymer and homopolymer material. The relatively small change in the sag for this material would lead to the conclusion that neither degradation mechanism is dominant in this resin.

The observations of the change in the PI provides a relative measure of the changes in the MWD. The change in the position and slope of the loss modulus curve may provide some evidence of the nature of the broadening of the distribution. The general increase in PI, driven by a drop in G_c, shows a broadening of the MWD for all materials. The inconsistent behaviour of the copolymer, relative to the other 3 resins would indicate that, while the MWD is broadening, the average MW is decreasing for the copolymer and increasing for the homopolymer and natural PCR. This observation provides some explanation on the change in the sag behaviour of the 4 resins. As the average MW decreases the resistance to sagging decreases, as occurred with the copolymer, while the opposite occurred with the homopolymer and natural PCR. The mixed colour average MW would have changed very little and as reported, the sag also changed very little.

From the thermal analysis, the decline in melt temperature from 0 to 4 passes is consistent with the previous discussion on the broadening of the MWD. The higher melt temperature and higher maximum endothermic temperature of the homopolymer / natural PCR distinguishes between their more linear nature and the slightly branched characteristics of the copolymer / mixed colour PCR. The decrease in crystallinity suggests that there is some decline in the very low molecular weight material which tends to conform easier to a crystalline structure. This material may be consumed in the oxidation process and is most likely be burned off with each pass.

The DSC measurement is very sensitive to the last cooling cycle experienced by the resin and the double heating cycle was done to remove any historical cooling effects. In essence, all of the samples were exposed to the same final thermal history. Operator input can contribute significantly to the variance in the measurements, especially the percentage crystallinity which is determined from a baseline established by the operator. Finally, the presence of inorganic fillers, such as pigments or contaminant, can also adversely affect DSC measurements. In the case of the PCR materials, the small sample size, operator variance and the greater degree of inorganic material present in the sample could explain the relatively large change in crystallinity and relatively small change in maximum endothermic temperature and heat flow compared to the virgin resins, which would tend to be more homogeneous polymeric material.

The magnitude of the changes in extrusion performance were quite low and arguably may be insignificant but there may be some molecular based explanation for the behaviour of the different materials. The increase in pressure drop for the homopolymer / natural materials is consistent with a material that is undergoing crosslinking while the drop in pressure for the copolymer suggests a loss of higher molecular weight material through chain scission. The lack of change in pressure drop for the mixed colour PCR is similar to the observations from the sag study. In effect, the amount of crosslinking is offset by a similar degree of chain scission, resulting in little change in the extrusion performance.

In many applications the ESCR property is a crucial performance requirement. The large decrease associated with the virgin copolymer can have a significant impact on the suitability of using this material, in the original primary application, after 4 passes. The high ESCR performance of this material is based on the high MW fraction and short chain branching, which is directly attributed to the presence of the copolymer. The interlamellae interaction of the high MW chains provides a strong resisting force to the cleaving action associated with stress cracking in an aggressive media. As the high MW chains are consumed during chain scission the resistance to cleaving also declines and the ESCR drops. The other materials do not have as large amount of high MW material initially and as result do not have as high initial ESCR. At the same, in earlier sections it has been suggested that crosslinking is occurring in the other materials. Crosslinked material tends to produce a rigid structure which is brittle. An increase in brittleness tends to lead to a decrease in ESCR because of a greater number of microvoids and larger surface area exposed to the aggressive media. Both the ESCR and the tensile properties, studied in the first set of experiments, are sensitive to the forming process in terms of part shape and cooling rate and can have a large variance in the data. The drop in ESCR for the copolymer is significantly larger than the variance.

7.3 Modelling multiple extrusion effects on a virgin copolymer HDPE

The effect of extrusion passes on the properties of the virgin copolymer resin, compared to the other materials, was not completely unexpected. The previously reported work by Moss indicated the nature of the effect of multiple pass degradation on the MWD for a Ziegler catalyst based material. There is nothing reported in the literature on how multiple pass degradation could be modelled. In this work the polydispersity index, extrusion pressure and ESCR F50 were compared against extrusion passes . A summary of the data is given in Table 7.1. Plots of the PI and F50 versus extrusion passes are shown in Figure 7.1.

Table 7.1 Multiple pass data for virgin copolymer

Pass	PI	ESCR F50	extrusion press. MPa
0	3.16	90	-
1	3.58	48	12.37
2	4.26	24	12.23
3	4.60	11	11.97
4	4.46	19	11.89

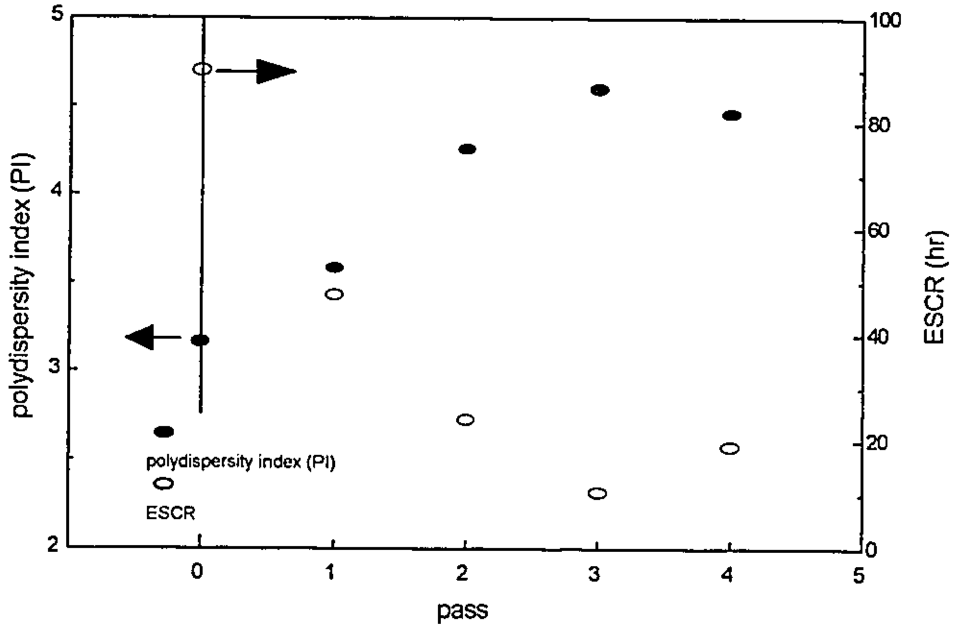


Figure 7.1: Polydispersity and ESCR versus pass for virgin copolymer

The ESCR data follows an exponential decay function of the form:

$$F(p) = e^{(-Ap + B)} + C \tag{36}$$

where F(p) is the F50 failure function, p is the extrusion pass, A is a decay constant, B is the 0 pass F50 constant and C is the asymptotic minimum 50% failure. The function was fitted to the data using the following assumptions:

i) at $p = 0$, $F(0) = F_{max}$

ii) C = 10% < minimum observed F50 at 4 passes

iii) by setting $p = 0$ and using C, B is solved at F(0)

iv) by setting $p = 4$, A is solved at F(4)

In the case of the copolymer, if

$F(0) = 90 \quad F(4) = 19 \quad C = 10$

the resulting function is

$$F(p) = e^{(-0.766p + 4.3)} + 10 \tag{37}$$

or

$$F(p) = 73.7e^{(-0.766p)} + 10 \tag{38}$$

Similar to the ESCR data, there is an apparent exponential growth relationship between PI and the number of extrusion passes. A logarithmic function of the form

$$PI(p) = A \ln(p+1) + PI_0 \qquad (39)$$

was fitted to the data where, PI(p) is the polydispersity index function, p is the extrusion pass, A is the MWD growth constant and PI_0 is the initial PI. The term (p+1) was used to ensure that at p = 0 the function was defined (i.e. ln(0) = undefined). Using the same approach as used for F(p) and the data in Table 6.6, the following function was determined,

$$PI(p) = 0.95\ln(p+1) + 3.2 \qquad (40)$$

This function approaches an asymptotic value and shows that there is a limit to the broadening of the distribution.

If the 2 equations are examined from a scientific perspective there is some support for using an asymptotic decay function, for the ESCR, and an asymptotic growth function for the polydispersity index. It is known that a high variance is possible with this test but the decrease in the F50 or median value in this case, is greater than the variance. The ESCR data in Figure 7.2 for this resin shows that a substantial amount of the effect from the multiple pass degradation damage occurs within the first 2 passes and then a limit may be reached at passes 3 and 4.

A limiting function is feasible for the ESCR because within any molecular structure a minimum level of resistance to stress exists. If the limit

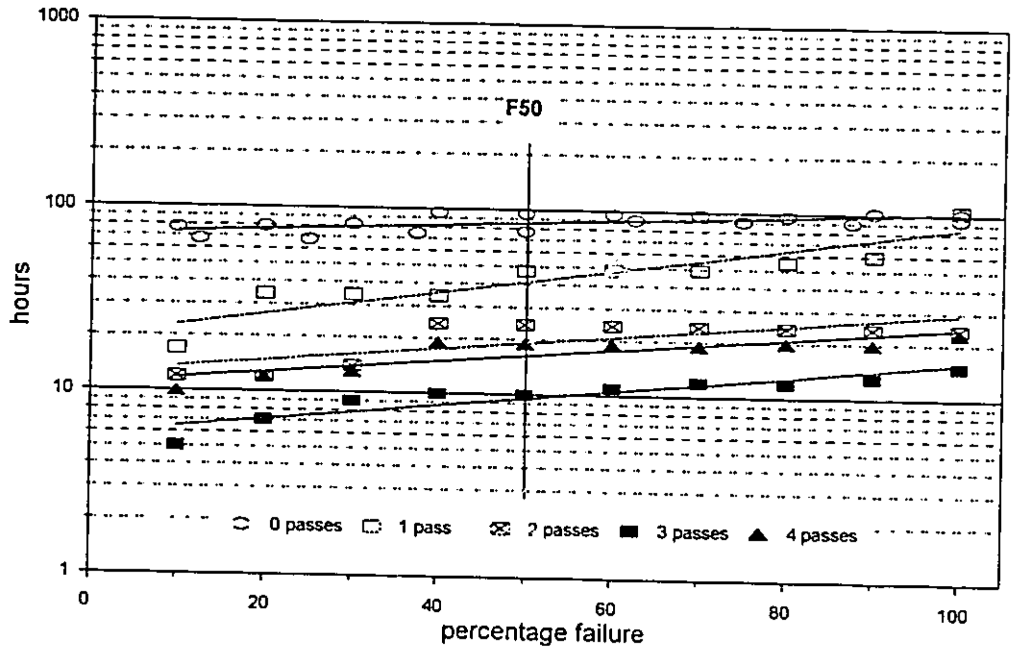


Figure 7.2: ESCR F50 multiple pass data for virgin copolymer

were 0 hours it would imply that the material would reach such a brittle state that it could not resist any deformation. It follows that the amount and severity of the degradation would have to reach a point where there is virtually no physical integrity to the molecular structure. Essentially, the material would be oxidized and not even capable of being extruded and blow moulded into any form. The same rationale could be applied to the limiting growth function for the PI. If there is not a limit, the logical extension is that all of the molecular chains could be reduced to an infinite number of chains of very short length. This argument is weak when considering the random and competitive nature of the degradation process. If the findings of Moss are applied and the primary degradation mechanism for this resin is chain scission, then with time, sites become available for chemical reactions and either branching or crosslinking may occur amongst the fractured chains. Therefore, in this instance, while an increase in the PI occurs within the first 3 passes the slight drop in PI at the fourth pass may indicates that a threshold limit may be reached and the chain scission mechanism is no longer the dominant degradation process. This result is consistent with the findings of Moss.

The reduction in extrusion pressure drop is less than 4% over 4 extrusion passes but there is a strong negative correlation (-0.98) between the pressure drop and passes for this particular resin. This relationship must be explored carefully because a number of factors can contribute to a change in pressure. In section 6.1.4, the change in pressure drop for the homopolymer was shown to be strongly dependent on the temperature and screw speed and had little dependence on the number of extrusion passes. In the second set of experiments the extruder setpoints were fixed. Therefore, a change in pressure drop would have to be associated with some structural change. A broadening of the distribution resulting from a predominantly chain scission degradation mechanism would lead to a decrease in pressure drop. This would result from the shorter, lower molecular weight chains tending to disentangle and conform to the flow regime easier than the longer, high molecular weight chains.

It cannot be assumed that either of the 2 functions, F(p) or PI(p) could be used as general functions for all HDPE blow moulding bottle resins especially if the degradation mechanism is different. The copolymer resin consistently displayed tendencies which support the theory that chain scission is the dominant degradation mechanism. The homopolymer and natural PCR exhibit a behaviour that is typical of material which is crosslinking and an entirely different model describing the relationship with multiple passes may have to be developed. The objective of this expansion of the original study was to roughly assess whether a model was plausible and had some theoretical basis for a more intensive investigation. It is apparent from the above analysis that there is justification for future work.

7.4 Statistical analysis of the response system

The objective of the experimental plan for this work was to extract as much information with a minimum number of experiments. An examination of the interdependent relationships between variables was an integral part of the plan and the following analysis explores these relationships from a statistical perspective.

There were no replicated runs but each measurement for a response was repeated at least twice and in most cases 5 times. This was done to obtain a measure of the measurement system variance. In the following presentation of the results only average values for each response are considered.

7.4.1 Statistical analysis of experimental set 1

A list of the responses used in the statistical analysis for the first set and their associated short forms is given in Table B-9. Included in the table is a summary of the analysis of variance (ANOVA), for all responses, done using the MINTAB software package. A factor's effect on a particular response, exclusive of any interactions, is expressed in terms of its level of significance (i.e. 1%, 5% and 10%) from a simple F-test. Initially, all main effects and interactions were studied for their statistical significance. It was found for all responses, except the extrusion pressure response, there were no interactions significant to less than $\alpha = 5\%$. Therefore, the interaction effects were pooled into the experimental error and the ANOVA was repeated.

In the extrusion pressure case, the temperature/extrusion shear interaction was significant to $\alpha = 5\%$ and was retained in the second ANOVA. Keeping this interaction in the ANOVA is scientifically plausible. As the temperature increases at a given extrusion shear rate, the pressure tends to decrease because of the temperature dependence of the polymer viscosity.

The outcome of the second ANOVA only is presented in Table 9. The swell ratio and power law coefficient responses were the only ones which showed a significant effect from extrusion passes. The UTS properties also had a significant effect from the number of passes but also had large sample variances within runs (in Table B-9, * - denotes a large within sample variance). The complete set of observed values for the responses for the designed experiment are given in Table B-10.

From the correlation matrix in Table B-11, over 11 pairs of variables, roughly 10%, of the possible combinations, showed at least a weak relationship (i.e. >70% correlation coefficient). This provided some evidence that using ANOVA as the primary analytical tool may miss the relationships that exist amongst the responses themselves.

Principal component analysis (PCA) allows for the rapid identification of those responses which are significantly influenced by a change in the levels of factors or conversely, identify those responses which indicate a change in a factor. A summary of the results of the PCA for the first set of experiments is provided in Tables B-12 to B-14. In Figure 7.3 a plot of the values of the characteristic roots of the principal components (PC's) and their cumulative contribution to the total experimental variance are shown. Eight of the possible 13 PC's accounted for 99% of the variance with the first 3 alone accounting for 80%.

Examination of the first PC (Figure 7.4 a) shows a strong positive influence from the change in the swell ratios, UTS, and high shear

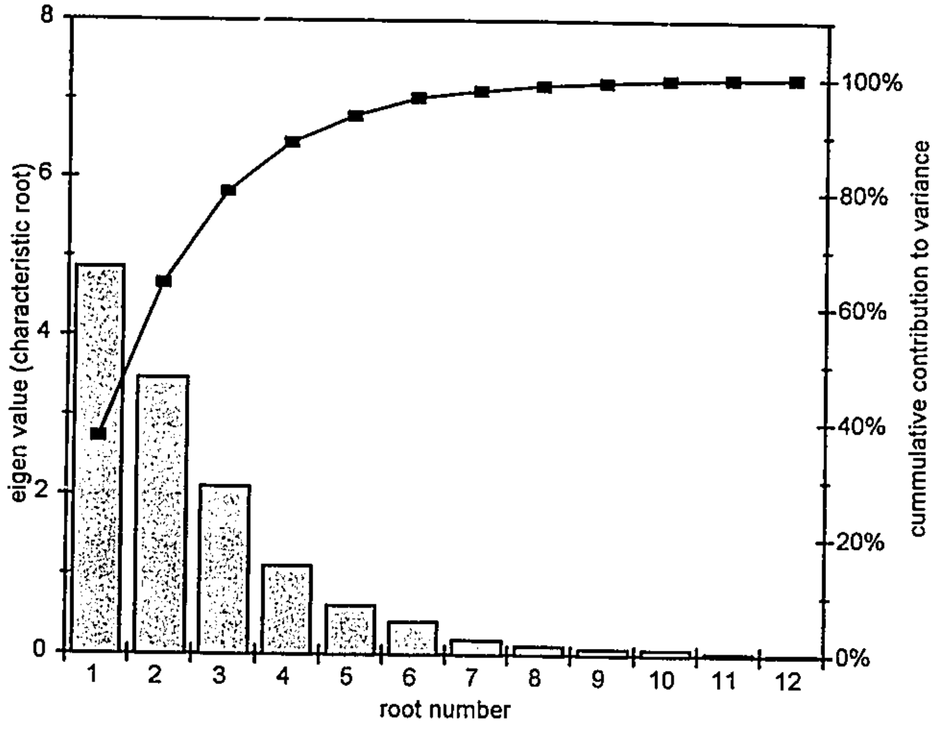
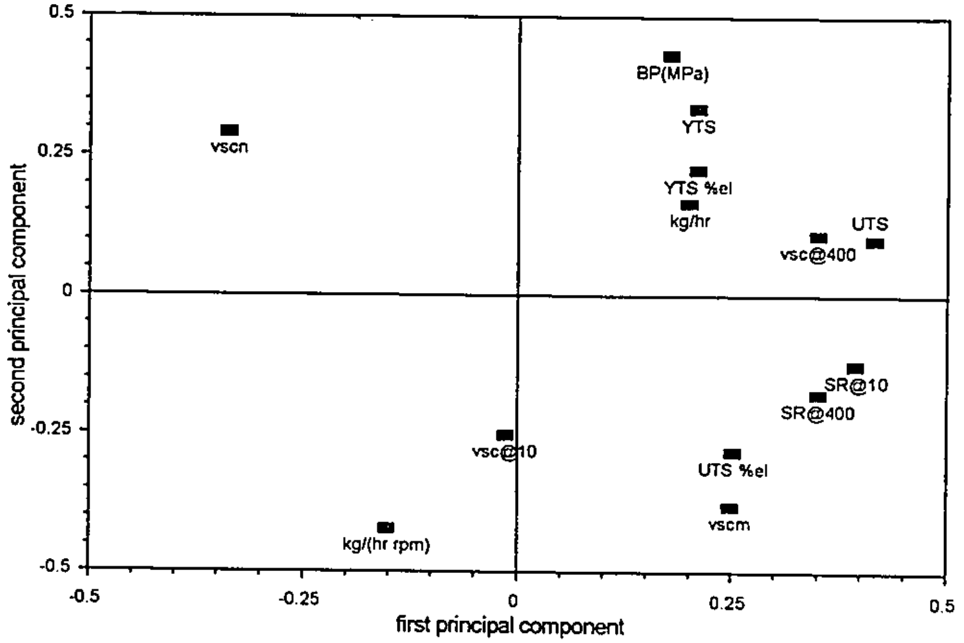
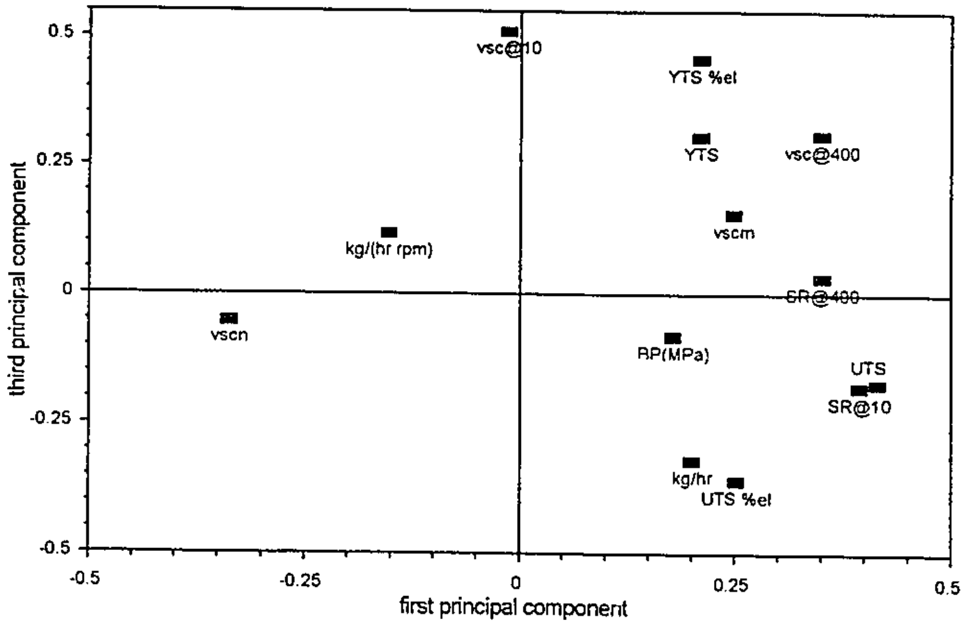


Figure 7.3: Characteristic root plot of principal components for experiment 1

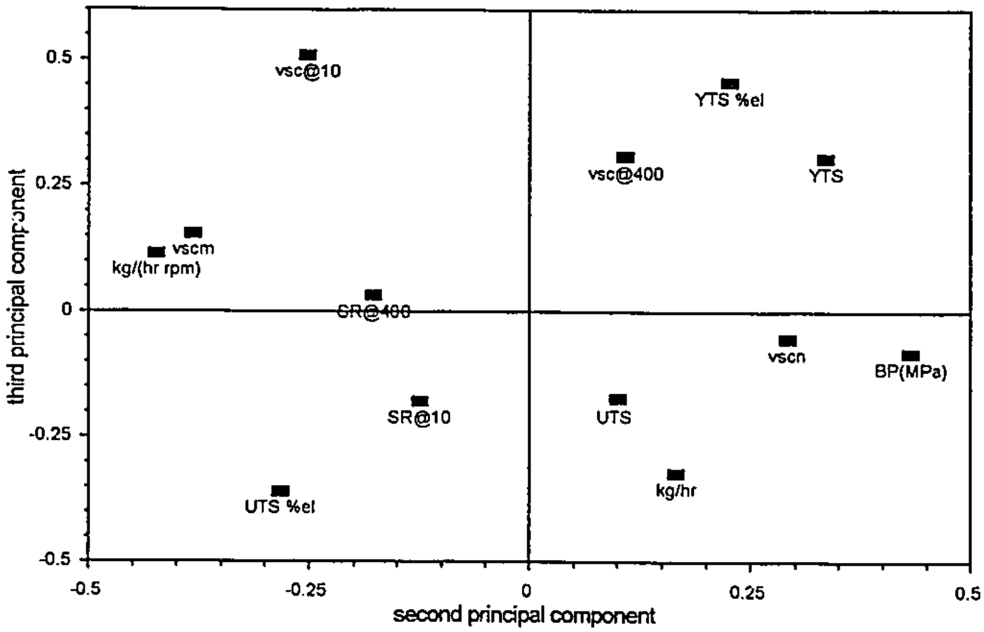


a) second versus first principal component



b) third versus first principal component

Figure 7.4: Scatter plots of experiment set 1 principal components



c) third versus second principal component

Figure 7.4 (cont.): Scatter plots of experiment set 1 principal components

viscosity, and a negative influence from the power law index. The second PC was positively influenced by the extruder pressure drop (BP) and negatively by the extrusion efficiency and power law coefficient responses. In Figure 7.4 b), the low shear viscosity and elongation at UTS have the greatest effect on the third PC.

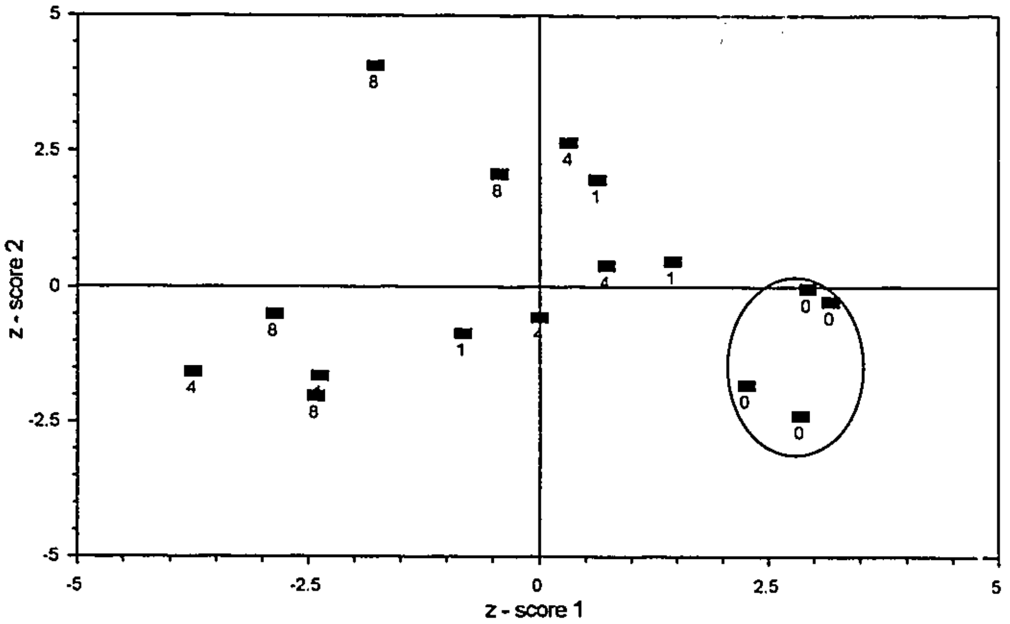
The PC's are used to generate new uncorrelated responses and these are referred to as the loadings or z-scores. Many different variations are used to calculate the loadings and in the MINITAB statistical package used for this study the following equation is used:

$$z_{ik}=\sum\frac{(y_{ij}-\bar{y}_j)}{s_j}PC_{jk} \qquad (41)$$

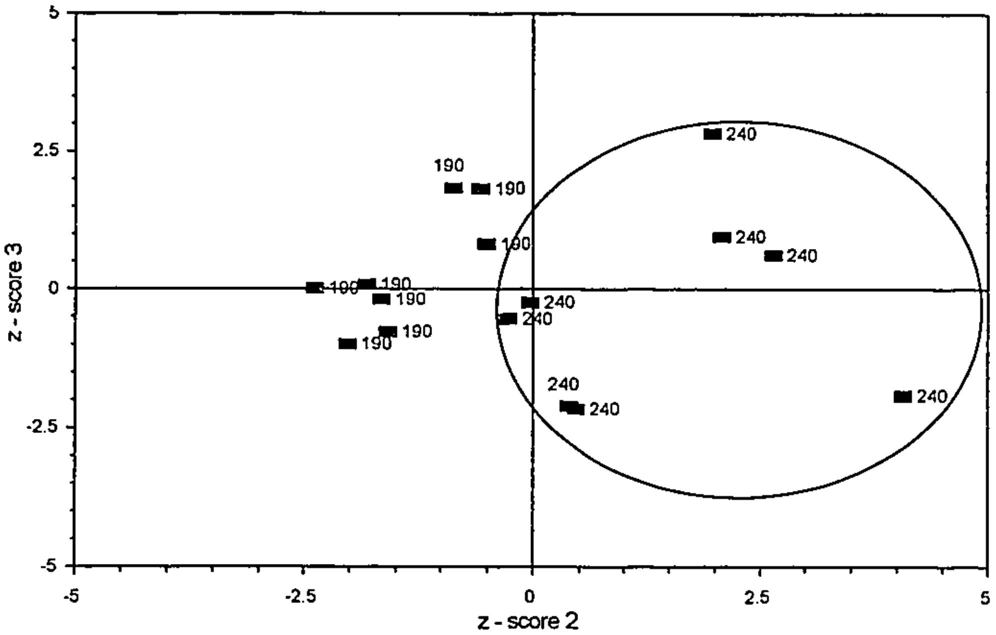
where i is the experimental run number, j is the response variable number, k is the principal component number, y_{ji} is an observed response, $\bar{y}_i$ and s_j are the average and standard deviation of a response, for all experimental runs, and PC_{jk} is the principal component associated with the response (MINITAB ref manual, 1989) (see sample in Table A-3).

A scatter plot of the loadings for the first two PC's are shown in Figure 7.5 a). The loading for first PC shows a definite distinction between the virgin, 0 pass material, and the other passes but there is no apparent break between the other passes. The clustering for the loadings of the second and third PC's are shown in Figure 7.5 b) and c). The second PC loading, z_2, shows the difference between the 2 levels of temperature. The combination of z_2 and z_3 shows that the transformed variables cluster into the 4 combinations of extrusion temperature and extruder speed.

While separating the analysis of the PC's and the loadings is useful, the power of PCA is in the consolidation of the 2 analysis. As discussed previously, the first PC shows that in the total response system, extrusion passes accounts for roughly 37% of the total variance and the primary responses contributing to this variance are the swell ratio, power law index and the UTS. Similarly, the second PC which is associated with a further 27% of the variance, is associated with the temperature factor

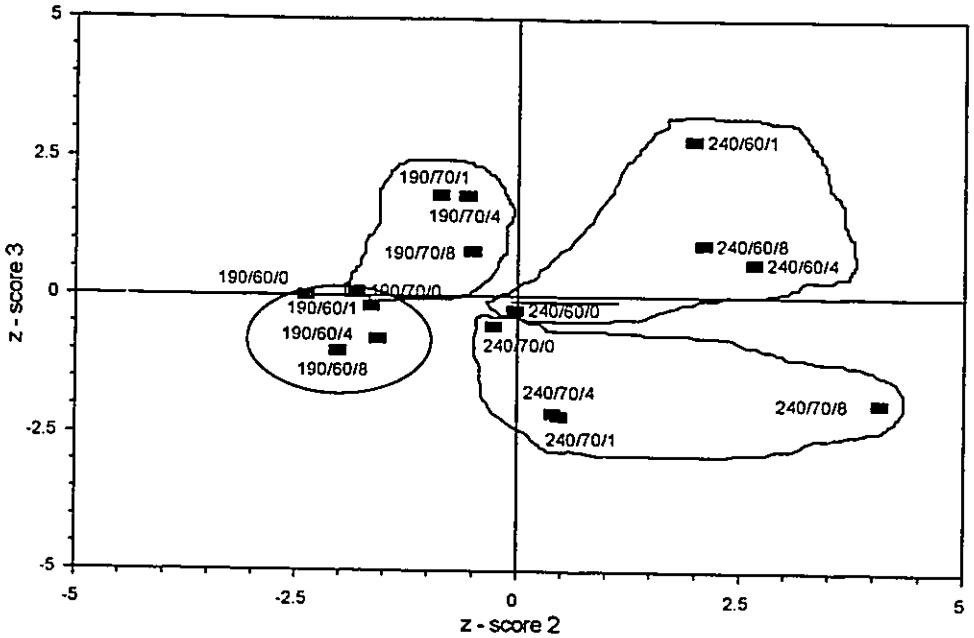


a) Z_2 versus Z_1



b) Z_3 versus Z_2 (temperature effect)

Figure 7.5: Principal component loadings for experiment set 1



c) Z_3 versus Z_2 (temperature / extruder speed combined effect)

Figure 7.5 (cont.): Principal component loadings for experiment set 1

and this effect is identified with the change in output efficiency and extruder pressure difference. The second and third PC loadings together, show a separation between the temperature/extrusion speed combinations. This distinction between experimental run combinations is measured by the effect on the low shear viscosity, YTS, elongation at YTS and elongation at UTS, which are at the extremes in 3 quadrants of the PC 3 versus PC 2 plot (Figure 7.4 c). There were no identifiable patterns or clustering amongst the other loadings or PC's , which account for 20% of the variance. This implies that these PC's can be attributed to noise or unexplained variance in the system of responses.

7.4.2 Statistical analysis of experiment set 2

Similar to section 7.4.1, a reference list of the short form notation used in the PCA for this data set and a summary of the level of significance for each response from the ANOVA is given in Table B-11. The responses for the designed experiment are given in Table B-12. From the correlation matrix (Table B-13), over 20 pairs of variables, roughly 15%, of the possible combinations showed at least some relationship (i.e. >70% correlation coefficient). As in the first set of experiments, this provided some evidence that PCA may be a better screening tool than ANOVA.

The statistical analysis of the rheology data was reduced to the low shear complex viscosity (0.2 Hz), high shear viscosity ($\dot{\gamma}$ = 400 s^{-1}), the power law coefficient and index and the elongational viscosity at a strain rate of 5 s^{-1} and 50 s^{-1}. As reported in section 6.2.3, the Bagley correction factors, for each set of experimental conditions, was reduced to an average Bagley correction factor.

A single parameter for the swell ratio was derived from the normalized swell ratio data to provide a unique measurement for the statistical analysis. Linear regression was used to fit a simple equation to all of the normalized data for a given set of experimental conditions. From the results of the regression a swell ratio index (SWRI) was derived from the equation, where

$$t_{L/D,\ \text{shear rate}(\dot{\gamma})} = \beta_0 + \beta_1\dot{\gamma}\text{; at a given pass} \quad (42)$$

$$\text{SWRI}_{\text{pass}} = \frac{\beta_0}{\beta_1} \quad (43)$$

Though a potential correlation could exist amongst many of these responses, each is associated with a different characteristic of a resin's viscoelastic properties that could be affected by multiple extrusions.

In Figure 7.6 the Eigenvalues for first 7 PC's and their contribution to the total variance are shown. The first 3 PC's contribute over 80% to the overall variance in the system. Scatter plots of the second and third

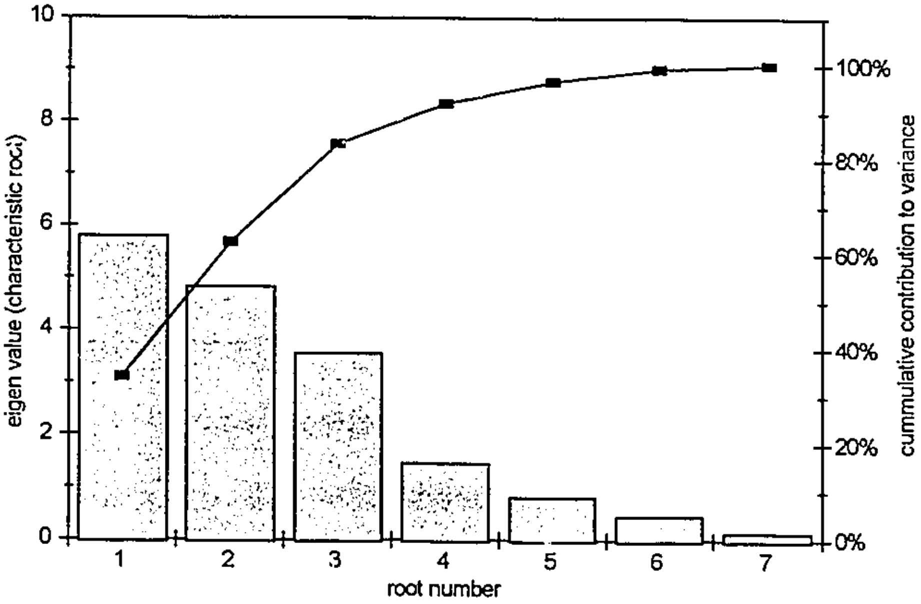
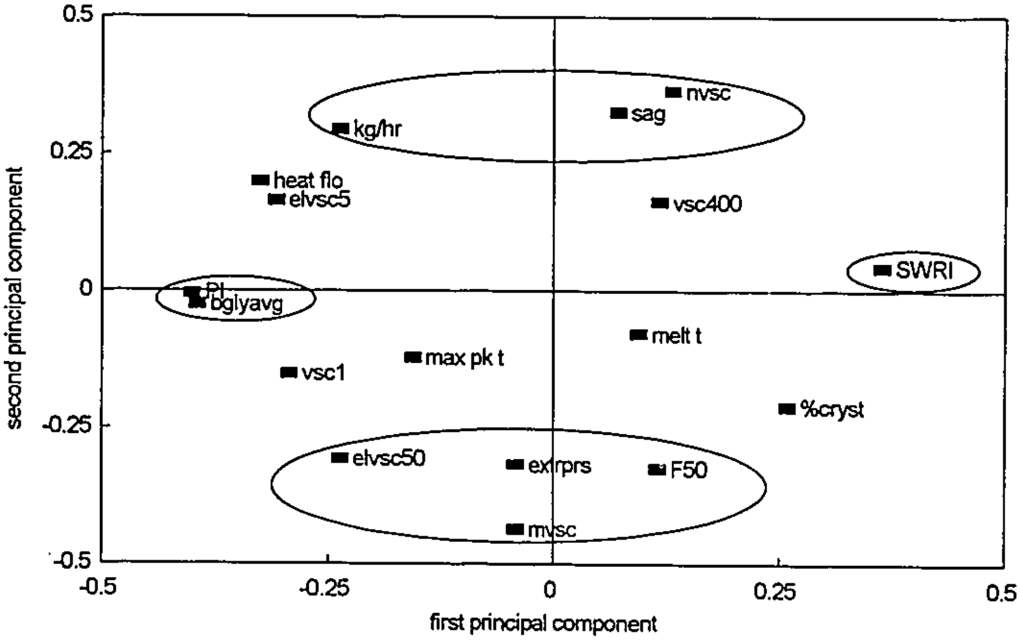


Figure 7.6: Characteristic root plot of principal components for experiment 2

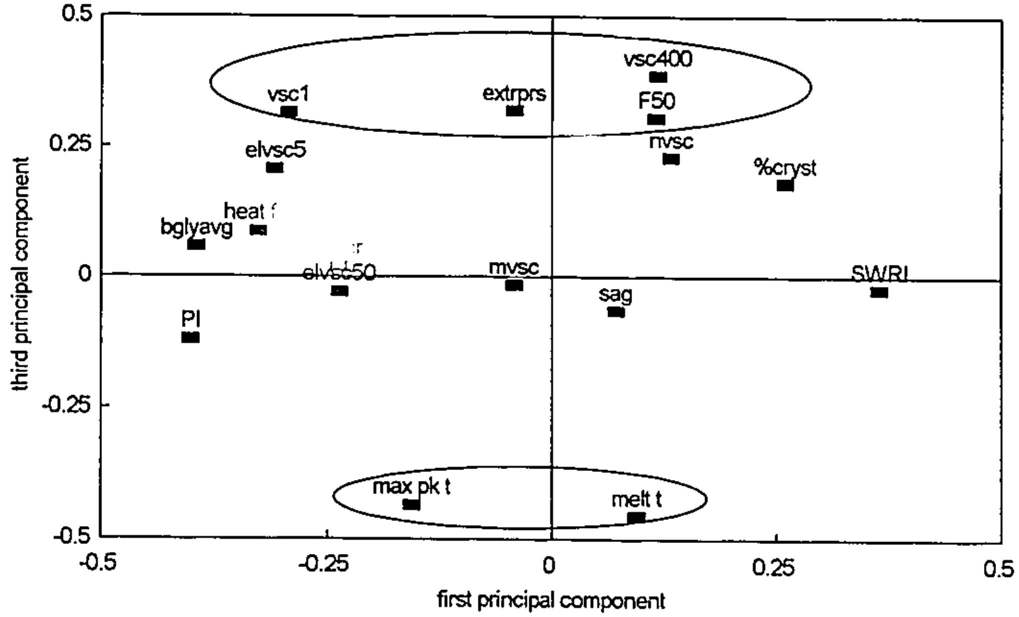
principal components versus the first principal component were generated (Figure 7.7).

From Figure 7.7 a), the first PC is strongly influenced by the change in the swell ratio, the Bagley correction factor (bglyavg) and polydispersity index (PI). This PC accounted for 34% of the total variance in the experiment. The second PC has a strong positive effect from the change in the power law index (nvsc), extruder output (kg/hr) and sag, and a strong negative effect from the change in the extrusion pressure (extprs), ESCR F50, elongational viscosity at 50 s^{-1} (elvsc50) and the power law coefficient (mvsc). In Figure 7.7 b), the third PC is negatively influenced by the peak endothermic temperature (max pk t) and melt temperature (melt t), as observed from the DSC, and positively by the low frequency complex viscosity (vsc1) and the high shear viscosity (vsc400), the F50 and extrusion pressure.

In Figure 7.8 a) a plot of the loadings for the first and second principal components, Z_1 and Z_2, is shown. From the Z_1 loading there is a clear distinction between the 0 pass or "as received" material and the same material after 4 extrusion passes. The 0 pass materials have positive Z_1 loadings and the 4 pass materials are negative.

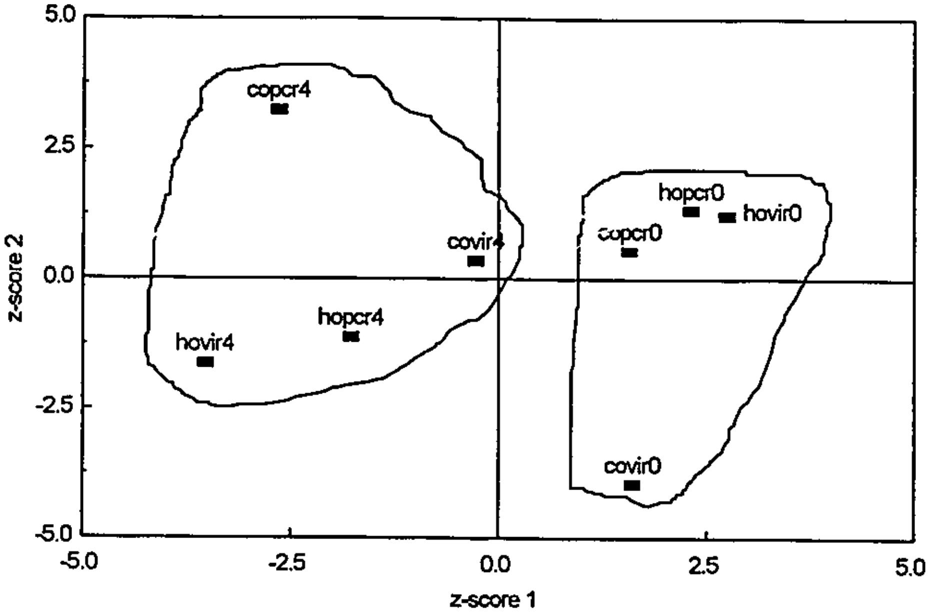


a) Second versus first principal component

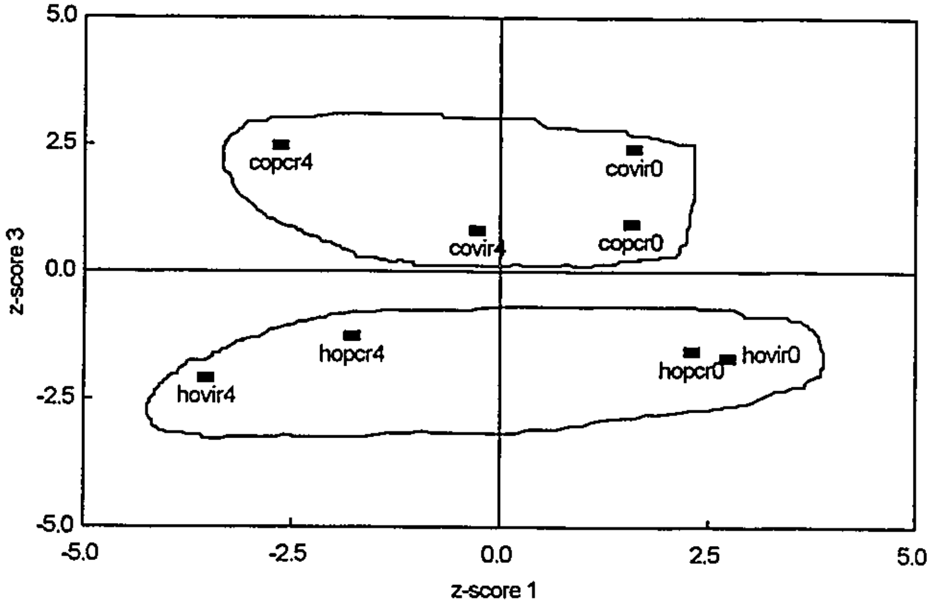


b) Third versus first principal component

Figure 7.7: Scatter plots of experiment set 2 principal components



a) Z_2 versus Z_1



b) Z_3 versus Z_1

Figure 7.8: Principal component loadings for experiment set 2
[hovir - homopolymer, virgin hopcr - natural bottle, pcr
covir - copolymer, virgin copcr - mixed colour bottle]

Analysis of Z_2 shows very little clustering which might lead to the conclusion that 28% of the variance explained by this PC is noise or experimental error. However, this would be erroneous because of the outlier loading associated with the 0 pass, copolymer virgin resin (covir0). In the previous discussion on the experimental results, it was clearly shown that this resin's properties prior to multiple extrusions and during its first pass, are unique and different from the other 3 resins. Examination of the Z_3 loadings in Figure 7.8 b) show a distinction between the homopolymer/natural PCR and the copolymer/mixed colour bottle resin systems. The homopolymer/natural PCR materials have negative loadings while the copolymer/mixed colour bottle loadings are positive.

As demonstrated in section 7.4.1, cluster analysis of principle components is done in conjunction with the analysis of their loadings. Combining the analysis of the 2 sets of diagrams in Figure 7.7 and 7.8, it could be concluded that the primary effect of multiple extrusion passes is manifested in changes in viscoelastic properties, especially swell and the Bagley correction factor, and in changes in the polydispersity index. A little finer analysis shows that the low frequency complex viscosity (vsc1), low strain rate elongational viscosity (elvsc5) and DSC heat flow (heat flo) also have a negative influence and percent crystallinity (%cryst) a positive influence on the first PC. As well, over a third of the variance in the entire response system is explained by the effect of the extrusion passes. The sag and ESCR properties and power law coefficient of the virgin copolymer is so distinct from the other materials that it is identified as an outlier in the Z_2 loadings. The differences between homopolymer/natural PCR and copolymer/mixed colour PCR are identified by the Z_3 loading and which is associated with DSC responses, in particular the melt temperature and maximum endothermic temperature.

With a complex process, such as multiple pass extrusion, which also incorporates PCR, principle component analysis takes advantage of the correlated set of interdependent variables. The use of PCA in this work provided statistical support of the conclusions drawn from the analysis of the individual responses. The scientific interdependence of some responses such as swell, the Bagley correction factor, PI, ESCR and sag was discussed in sections 7.1 and 7.2. The PCA reached the same conclusions from a data based perspective, including consideration for system variance. This finding should lead to more applications of this statistical tool in the study of plastics recycling.

Chapter 8 - Conclusions

This dissertation is a summary of a systematic study into the effect of multiple extrusion passes during recycling. In two sets of experiments the effect of multiple extrusion passes on virgin and post consumer HDPE blow moulding resin properties was examined. In general, it can be concluded that multiple extrusion passes has the greatest effect on low shear, viscoelastic properties, molecular weight distribution and, relative to a specific materials, crystallinity and environmental stress crack resistance (ESCR). However, extrusion processability, within typical manufacturing shear rates, is not greatly affected.

In the first set of experiments, a virgin homopolymer resin based on the Phillips catalyst technology was extruded through a single screw extruder and responses were recorded and analyzed at 0, 1, 4 and 8 passes. The shear viscosity curve, as measured with a capillary rheometer, showed little effect from multiple extrusion passes but a significant change in the extrudate swell ratio was observed.

In the second set of experiments, the effect of multiple extrusions on 4 different resins was studied, at a fixed set of extrusion conditions, up to 4 passes. The virgin homopolymer used in the first set was studied along with a natural PCR, virgin copolymer (Ziegler catalyst technology) and mixed colour bottle PCR. The performance of the PCR materials at the "as received" or 0 pass state differed from the virgin materials but it can be concluded that the changes they experienced during multiple passes was consistent with the changes in the virgin materials.

The Bagley correction factor and swell ratio were used to investigate changes in viscoelastic behaviour. The correction factor dropped for the homopolymer and increased for the copolymer and changed slightly for the PCR materials after 4 extrusion passes. The greatest change in swell was observed for the virgin homopolymer and natural PCR. Based on the results of this work, multiple pass studies which measure swell and viscoelastic behaviour should take into consideration primary polymerization processes and degradation mechanisms relative to a specific resin.

The elastic storage and loss modulus, G' and G", were measured and used to obtain the crossover point, G_c, which was in turn used to determine the polydispersity index (PI). The PI increased for all resins, corresponding to a broadening of MWD, with the homopolymer and natural PCR displaying the greatest change. While the G_c method is considered suitable for measuring PI, for this work it can be concluded that it was a useful measure of the relative change in MWD.

Using a differential scanning calorimeter, it was found that the PCR materials had a significant drop in percentage crystallinity with passes and the virgin resins decreased slightly. Changes in melt temperature, peak endothermic temperature and peak endothermic heat flow were not large. With the variety of materials and contaminants that could be present in PCR, the value of the DSC analysis needs further study.

The virgin copolymer exhibited a significant loss in ESCR from 0 to 4 passes, where a 70% drop was observed. The other resins had a small drop or no change in ESCR. Since the virgin coploymer material is marketed as having high ESCR, this result is a decidely significant finding. It is recommended that caution be used, particularily if ESCR is a critical product property and it is suspected that this type of copolymer resin could be a primary constituent of the PCR content.

The unique application of principal component analysis to this plastics recycling study showed that multiple pass extrusion of HDPE accounts for more variance than the difference in base resins or the source of the resin. Studying the entire system of responses using PCA provided data based evidence to support the PI, Bagley correction factor and swell ratio as the most sensitive responses to the effects of multiple extrusions.

Plastics recycling studies involving a large number of responses and correlated variables would benefit from the inclusion of PCA as part of the analytical strategy.

Social, economic and legislative pressures have increased the demand for recycled content in many products. In order to meet those demands, designers and processors of blow molded HDPE products must account for the effects of multiple extrusion passes and must know which properties are most affected. Unless some standard on the number of extrusion passes a polymer can endure, before it should leave the recycling phase, is established, plastics recycling in terms of re-extrusion will be considered an imposition as opposed to a viable, long term technology. By identifying some of the properties affected by multiple extrusion passes, which could be used in the development of standards, the results of this work have contributed to advancing plastics recycling technology.

References

Adewole, A., Dackson, K., Wolkowicz, M., "Response surface modeling in compounding recycled polyolefinic blends", proceedings of SPE-ANTEC'94, San Francisco (1994)

Akoh Y., Tabata, H., "Materials recycling in the automotive production process", International Journal of Vehicle Design, April (1985) 277

Allen, N,S., Degradation and Stabilisation of Polyolefins, Applied Science Publishers, New York (1983)

ASTM D3835-79, "Standard Test Method for Rheological Properties of Thermoplastics with a Capillary Rheometer"

ASTM D638-90, "Standard Test Method for Tensile Properties of Plastics"

ASTM D1693-80, "Standard Test Method for Environmental Stress Cracking of Ethylene Plastics"

ASTM D3536-76, Standard Test Method for Molecular Weight Average and Molecular Weight Distribution by Light Exclusion Chromatography, (GEL Permeation Chromatography)

Babinchak, S.R., "The truth about recycling post-consumer waste", proceeding of "Plastic Waste Management Recycling Alternatives" SPE-RETEC, October (1990)

Bagley, E.B., *J. Appl. Phys.*, **28**, 624 (1957)

Bagley, E., Duffey, H., *Trans. Soc. Rheol.*, **10** 299 (1966)

Basta N., Johnston, E., "Plastics recycling picks up momentum", Chemical Engineering, July (1989) 30

Beasley, J.K., "Polymerization at high Pressure", Comprehensive Polymer Science, vol. 3, Pegamon Press, Oxford (1989)

Boldizar, A., "Evaluation of repeated processing and ageing of LDPE", proceedings of Rec '93, Geneva, January (1993)

Bond, B.E., "Recycling Plastics in Akron, Ohio", proceedings of SPE - RETEC, Toronto, April (1990)

Box, G.E., Hunter, W.G., Hunter, S., Statistics for Experimenters, John Wiley and Sons, Toronto, (1978)

Brewer, G., "European plastics recycling, parts 1 and 2", Resource Recycling (1987)

Brooke, L., Kobe, G., Sawyer, C., "Recycability", Automotive Industries, September (1990)

Chen I.M., Shiah, C.M., "Producing tough PET/HDPE blends from recycled beverage bottles", Plastics Engineering, October (1989)

Christensen, R.E., Cheng, C.Y., "Processing polyolefins on single-screw extruders", Plastics Engineering, June (1991)

Cogswell, F.N., *Poly. Eng. and Sci.*, **12** 64 (1972)

Cornell, D., "Computer model for comprehensive curbside recycling", proceeding of "Plastic Waste Management Recycling Alternatives" SPE-RETEC, October (1990)

Deloitte and Touche, "Summary Report - Energy and environmental impact profiles in Canada of TETRA BRIK ASEPTIC carton and glass bottle packaging systems", Toronto (1991)

Denny, R., "Regulatory impacts on packaging in the US and recycling/reuse options", Plastic Drum Institute - SPI Spring Conference, Florida (1994)

Dole, M., Milner, D. and Williams, T., *J. Amer. Chem. Soc.*, **20**, 1580, (1958)

Ehrig, R., Plastics Recycling, Hanser, New York, (1992)

Engleman, P.V., et al, "Extrusion - compression of commingled resin blends", Plastics Engineering, February (1992)

Ezrin, M., Wyatt, D., Lavigne, G., Garton, A., "Quantification and control of contaminants in recycled HDPE", proceedings of SPE-ANTEC'94., San Francisco (1994)

Fawcett, E.W., Gibson, R.O., Perrom, M.W., Paton, J.G., Williams. E.G., Brit. Patent 471590 1937, ICI invs.; Chem. Abstr. 32, 13626 (1938)

Fleissner, M., *Agnew Makromol. Chem.*, (1973)

Gachter, R., Muller, H., Plastics Additives Handbook, Collier Macmillan Canada, Toronto (1987)

Ghijsels, A., Ente, J., Raadsen, J., *Int. Poly. Process.*, **5** p284 (1990)

Ghijsels, A., De Clippeleir, J., *Int. Poly. Process.*, **9** p252 (1994)

Gibbs, M.L., "Post consumer recycled HDPE: suitable for blowmolding?", Plastics Engineering, July (1990) p57

Goetsch, D.L., Davis, S., Introduction to total quality, Maxwell MacMillan Canada, Toronto (1994)

Hamielec, L.A., Vlachopoulos, J., "Influence of Long Chain Branching on Extrudate Swell of Low Density Polyethylene", J. Appl. Polym. Sci., **28** (1983)

Han, C.D., Rheology in Polymer Processing, Academic Press, New York (1976)

Han, C.D, Villamizar, C.A., *J. Appl. Polym. Sci.* **22** 1677 (1978)

HInsken, H., Moss, S., Paquet, J-R., Zweifel, H., *Poly. Deg. Stab.*, **34** 279 (1991)

Ishikawa, Dr. K., Guide to Quality Control, Asian Productivity Organization, Tokyo, (1980

Jackson, J.E., A User's Guide to Principal Components, John Wiley and Sons Inc. (1991)

Kelen, T., Polymer Degradation, Van Nostrand Reinhold Co., Toronto (1983)

Kenny, G.R., Bruner, R.S., "Experience and Advances in Automated Separation of Plastics for Recycling", proceedings of SPE-RETEC, Chicago (1993)

Koch, P.E., Ross, M., "Separation of PET and Aluminum", proceedings of ANTEC '90, **1457** (1990)

La Mantia, F.,Citia, V. and Valenza, A., *Poly. Degr. and Stab.*, **109**, (1989)

Laun, H.M., Munstedt, H., *Rheol. Acta,* **17**, 415 (1978)

Leaversuch, R.D., "PVC recycling - landfill fodder? It doesn't have to be.", Modern Plastics, March (1989)

Lutz, J.T., Thermoplastic Polymer Additives - Theory and Practice, Marcel Dekker Inc., New York (1989)

Lynch, M., "Drinking boxes now recyclable", Canadian Plastics, July/August (1990)

Maczko, J., "An update on commingled, mixed plastic extrusion system", proceedings of "Plastic Waste Management Recycling Alternatives" SPE-RETEC, October (1990)

McCrum, N.G., Buckley, C.P., Bucknall, C.B., Principles of Polymer Engineering, Oxford University Press, New York (1988)

McTigue, F.H., "Environmental stress cracking resistance of high density polyethylene", Plastics Technology, February (1959)

Mendelson, R.A., Finger, F.L., *J. Appl. Polym. Sci.* **19** 1061 (1975)

Meyers, G.E., Chahyadi, I.S., "Wood flour/polyppropylene composites", Inter. J. Polyer Mater., **15** (1991)

Modern Plastics International, Jan., 1991 p51-65

Modern Plastics Encyclopedia '95, mid-November (1994)

Modern Plastics, "Chlorine fingerprint", (1990)

Montgomery, D.C., Design and Analysis of Experiments - 3rd Ed., John Wiley and Sons, Toronto (1991)

Montgomery, D.C., Introduction to Statistical Quality Control - 2nd Ed., John Wiley and Sons, Toronto (1991)

Morton, M., Schafer, R., Isringhaus, Rubber Technology 3rd ed, Van Nostrand Reinhold, New York, 1987.

Moss, S. and Zweifel, H., *Poly. Degr. and Stab.*, **25**, (1989)

Nakajima, N., Shida, M., , Trans. Soc. Rhe.ol, **10** 299 (1966)

Nir, M.M., "Implications of post consumer waste", Plastics Engineering, September (1990)

NRC/SPI White Paper #2 on the SPI Resin Identification Code, Washington DC (1994)

Packaging Without Plastics, German Society for Research into Packaging Market, 1987.

"Pilot Project - Barhaven Demonstration Project", Canadian Plastics, March (1990)

Paudich, C.W., Ritzman, H.B., "Rapid identification of plastics utilizing fast NIR-spectroscopy", proceedings of ReC'93, Geneva, January (1993)

Portugués, M.M., "Situación del reciclaje de los materiales plásticos utilizados para el cultivo del banano en Costa Rica", I Coloquio de Reciclado de Plasticos, Guadalajara,Mexico, March (1994)

Rabinowitsch, B. Z., *Physik. Chem.*, **145**, 1 (1929)

Rathje, W.L., "Rubbish!", The Atlantic Monthly, December, 1989

Renfree R.W. et al, "Physical characteristics and properties of profile extrusions produced from post consumer commingled plastic wastes", proceedings of SPE-ANTEC'89, **1809** (1989)

Richardson, J.T., Projections based on presentations from the Third World Chemical Engineering Congress, Tokyo, Japan, 1986 (1989)

Salas, M., et al, "A study on the effects of fillers and reinforcements on the properties of post consumer plastic waste profiles", proceedings of SPE-ANTEC'90, **1430** (1990)

Schott, H., Kaghan, W.S., "Viscous Flow of Molten Polyethylene Resins", *J. Appl. Polymer Sci.*, **14** (1961)

Selke, S., Yam, K., Nieman, K., "Effects of additives on mechanical properties of wood fiber/high density polyethylene composites", proceedings of SPE-ANTEC'89, **1813** (1989)

Shang, S.W., *Adv. in Poly. Tech.*, **12**, (4) 389 (1993)

Shroff, R., Shida, M., "Effect of Molecular Weight and Molecular Weight Distribution on Elasticity of Polymer Melts", ANTEC (1977)

Stahle, L., Wold, S., "Multivariate Data Analysis and Experimental Design in Biomedical Research", Progress in Medicinal Chemistry, Elsevier (1988)

Summers, S.W., Mikofalvy B. et al, "Recycling vinyl packaging materials from the City of Akron Municipal Wastes", proceedings of SPE-ANTEC'90, **1422**, (1990)

Tadmor, Z., Gogos, C., Principles of Polymer Processing, John Wiley & Sons, Toronto, (1979)

Today's Generation, "Did the earth get a break today or did the public misdirect MacDonald's?", March (1991)

Tuminello, W.H., *Poly. Eng. and Sci.*, **26** (19) 1339 (1986)

Tuminello, W.H., Cudre-Mauroux, N., *Poly. Eng. and Sci.*, **31** (20) 1496 (1991)

Uxa, R., "Metal Market Conditions", 5th Annual New York State Recycling Conference, Syracuse, New York, September (1993)

Van Eijk, J., et al, "Reusable vs Disposable, A Comparison of the Environmental Impact of Polystyrene/Paper/ Cardboard/Porcelain Crockery", Dutch Ministry of Housing, Deventer, 1992.

Vink, P., Rotteveel, R.T., Wisse, J., "Ageing and recycling of plastic crates", Die Ang. Makro. Chemie, **137** (1985)

Vlachopoulos, J., "Extrudate Swell in Polymers", Rev. Dif. Beh. Mat., (1981)

Vlachopoulos, J., Horie, M., Lidorikis, S., *Trans. Soc. Rheol.* **16** 669 (1972)

Voluntary Guidelines - Plastic Bottle & Container Material Code System - Mold Modification Drawings, Technical Bulletin SPI, Jan. 1, (1989)

Waters, K., "Bottles, plastic coextrustion, multilayer and high barier", Packaging's Encyclopedia (1989)

Whelan, A., Craft, J.L., Developments in PVC Production and Processing - 1, Applied Science Publishers Ltd., London (1977)

Wilder, R.V., "How sound an investment are turnkey recycling plants?", Modern Plastics, July (1990)

Williams, J.G., Facture Mechanics of Polymers, John Wiley and Sons, Toronto (1984)

Yu, T.L., Ma, S.C., *Poly. J.*, **24** (12) 1321 (1992)

Zeichner, G.R., Macosko, C.W., "On line viscoelastic measurements for polymer melt processing", proceedings of SPE-ANTEC'82, San Francisco (1982)

Appendix A - Sample Calculations

Table A-1 Shear rate through extruder die system

assume:

$Q = 4.5$ kg/h
$\rho_m = 0.750$ g/cc
die: $R = 0.635$ cm
breaker plate: $R = 0.08$ cm

shear rate through a cylindrical die:

$$\dot{\gamma} = \frac{4V}{\pi R^3}$$

where

$$V = \frac{Q \times 1000}{\rho m \times 3600}$$

$$= 1.67 \text{ cc/s}$$

shear rate at 60 rpm (no breaker plate):

$$\dot{\gamma} = \frac{4(1.67)}{\pi(0.635)^3}$$

$$= 8.3 \text{ s}^{-1}$$

shear rate at 70 rpm (with breaker plate, 9 holes):

$$\dot{\gamma} = \frac{4(1.67)/9}{\pi(0.08)^3}$$

$$= 461 \text{ s}^{-1}$$

Table A-2 Experiment set 2 observed and theoretical pressure drop comparison using the average Bagley correction factor

Observed extrusion responses - virgin copolymer

polymer	value	calculation / reference
pass	0	
extruder output (kg/h)	5.2	(Table 6.4)
observed extruder ΔP	**12.4**	(Table 6.4)
V cc/s @ $\rho_m = 0.725$ g/cc	V	$= \frac{5.2\,(100)}{0.725\,(3600)}$ $= 1.99$

THEORETICAL PRESSURE DROP THROUGH DIE SYSTEM

n - power law index	0.38	(Table B-17)
m - power law coefficient	25493	(Table B-17)
average Bagley factor	**3.9**	(Table B-18)

Breaker Plate (9 holes) R = (1/32") 0.07938 cm, L =1 cm

pressure drop (MPa)

$$\Delta P_{BP} = 2mL\left[\frac{3n+1}{n}\,\frac{1}{\pi}\,\frac{V}{9}\,R^{-(\frac{3n+1)}{n}}\right]^{n}\frac{1}{10^6}$$

$$= 2(25493)1\left[\frac{3(0.38)+1}{0.38}\,\frac{1}{\pi}\,\frac{1.99}{9}\,0.08^{-\frac{(3(0.38)n+1}{0.38}}\right]^{.38}\frac{1}{10^6}$$

$$= 8.1$$

entrance loss

$$\Delta P_e = \Delta P_{BP} \times \frac{n_B}{2\,L/R}$$

$$= 8.1\left(\frac{3.9}{2(1/0.08)}\right)$$

$$= 1.3$$

Reservoir R = (1/2") 1.252 cm, L = 2.81 cm

pressure drop (MPa)

$$\Delta P_{Res} = 2mL\left[\frac{3n+1}{n}\,\frac{1}{\pi}\,V\,R^{-(\frac{3n+1)}{n}}\right]^{n}\frac{1}{10^6}$$

$$= 2(25493)2.81\left[\frac{3(0.38)+1}{0.38}(1.99)\,2.81^{-\frac{(3(0.38)n+1}{0.38}}\right]^{.38}\frac{1}{10^6}$$

$$= 0.1$$

entrance loss

$$\Delta P_e = \Delta P_{Res} \times \frac{n_B}{2\,L/R}$$

$$= 0.1\left(\frac{3.9}{2(2.81/1.252)}\right)$$

$$= 0.1$$

Table A-2 (cont.) Experiment set 2 observed and theoretical pressure drop comparison using the average Bagley correction factor

Die R = (1/4") 0.635 cm, L = 3.81 cm

pressure drop (MPa)

$$\Delta P_{Die} = 2mL\left[\frac{3n+1}{n}\frac{1}{\pi}V\,R^{-(\frac{3n+1}{n})}\right]^{n}\frac{1}{10^6}$$

$$= 2(25493)3.81\left[\frac{3(0.38)+1}{0.38}\frac{1}{\pi}(1.99)\ .635^{-\frac{(3(0.38)+1)}{0.38}}\right]^{.38}\frac{1}{10^6}$$

$$= 0.8$$

entrance loss

$$\Delta P_e = \Delta P_{Die} \times \frac{n_B}{2\,L/R}$$

$$= 0.8\left(\frac{3.9}{2(3.81/0.635)}\right)$$

$$= 0.3$$

Theoretical dP

$$\Delta P_{theor} = \sum \Delta P$$

$$= (8.1 + 0.1 + 0.8)$$

$$= 9.0$$

Bagley corrected dP

$$\Delta P_{Bgly} = \sum \Delta P_e$$

$$= (1.3 + 0.1 + 0.3)$$

$$= 1.7$$

Total Corrected Theoretical

$$\Delta P_{corr} = \Delta P_{theor} + \Delta P_{Bgly}$$

$$= 9.0 + 1.7$$

$$= 10.7$$

difference from observed

$$\Delta P_{diff} = \Delta P_{observed} - \Delta P_{theor}$$

$$= 12.4 - 10.7$$

$$= 1.7$$

% difference from observed

$$\%diff = \frac{\Delta P_{diff}}{\Delta P_{observed}}$$

$$= \frac{1.7}{12.4}$$

$$= 13\%$$

Table A-3 Loading calculation for experiment set 1 PCA

loading formula (equation 40)

$$z_{ik} = \sum \frac{(y_{ij} - \bar{y}_j)}{s_j} PC_{jk}$$

z_{11} calculation
(data taken from Table B-10
and Table B-14, loading in
Table B-13)

$$z_{11} = \frac{(\text{vsc@10}_1 - \text{vsc@10 avg})}{\text{vsc@10 st. dev.}} PC_{11} + \ldots + \frac{(BP_1 - \text{BP avg})}{\text{BP st. dev.}} PC_{1\,13}$$

$$= \frac{(2953 - 2965)}{117}(-0.013) + \ldots + \frac{(2.20 - 8.61)}{6.81}(0.179)$$

$$= 2.859$$

Appendix B - Raw Data Tables

Table B-1 Experimental set 1 viscosity data (60 rpm, 190 °C)

	Barrel diameter -				Capillary die dimensions -				
	0.375	in	9.525	mm	Length	1.2	in	31.7	mm
60/190					Diameter	0.052		1.321	
Pass No.	shear rate sec^{-1}	load lb	N	std	shear stress kPa	apparent viscosity Pa s	power law index	corrected shear rate sec^{-1}	viscosity Pa s
0	13	75	334		49	3752	0.48	17	2953
	40	137	609	3.8	89	2227	0.48	51	1753
	133	238	1059	2.9	155	1164	0.48	169	916
	400	383	1702	5.0	249	622	0.48	508	489
1	13	80	356	7.1	52	4002	0.46	17	3082
	40	129	574	3.5	84	2097	0.46	52	1615
	133	230	1023	7.6	150	1125	0.46	173	866
	400	368	1635	3.5	239	597	0.46	519	460
4	13	78	347	7.1	51	3902	0.43	17	2930
	40	126	560	5.1	82	2048	0.43	53	1538
	133	225	1001	0.0	146	1100	0.43	177	826
	400	350	1557	3.5	228	569	0.43	533	427
8	13	80	354	3.5	52	3977	0.44	17	3009
	40	126	560	3.5	82	2048	0.44	53	1550
	133	223	990	0.0	145	1088	0.44	176	823
	400	355	1579	3.5	231	577	0.44	529	437

Table B-1 (cont.) Experimental set 1 viscosity data (60 rpm, 240 °C)

	Barrel diameter -				Capillary die dimensions -				
	0.375	in	9.525	mm	Length	1.2	in	31.7	mm
60/240					Diameter	0.052		1.321	
Pass No.	shear rate sec^{-1}	load lb	N	std	shear stress kPa	apparent viscosity Pa s	power law index	corrected shear rate sec^{-1}	viscosity Pa s
0	13	75	334		49	3752	0.48	17	2953
	40	137	609	3.8	89	2227	0.48	51	1753
	133	238	1059	2.9	155	1164	0.48	169	916
	400	383	1702	5.0	249	622	0.48	508	489
1	13	79	351	1.4	51	3952	0.47	17	3092
	40	130	578	0.0	85	2113	0.47	51	1653
	133	235	1045	7.1	153	1149	0.47	170	899
	400	378	1679	3.5	245	614	0.47	511	480
4	13	78	345	3.5	50	3877	0.48	16	3061
	40	135	601	3.5	88	2195	0.48	51	1733
	133	239	1063	1.4	155	1169	0.48	168	923
	400	385	1713	3.5	250	626	0.48	507	494
8	13	78	345	3.5	50	3877	0.46	17	3011
	40	133	589	3.5	86	2154	0.46	52	1673
	133	235	1045	7.1	153	1149	0.46	171	892
	400	373	1659	0.0	243	606	0.46	515	471

Table B-1 (cont.) Experimental set 1 viscosity data (70 rpm, 190 °C)

	Barrel diameter -				Capillary die dimensions -				
	0.375	in	9.525	mm	Length	1.2	in	31.7	mm
70/190					Diameter	0.052		1.321	
Pass No.	shear rate sec^{-1}	load lb	N	std	shear stress kPa	apparent viscosity Pa s	power law index	corrected shear rate sec^{-1}	viscosity Pa s
0	13	75	334		49	3752	0.48	17	2953
	40	137	609	3.8	89	2227	0.48	51	1753
	133	238	1059	2.9	155	1164	0.48	169	916
	400	383	1702	5.0	249	622	0.48	508	489
1	13	80	356	7.1	52	4002	0.48	17	3152
	40	135	601	0.0	88	2195	0.48	51	1728
	133	245	1090	7.4	159	1198	0.48	169	943
	400	385	1713	14.1	250	626	0.48	508	493
4	13	74	327	2.1	48	3677	0.48	17	2890
	40	130	578	0.0	85	2113	0.48	51	1661
	133	243	1081	10.6	158	1188	0.48	169	934
	400	378	1681	3.5	246	615	0.48	509	483
8	13	77	343	2.1	50	3852	0.46	17	2988
	40	133	592	3.5	86	2162	0.46	52	1678
	133	238	1059	3.5	155	1164	0.46	171	903
	400	373	1657	3.5	242	606	0.46	516	470

Table B-1 (cont.) Experimental set 1 viscosity data (70 rpm, 240 °C)

Barrel diameter -					Capillary die dimensions -				
	0.375	in	9.525	mm	Length	1.2	in	31.7	mm
70/240					Diameter	0.052		1.321	
Pass No.	shear rate sec^{-1}	load lb	N	std	shear stress kPa	apparent viscosity Pa s	power law index	corrected shear rate sec^{-1}	viscosity Pa s
0	13	75	334		49	3752	0.48	17	2953
	40	137	609	3.8	89	2227	0.48	51	1753
	133	238	1059	2.9	155	1164	0.48	169	916
	400	383	1702	5.0	249	622	0.48	508	489
1	13	75	334	7.1	49	3752	0.47	17	2917
	40	133	589	[illegible]5	86	2154	0.47	51	1675
	133	237	1053	7.6	154	1157	0.47	171	900
	400	373	1657	3.5	242	606	0.47	514	471
4	13	73	326	7.1	48	3667	0.47	17	2860
	40	131	581	5.1	85	2125	0.47	51	1657
	133	230	1023	0.0	150	1125	0.47	171	877
	400	373	1657	3.5	242	606	0.47	513	472
8	13	68	300	3.5	44	3377	0.47	17	2641
	40	123	545	3.5	80	1992	0.47	51	1557
	133	225	1001	0.0	146	1100	0.47	170	860
	400	368	1635	3.5	239	597	0.47	511	467

Table B-2 Experiment set 1 swell ratio data

capillary die diam. (in) -		0.052		L\D =	24:1								
Pass	rheometer shear rate	60 rpm, 190 °C			60 rpm, 240 °C			70 rpm, 190 °C			70 rpm,240 °C		
		strand dia. (in)	std	swell ratio	strand dia. (in)	std	swell ratio	strand dia. (in)	std	swell ratio	strand dia. (in)	std	swell ratio
0	13	0.073	0.002	1.40									
	40	0.074	0.001	1.43									
	133	0.078	0.002	1.51									
	400	0.083	0.003	1.59									
1	13	0.071	0.001	1.37	0.071	0.002	1.37	0.071	0.001	1.37	0.073	0.000	1.39
	40	0.073	0.001	1.41	0.074	0.001	1.42	0.074	0.001	1.42	0.074	0.001	1.43
	133	0.077	0.001	1.49	0.077	0.002	1.48	0.078	0.001	1.50	0.078	0.001	1.50
	400	0.082	0.002	1.57	0.081	0.003	1.56	0.082	0.001	1.57	0.082	0.002	1.57
4	13	0.071	0.001	1.36	0.072	0.002	1.38	0.071	0.001	1.37	0.072	0.001	1.38
	40	0.073	0.001	1.40	0.074	0.001	1.42	0.074	0.001	1.42	0.074	0.001	1.41
	133	0.077	0.001	1.49	0.077	0.002	1.48	0.078	0.001	1.50	0.077	0.001	1.48
	400	0.081	0.001	1.57	0.081	0.003	1.56	0.082	0.000	1.58	0.082	0.001	1.57
8	13	0.071	0.000	1.36	0.070	0.002	1.35	0.071	0.001	1.36	0.071	0.001	1.37
	40	0.073	0.001	1.39	0.073	0.001	1.40	0.073	0.001	1.41	0.073	0.001	1.41
	133	0.076	0.001	1.47	0.076	0.002	1.45	0.077	0.001	1.47	0.076	0.001	1.46
	400	0.082	0.026	1.57	0.081	0.003	1.55	0.082	0.001	1.57	0.080	0.002	1.54

Table B-3 Experiment set 1 strength properties (60 rpm, 190 °C)

60/190	Dimensions			Load and Extension Responses				Yield Properties						Ultimate tensile strength properties					
Pass No.	sample thick. mm	sample width mm	cross sect. area mm^2	load at yield N	exten. at yield mm	load at break N	exten. at break mm	YTS MPa	avg YTS MPa	std	yield elong.	avg yield elong. %	std	UTS MPa	avg UTS MPa	std	UTS elong.	avg UTS elong. %	std
0	3.00	12.62	37.84	916	10.0	392.0	114.3	24.2	24.0	0.2	20.0	21.1	1.7	10.4	10.5	0.2	228.6	287.2	113.5
	3.05	12.52	38.17	911	10.1	396.0	107.5	23.9			20.3			10.4			215.0		
	3.00	12.57	37.68	907	11.5	407.0	209.0	24.1			23.1			10.8			418.0		
1	3.00	12.55	37.61	884	9.7	229.0	94.8	23.5	23.5	0.2	19.5	20.0	0.6	6.1	5.7	1.1	189.6	189.7	52.4
	3.07	12.45	38.25	890	9.9	253.0	121.1	23.3			19.8			6.6			242.2		
	3.00	12.45	37.30	881	10.3	169.0	68.7	23.6			20.7			4.5			137.4		
4	3.00	12.60	37.76	884	9.7	226.0	81.4	23.4	23.6	0.5	19.4	19.5	0.7	6.0	5.2	1.1	162.7	190.9	39.8
	3.02	12.55	37.93	915	10.2	104.0	69.7	24.1			20.3			2.7 *			139.4		
	2.97	12.57	37.36	868	9.4	163.0	109.5	23.2			18.8			4.4			219.1		
8	3.05	12.50	38.09	879	9.9	254.0	105.3	23.1	23.4	0.5	19.8	20.0	0.4	6.7	7.2	0.8	210.5	267.0	79.9
	3.00	12.52	37.53	893	10.2	291.0	161.8	23.8			20.3			7.8			323.5		

Table B-3 (cont.) Experiment set 1 strength properties (60 rpm, 240 °C)

60/240	Dimensions			Load and Extension Responses				Yield Properties						Ultimate tensile strength properties					
Pass No.	sample thick. mm	sample width mm	cross sect. area mm²	load at yield N	exten. at yield mm	load at break N	exten. at break mm	YTS MPa	avg YTS MPa	std	yield elong.	avg yield elong. %	std	UTS MPa	avg UTS MPa	std	UTS elong.	avg UTS elong. %	std
0	3.00	12.62	37.84	916	10.0	392.0	114.3	24.2	24.0	0.2	20.0	21.1	1.7	10.4	10.5	0.2	228.6	287.2	113.5
	3.05	12.52	38.17	911	10.1	396.0	107.5	23.9			20.3			10.4			215.0		
	3.00	12.57	37.68	907	11.5	407.0	209.0	24.1			23.1			10.8			418.0		
1	3.02	12.57	38.00	906	10.0	371.0	75.0	23.8	24.0	0.2	20.0	21.1	1.1	9.8	7.7	2.4	150.0	139.3	9.2
	3.00	12.57	37.68	902	10.7	189.0	67.0	23.9			21.3			5.0			134.0		
	3.00	12.67	37.99	920	11.1	318.0	67.0	24.2			22.2			8.4			134.0		
4	3.00	12.55	37.61	913	10.1	309.0	100.0	24.3	24.3	0.2	20.2	20.9	0.7	8.2	7.8	1.3	200.0	148.0	45.1
	3.00	12.62	37.84	927	10.5	334.0	62.0	24.5			20.9			8.8			124.0		
	3.00	12.55	37.61	909	10.8	240.0	60.0	24.2			21.5			6.4			120.0		
	2.97	12.57	37.36	906	11.4	243.0	55.0	24.2			22.8			6.5			110.0		
8	3.02	12.60	38.08	916	9.3	282.0	75.0	24.1	23.9	0.3	18.7	20.1	2.1	7.4	6.4	1.4	150.0	153.0	4.2
	3.00	12.95	38.83	920	10.8	211.0	78.0	23.7			21.6			5.4			156.0		

Table B-3 (cont.) Experiment set 1 strength properties (70 rpm, 190 °C)

70/190	Dimensions			Load and Extension Responses				Yield Properties						Ultimate tensile strength properties					
Pass No.	sample thick. mm	sample width mm	cross sect. area mm^2	load at yield N	exten. at yield mm	load at break N	exten. at break mm	YTS MPa	avg YTS MPa	std	yield elong.	avg yield elong. %	std	UTS MPa	avg UTS MPa	std	UTS elong.	avg UTS elong. %	std
0	3.00	12.62	37.84	916	10.0	392.0	114.3	24.2	24.0	0.2	20.0	21.1	1.7	10.4	10.5	0.2	228.6	287.2	113.5
	3.05	12.52	38.17	911	10.1	396.0	107.5	23.9			20.3			10.4			215.0		
	3.00	12.57	37.68	907	11.5	407.0	209.0	24.1			23.1			10.8			418.0		
1	3.00	12.52	37.53	932	10.1	327.0	60.0	24.8	24.5	0.5	20.2	22.0	2.5	8.7	8.1	0.8	120.0	132.0	17.0
	3.00	12.47	37.38	904	11.9	282.0	72.0	24.2			23.7			7.5			144.0		
4	3.05	12.42	37.86	911	10.2	359.0	68.0	24.1	24.1	0.1	20.5	22.1	2.3	9.5	9.1	0.6	136.0	140.0	5.7
	3.05	12.50	38.09	920	11.9	330.0	72.0	24.2			23.8			8.7			144.0		
8	3.00	12.57	37.68	925	10.7	330.0	74.0	24.5	24.1	0.6	21.5	21.8	0.4	8.8	8.6	0.2	148.0	153.0	7.1
	2.95	12.47	36.75	870	11.0	309.0	79.0	23.7			22.0			8.4			158.0		

Table B-3 (cont.) Experiment set 1 strength properties (70 rpm, 240 °C)

70/240	Dimensions			Load and Extension Responses				Yield Properties						Ultimate tensile strength properties					
Pass No.	sample thick. mm	sample width mm	cross sect. area mm^2	load at yield N	exten. at yield mm	load at break N	exten. at break mm	YTS MPa	avg YTS MPa	std	yield elong.	avg yield elong. %	std	UTS MPa	avg UTS MPa	std	UTS elong.	avg UTS elong. %	std
0	3.00	12.62	37.84	916	10.0	392.0	114.3	24.2	24.0	0.2	20.0	21.1	1.7	10.4	10.5	0.2	228.6	287.2	113.5
	3.05	12.52	38.17	911	10.1	396.0	107.5	23.9			20.3			10.4			215.0		
	3.00	12.57	37.68	907	11.5	407.0	209.0	24.1			23.1			10.8			418.0		
1	3.00	12.60	37.76	914	10.0	423.0	125.4	24.2	23.9	0.3	20.0	19.8	0.3	11.2	10.8	0.9	250.8	212.9	39.3
	3.02	12.67	38.31	902	9.9	437.0	107.8	23.5			19.9			11.4			215.6		
	3.05	12.65	38.55	927	9.7	373.0	86.2	24.1			19.4			9.7			172.4		
4	3.05	12.57	38.32	902	9.9	335.0	79.7	23.5	23.8	0.3	19.9	19.8	0.5	8.7	9.5	0.6	159.3	256.6	131.6
	3.05	12.62	38.48	913	9.7	376.0	203.2	23.7			19.4			9.8			406.4		
	3.00	12.57	37.68	915	9.7	402.0	269.3	24.3			19.5			10.7 *			538.6 *		
	3.05	12.70	38.71	923	10.2	382.0	102.1	23.8			20.4			9.9			204.2		
8	3.05	12.70	38.71	925	9.9	350.0	80.5	23.9	24.3	0.6	19.8	20.6	1.1	9.0	8.9	0.3	161.0	160.3	1.0
	3.00	12.52	37.53	930	10.7	326.0	79.8	24.8			21.4			8.7			159.6		

Table B-4 Experiment set 1 extrusion responses

Processing responses					
Melt Temperature (°C)	**Screw Speed** (rpm)	**Extrusion passes**	**Output** kg/hr	**Output Efficiency** kg/(hr rpm)	**Extrusion Pressure** (MPa)
190	60	0	4.48	0.745	2.2
190	60	1	4.45	0.735	2.2
190	60	4	4.30	0.712	2.3
190	60	8	4.35	0.720	2.2
190	70	0	4.40	0.731	2.0
190	70	1	4.38	0.729	2.0
190	70	4	4.42	0.734	2.0
190	70	8	4.37	0.724	2.0
240	60	0	4.37	0.621	16.3
240	60	1	4.40	0.626	17.2
240	60	4	4.46	0.634	16.2
240	60	8	4.40	0.626	16.5
240	70	0	4.46	0.635	13.3
240	70	1	4.59	0.653	13.3
240	70	4	4.51	0.641	14.0
240	70	8	4.48	0.638	14.1

Table B-5 Experimental set 2 viscosity data

QUANTUM LM6007, HOMOPOLYMER
0 PASS

shear rate 1/sec	load lb	dP KPa	wall stress KPa	Bagley factor	viscosity (Bgly corr.) Pa s	corrected shear rate 1/sec	viscosity (Bgly & Rab.) Pa s	dP entrance KPa	strain rate 1/sec	elong. visc. (Bgly corr.) Pa s	corrected strain rate 1/sec	elong. visc. (Bgly & Rab.)
10	84	5244	55		4202	17	3124					
50	130	8116	77	4.6	1929	54	1434	710	4	91131	6	67743
150	223	13890	136	3.1	1022	179	760	843	20	21930	27	16302
400	358	22318	221	2.5	552	538	411	1105	76	7710	102	5731
			power law index		m (Bgly)		m (Bgly & Rab.)		v1/v150			
			0.42		17546		15873		10.4			

QUANTUM LM6007, HOMOPOLYMER
4 PASS

shear rate 1/sec	load lb	dP KPa	wall stress KPa	Bagley factor	viscosity (Bgly corr.) Pa s	corrected shear rate 1/sec	viscosity (Bgly & Rab.) Pa s	dP entrance KPa	strain rate 1/sec	elong. visc. (Bgly corr.) Pa s	corrected strain rate 1/sec	elong. visc. (Bgly & Rab.)
10	110	6867	72		5502	19	3717					
50	142	8865	81	6.7	2026	59	1368	1086	3	203069	4	137175
150	230	14359	134	5.5	1009	197	682	1476	11	68155	17	46040
400	360	22474	216	4.0	540	592	365	1729	47	19302	70	13039
			power law index		m (Bgly)		m (Bgly & Rab.)		v1/v150			
			0.34		27315		21031		18.2			

Table B-5 (cont.) Experimental set 2 viscosity data

RP NATURAL HDPE

0 PASS

shear rate 1/sec	load lb	dP KPa	wall stress KPa	Bagley factor	viscosity (Bgly corr.) Pa s	corrected shear rate 1/sec	viscosity (Bgly & Rab.) Pa s	dP entrance KPa	strain rate 1/sec	elong. visc. (Bgly corr.) Pa s	corrected strain rate 1/sec	elong. visc. (Bgly & Rab.)
10	85	5306	55		4252	18	3123					
50	125	7804	74	4.4	1862	54	1367	655	4	80478	5	59113
150	225	14046	139	2.6	1044	181	767	722	24	15754	24	11571
400	343	21382	210	3.0	524	545	385	1258	63	10532	108	7736
			power law index		m (Bgly)		m (Bgly & Rab.)		v1/v150			
			0.41		18149		16431		10.4			

RP NATURAL HDPE

4 PASS

shear rate 1/sec	load lb	dP KPa	wall stress KPa	Bagley factor	viscosity (Bgly corr.) Pa s	corrected shear rate 1/sec	viscosity (Bgly & Rab.) Pa s	dP entrance KPa	strain rate 1/sec	elong. visc. (Bgly corr.) Pa s	corrected strain rate 1/sec	elong. visc. (Bgly & Rab.)
10	93	5806	60		4652	19	3254					
50	145	9052	86	4.6	2151	57	1505	792	4	101646	6	71090
150	235	14671	141	4.0	1061	190	742	1129	16	37895	22	26504
400	335	20913	201	4.1	502	572	351	1646	48	18835	66	13173
			power law index		m (Bgly)		m (Bgly & Rab.)		v1/v150			
			0.37		23529		21031		16.9			

Table B-5 (cont.) Experimental set 2 viscosity data

DOW 32060C, HDPE COPOLYMER

0 PASS

shear rate 1/sec	load lb	dP KPa	wall stress KPa	Bagley factor	viscosity (Bgly corr.) Pa s	corrected shear rate 1/sec	viscosity (Bgly & Rab.) Pa s	dP entrance KPa	strain rate 1/sec	elong. visc. (Bgly corr.) Pa s	corrected strain rate 1/sec	elong. visc. (Bgly & Rab.)
10	104	6493	68		5202	18	3695					
50	168	10457	100	4.3	2499	56	1775	860	4	103191	6	73295
150	260	16231	157	3.6	1183	187	840	1132	17	34224	25	24309
400	395	24659	238	3.7	596	563	423	1765	51	18226	72	12946
			power law index		m (Bgly)		m (Bgly & Rab.)		v1/v150			
			0.38		24777		22915		16.1			

DOW 32060C, HDPE COPOLYMER

4 PASS

shear rate 1/sec	load lb	dP KPa	wall stress KPa	Bagley factor	viscosity (Bgly corr.) Pa s	corrected shear rate 1/sec	viscosity (Bgly & Rab.) Pa s	dP entrance KPa	strain rate 1/sec	elong. visc. (Bgly corr.) Pa s	corrected strain rate 1/sec	elong. visc. (Bgly & Rab.)
10	85	5306	55		4252	18	3092					
50	140	8740	81	5.8	2031	55	1477	942	3	152544	4	110941
150	220	13734	133	3.7	999	183	726	983	17	30531	23	22204
400	340	21226	209	2.7	523	550	381	1130	70	8519	96	6196
			power law index		m (Bgly)		m (Bgly & Rab.)		v1/v150			
			0.40		19732		17496		17.8			

Table B-5 (cont.) Experimental set 2 viscosity data

RP MIXED COLOUR HDPE 0 PASS												
shear rate 1/sec	load lb	dP KPa	wall stress KPa	Bagley factor	viscosity (Bgly corr.) Pa s	corrected shear rate 1/sec	viscosity (Bgly & Rab.) Pa s	dP entrance KPa	strain rate 1/sec	elong. visc. (Bgly corr.) Pa s	corrected strain rate 1/sec	elong. visc. (Bgly & Rab.)
10	99	6180	64		4952	18	3602					
50	145	9052	85	5.5	2115	55	1538	931	3	142867	5	103903
150	242	15076	146	3.6	1098	183	799	1052	17	31789	24	23119
400	390	24347	242	2.4	604	550	439	1159	79	7767	108	5649
			power law index		m (Bgly)		m (Bgly & Rab.)		v1/v150			
			0.40		21220		19275		12.4			

RP MIXED COLOUR HDPE 4 PASS												
shear rate 1/sec	load lb	dP KPa	wall stress KPa	Bagley factor	viscosity (Bgly corr.) Pa s	corrected shear rate 1/sec	viscosity (Bgly & Rab.) Pa s	dP entrance KPa	strain rate 1/sec	elong. visc. (Bgly corr.) Pa s	corrected strain rate 1/sec	elong. visc. (Bgly & Rab.)
10	79	4932	51		3952	17	3034					
50	140	8740	79	7.1	1983	52	1522	1126	3	223196	3	171381
150	232	14483	137	4.8	1031	173	792	1317	13	53056	17	40739
400	385	24035	236	3.0	589	521	452	1414	63	11839	82	9091
			power law index		m (Bgly)		m (Bgly & Rab.)		v1/v150			
			0.45		15928		14112		17.6			

Table B-6 Experiment set 2 Bagley correction factor data

QUANTUM HDPE HOMOPOLY LM6007

	50 s-1				150 s-1				400 s-1			
	0 pass		4 pass		0 pass		4 pass		0 pass		4 pass	
	load	dP	load	dP	load	dP	load	dP	load	dP	load	dP
L/D	lb	MPa	lb	MPa	lb	MPa	lb	MPa	lb	MPa	lb	MPa
1	30	1.9	32	2.0	35	2.2	45	2.8	45	2.8	55	3.4
8	55	3.4	75	4.7	95	5.9	115	7.2	150	9.4	170	10.6
16	95	5.9	110	6.9	155	9.7	175	10.9	250	15.6	280	17.5
24	130	8.1	142	8.9	230	14.4	230	14.4	355	22.2	360	22.5
1	25	1.6			32	2.0			45	2.8		
8	53	3.3			88	5.5			145	9.1		
16	85	5.3			145	9.1			240	15.0		
24	130	8.1			215	13.4			360	22.5		
Bagley		4.6		6.7		3.1		5.5		2.5		4.0

0 pass Bagley average 3.4 4 pass Bagley average 5.4

RP HOMOPOLY BOTTLES

	50 s-1				150 s-1				400 s-1			
	0 pass		4 pass		0 pass		4 pass		0 pass		4 pass	
	load	dP	load	dP	load	dP	load	dP	load	dP	load	dP
L/D	lb	MPa	lb	MPa	lb	MPa	lb	MPa	lb	MPa	lb	MPa
1	23	1.4	25	1.6	30	1.9	40	2.5	55	3.4	55	3.4
8	55	3.4	70	4.4	83	5.2	105	6.6	135	8.4	155	9.7
16	90	5.6	105	6.6	155	9.7	152	9.5	250	15.6	240	15.0
24	130	8.1	145	9.1	230	14.4	235	14.7	345	21.5	335	20.9
1	25	1.6			30	1.9			45	2.8		
8	55	3.4			90	5.6			150	9.4		
16	63	3.9			125	7.8			205	12.8		
24	120	7.5			205	12.8			340	21.2		
Bagley		4.4		4.6		2.6		4.0		3.0		4.1

0 pass Bagley average 3.3 4 pass Bagley average 4.2

Table B-6 (cont.) Experiment set 2 Bagley correction factor data

DOW HDPE COPOLYMER 32060C												
	50 s-1				150 s-1				400 s-1			
	0 pass		4 pass		0 pass		4 pass		0 pass		4 pass	
L/D	load lb	dP MPa	load lb	dP MPa	load lb	dP MPa	load lb	dP MPa	load lb	dP MPa	load lb	dP MPa
1	28	1.7	32	2.0	40	2.5	30	1.9	62	3.9	40	2.5
8	66	4.1	65	4.1	110	6.9	105	6.6	165	10	150	9
16	135	8.4	105	6.6	200	12.5	170	10.6	320	20	225	14
24	165	10.3	140	8.7	265	16.5	220	13.7	395	25	340	21
1	30	1.9			36	2.2			61	3.8		
8	85	5.3			125	7.8			185	12		
16	130	8.1			202	12.6			290	18		
24	170	10.6			255	15.9			395	25		
Bagley		4.3		5.8		3.6		3.7		3.7		2.7
	0 pass Bagley average				3.9		4 pass Bagley average				4.1	

RP MIXED COLOUR BOTTLES												
	50 s-1				150 s-1				400 s-1			
	0 pass		4 pass		0 pass		4 pass		0 pass		4 pass	
L/D	load lb	dP MPa	load lb	dP MPa	load lb	dP MPa	load lb	dP MPa	load lb	dP MPa	load lb	dP MPa
1	27	1.7	30	1.9	37	2.3	40	2.5	47	2.9	50	3.1
8	80	5.0	80	5.0	110	6.9	115	7.2	155	9.7	170	10.6
16	120	7.5	105	6.6	185	11.5	172	10.7	295	18.4	272	17.0
24	150	9.4	140	8.7	235	14.7	232	14.5	420	26.2	385	24.0
1	27	1.7			32	2.0			49	3.1		
8	70	4.4			110	6.9			160	10.0		
16	115	7.2			175	10.9			260	16.2		
24	140	8.7			248	15.5			360	22.5		
Bagley		5.5		7.1		3.6		4.8		2.4		3.0
	0 pass Bagley average				3.8		4 pass Bagley average				5.0	

Table B-7 Sag observations

distance from die (m)	Sag from horizontal (cm)							
	virgin homopolymer		natural pcr		virgin copolymer		mixed colour pcr	
	0 pass	4 pass	0 pass	4 pass	0 pass	4 pass	0 pass	4 pass
0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.41	-18.1	-14.6	-22.2	-14.6	-11.1	-23.5	-19.1	-17.1
0.61	-21.0	-17.1	-24.8	-15.9	-13.7	-26.7	-21.0	-19.7
0.81	-20.3	-17.1	-24.1	-15.9	-12.7	-26.0	-21.0	-19.7
1.02	-17.5	-15.2	-20.0	-14.6	-10.5	-22.9	-17.1	-17.1
1.22	-12.7	-11.4	-14.9	-11.4	-8.3	-17.8	-12.4	-12.7
1.63	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

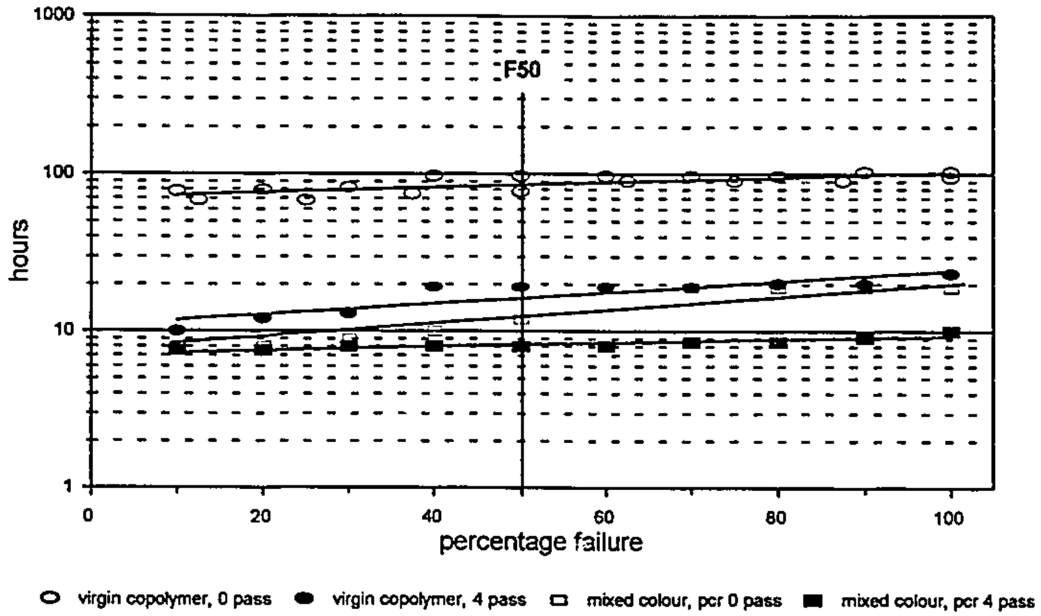
Table B-8 Experiment set 2 swell ratio data

QUANTUM LM6007, HOMOPOLYMER											
	shear rate	observed average swell ratio				normalized swell ratio					
		L/D				L/D					
	s^{-1}	1	8	16	24	1	8	16	24		
0 PASS	50	2.05	1.56	1.49	1.44	-0.11	0.16	0.08	0.44	intercept	-1.7
	150	2.22	1.64	1.56	1.43	0.93	1.00	0.90	0.39	coefficient	0.5
	400	2.32	1.65	1.60	1.49	1.47	1.09	1.39	1.37	SWRI	-3.4
4 PASS	50	1.88	1.39	1.38	1.31	-1.14	-1.44	-1.30	-1.52	intercept	-3.1
	150	1.96	1.46	1.44	1.37	-0.65	-0.84	-0.57	-0.70	coefficient	0.5
	400	1.99	1.54	1.45	1.41	-0.49	0.03	-0.49	0.03	SWRI	-6.4
RP NATURAL HDPE											
	shear rate	observed average swell ratio				normalized swell ratio					
		L/D				L/D					
	s^{-1}	1	8	16	24	1	8	16	24		
0 PASS	50	2.11	1.58	1.51	1.46	0.09	0.07	0.24	0.11	intercept	-1.7
	150	2.24	1.63	1.56	1.49	0.97	0.68	0.72	0.48	coefficient	0.5
	400	2.29	1.71	1.62	1.54	1.37	1.42	1.34	1.03	SWRI	-3.4
4 PASS	50	1.93	1.44	1.35	1.31	-1.14	-1.34	-1.49	-1.62	intercept	-3.6
	150	2.01	1.49	1.44	1.38	-0.57	-0.84	-0.59	-0.74	coefficient	0.6
	400	1.99	1.57	1.47	1.51	-0.72	0.01	-0.21	0.74	SWRI	-6.1

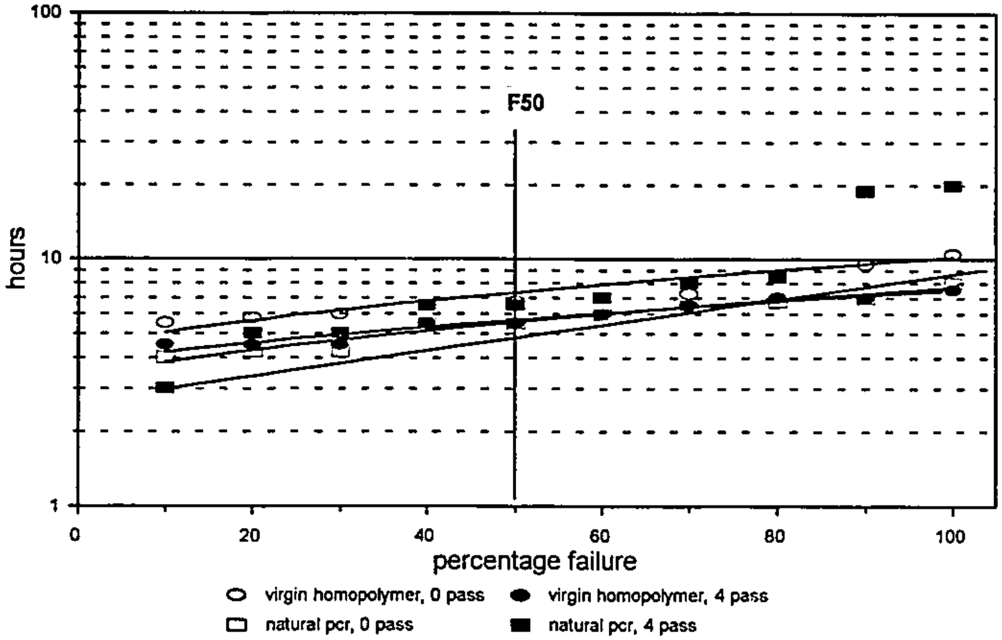
Table B-8 (cont.) Experiment set 2 swell ratio data

DOW 32060C, HDPE COPOLYMER											
		observed average swell ratio				normalized swell ratio					
	shear rate	L/D				L/D					
	s^{-1}	1	8	16	24	1	8	16	24		
0 PASS	50	1.96	1.46	1.43	1.37	-0.13	-0.55	0.01	-0.35	intercept	-3.4
	150	2.10	1.54	1.45	1.40	0.92	0.61	0.16	0.29	coefficient	0.8
	400	2.17	1.63	1.58	1.47	1.46	1.77	1.77	1.63	SWRI	-4.1
4 PASS	50	1.82	1.44	1.35	1.34	-1.17	-0.76	-1.03	-0.99	intercept	-2.5
	150	1.88	1.45	1.36	1.34	-0.69	-0.66	-0.88	-0.99	coefficient	0.4
	400	1.92	1.47	1.43	1.41	-0.39	-0.42	-0.03	0.42	SWRI	-6.5

RP MIXED COLOUR HDPE											
		observed average swell ratio				normalized swell ratio					
	shear rate	L/D				L/D					
	s^{-1}	1	8	16	24	1	8	16	24		
0 PASS	50	2.02	1.52	1.44	1.38	-0.37	-0.65	-0.44	-0.83	intercept	-3.8
	150	2.17	1.63	1.50	1.43	0.90	0.80	0.36	0.10	coefficient	0.9
	400	2.24	1.68	1.61	1.48	1.47	1.45	1.75	1.23	SWRI	-4.3
4 PASS	50	1.92	1.46	1.38	1.35	-1.26	-1.34	-1.20	-1.50	intercept	-3.4
	150	2.01	1.55	1.44	1.44	-0.45	-0.21	-0.44	0.37	coefficient	0.6
	400	2.03	1.56	1.47	1.46	-0.29	-0.05	-0.02	0.63	SWRI	-5.6

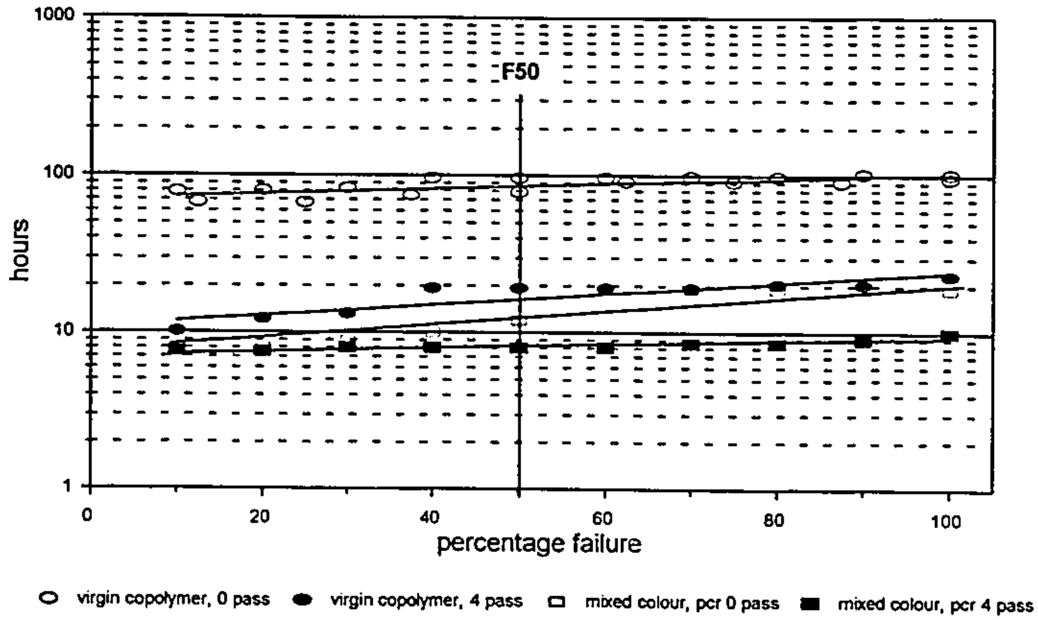


a) copolymer and mixed colour bottle PCR

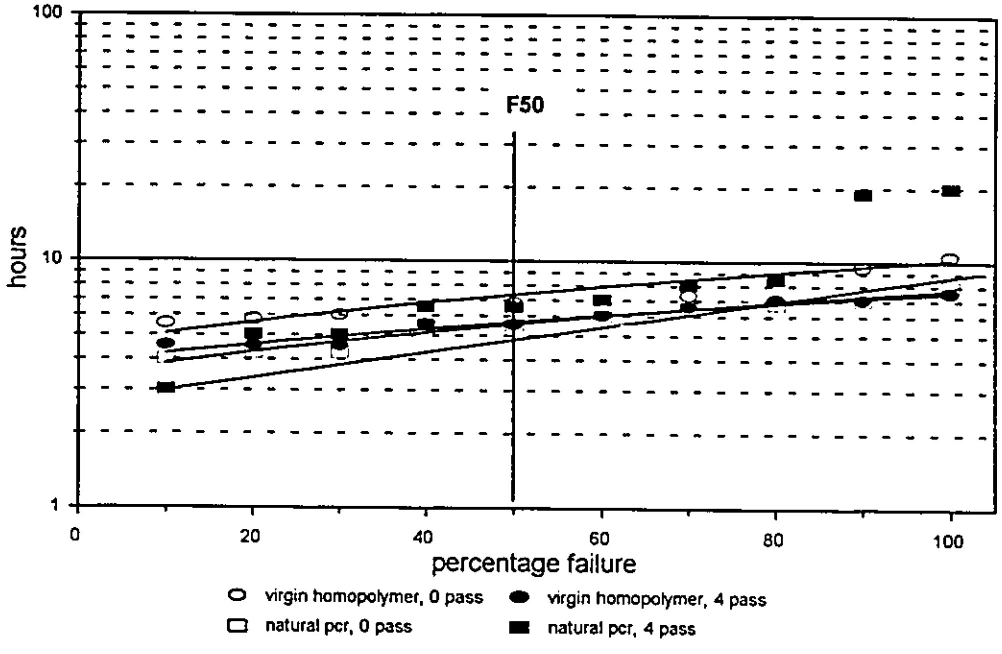


b) homopolymer and natural PCR

Figure B-1: ESCR F50 plots



a) copolymer and mixed colour bottle PCR



b) homopolymer and natural PCR

Figure B-1: ESCR F50 plots

Table B-9 Reference list of short forms and ANOVA summary for experiment set 1 statistical analysis

Short form	**Variable Description**	**ANOVA Signficance**		
		temp	extrusion speed	pass
temp	- extrusion melt temperature (controlled factor)	-	-	-
ext speed	- extruder speed (controlled factor)	-	-	-
pass	- extrusion passes (controlled factor)	-	-	-
vsc@10	- viscosity at 10 s^{-1} (response)	not	not	not
vsc@400	- viscosity at 400 s^{-1} (response)	not	not	not
vscm	- power law coeffiecient (response)	not	not	not
vscn	- power law index (response)	not	not	5%
SR@10	- swell ratio at 10 s^{-1} (response)	not	10%	5%
SR@400	- swell ratio at 400 s^{-1} (response)	not	1%	1%
YTS	- yield tensile strength (response)	not	not	not
YTS %el	- elongation at yield tensile strength (response)	not	not	not
UTS	- ultimate tensile strength (response)	1%*	10%*	5%*
UTS %el	- elongation at ultimate tensile strength (response)	not	not	5%*
kg/hr	- extrusion output (response)	not	not	not
kg/(hr rpm)	- extrusion efficiency (response)	1%	not	not
BP(MPa)	- extrusion pressure (response)	1%	1%	not

* - indicates high within run variance

Table B-10 Designed experiment and responses for experiment set 1

Factors			Responses												
temp °C	extruder speed (rpm)	pass	vsc@10	vsc@ 400	vscm	vscn	SR@10	SR@ 400	YTS	YTS %el	UTS	UTS %el	kg/hr	kg/(hr rpm)	BP(MPa)
190	60	0	2953	489	9.60	-0.55	1.40	1.59	24.0	21.1	10.5	287.2	4.48	0.74	2.20
190	60	1	3082	460	9.37	-0.53	1.37	1.57	23.5	20.0	5.7	189.7	4.45	0.73	2.20
190	60	4	2930	427	9.37	-0.53	1.36	1.57	23.6	19.5	5.2	190.9	4.30	0.71	2.27
190	60	8	3009	437	9.37	-0.53	1.36	1.57	23.4	20.0	7.2	267.0	4.35	0.72	2.16
190	70	0	2953	489	9.44	-0.55	1.40	1.59	24.0	21.1	10.5	287.2	4.40	0.73	1.99
190	70	1	3092	480	9.42	-0.54	1.37	1.56	24.0	21.1	7.7	139.3	4.38	0.73	1.99
190	70	4	3061	494	9.44	-0.54	1.38	1.56	24.3	20.9	7.8	148.0	4.42	0.73	1.99
190	70	8	3011	471	9.36	-0.53	1.35	1.55	23.9	20.1	6.4	153.0	4.37	0.72	2.03
240	60	0	2953	489	9.41	-0.56	1.40	1.59	24.0	21.1	10.5	287.2	4.37	0.62	16.32
240	60	1	3152	493	9.40	-0.53	1.37	1.57	24.5	22.0	8.1	132.0	4.40	0.63	17.23
240	60	4	2890	483	9.32	-0.52	1.37	1.58	24.1	22.1	9.1	140.0	4.46	0.63	16.25
240	60	8	2988	470	9.33	-0.53	1.36	1.57	24.1	21.8	8.6	153.0	4.40	0.63	16.46
240	70	0	2953	489	9.43	-0.56	1.40	1.59	24.0	21.1	10.5	287.2	4.46	0.64	13.33
240	70	1	2917	471	9.41	-0.54	1.39	1.57	23.9	19.8	10.8	212.9	4.59	0.65	13.26
240	70	4	2860	472	9.40	-0.54	1.38	1.57	23.8	19.8	9.5	256.6	4.51	0.64	13.98
240	70	8	2641	467	9.19	-0.50	1.37	1.54	24.3	20.6	8.9	160.3	4.48	0.64	14.09
response average			2965	474	9.39	-0.53	1.38	1.57	24.0	20.8	8.6	205.7	4.43	0.68	8.61
response st. dev.			117	19	0.08	0.01	0.02	0.01	0.3	0.8	1.8	62.5	0.07	0.05	6.81

Table B-11 Correlation matrix for experimental set 1

	temp	ext speed	pass	vsc@10	vsc @400	vscm	vscn	SR@10	SR @400	YTS	YTS %el	UTS	UTS %el	kg/hr	kg/(hr rpm)
temp	1														
ext speed	0.000	1													
pass	0.000	0.000	1												
vsc@10	-0.408	-0.260	-0.320	1											
vsc@400	0.287	0.284	-0.509	0.161	1										
vscm	-0.383	-0.072	-0.653	0.486	0.377	1									
vscn	0.059	-0.178	0.721	-0.341	-0.493	-0.760	1								
SR@10	0.169	0.265	-0.729	-0.145	0.559	0.560	-0.744	1							
SR@400	0.148	-0.315	-0.668	0.212	0.404	0.635	-0.720	0.645	1						
YTS	0.472	0.238	-0.113	-0.101	0.757	-0.041	-0.028	0.223	0.000	1					
YTS %el	0.336	-0.242	-0.181	0.198	0.676	0.059	-0.087	0.107	0.384	0.701	1				
UTS	0.532	0.257	-0.44	-0.337	0.647	0.312	-0.538	0.822	0.599	0.462	0.366	1			
UTS %el	-0.034	-0.003	-0.403	-0.181	0.038	0.502	-0.671	0.686	0.657	-0.326	-0.234	0.538	1		
kg/hr	0.475	0.366	-0.225	-0.398	0.333	0.053	-0.016	0.478	0.077	0.216	-0.071	0.597	0.196	1	
kg/(hr rpm)	-0.981	0.085	-0.060	0.362	-0.215	0.440	-0.081	-0.065	-0.134	-0.445	-0.358	-0.439	0.003	-0.297	1
BP(MPa)	0.987	-0.118	0.009	-0.329	0.302	-0.380	0.084	0.104	0.173	0.502	0.427	0.489	-0.028	0.379	-0.987

Table B-12 Eigenvalue analysis for experimental set 1 principal components

	l_1	l_2	l_3	l_4	l_5	l_6	l_7	l_8	l_9	l_{10}	l_{11}	l_{12}
Eigen-value	4.859	3.459	2.092	1.106	0.606	0.403	0.181	0.109	0.077	0.064	0.028	0.015
Prop.	0.374	0.266	0.161	0.085	0.047	0.031	0.014	0.008	0.006	0.005	0.002	0.001
Cumul.	0.374	0.640	0.801	0.886	0.933	0.964	0.977	0.986	0.992	0.997	0.999	1.000

Table B-13 Loadings for experimental set 1 principal components

Run Conditions	z1	z2	z3	z4	z5	z6	z7	z8
190/60/0	2.859	-2.383	0.014	1.195	0.337	0.982	-0.863	0.183
190/60/1	-2.368	-1.648	-0.188	0.223	-1.128	0.505	0.764	-0.057
190/60/4	-3.747	-1.574	-0.775	-1.118	0.457	-0.292	-0.691	-0.591
190/60/8	-2.411	-2.021	-0.995	-1.246	0.228	0.489	0.045	0.160
190/70/0	2.263	-1.810	0.078	0.244	1.308	0.218	0.484	-0.020
190/70/1	-0.816	-0.864	1.829	0.725	0.016	-0.228	0.355	-0.175
190/70/4	0.010	-0.564	1.816	1.740	0.157	-0.502	0.005	-0.329
190/70/8	-2.865	-0.506	0.818	0.590	0.038	-0.671	0.021	0.824
240/60/0	2.939	-0.028	-0.245	-1.668	0.536	-0.907	0.242	-0.075
240/60/1	0.635	1.979	2.824	-0.579	-0.795	-0.312	-0.508	-0.010
240/60/4	0.320	2.654	0.612	-0.563	0.038	1.525	0.237	-0.039
240/60/8	-0.425	2.088	0.949	-1.145	-0.159	0.313	-0.099	0.042
240/70/0	3.187	-0.265	-0.537	-0.784	-0.061	-0.450	0.259	0.065
240/70/1	1.455	0.474	-2.160	1.057	-1.537	-0.201	0.010	-0.404
240/70/4	0.731	0.399	-2.117	-0.040	-0.775	-0.286	-0.302	0.469
240/60/8	-1.766	4.070	-1.922	1.370	1.340	-0.183	0.043	-0.042

Table B-14 Principal components for experimental set 1

Response	pcoef1	pcoef2	pcoef3	pcoef4	pcoef5	pcoef6	pcoef7	pcoef8
vsc@10	-0.013	-0.252	0.509	-0.142	-0.545	-0.115	0.200	-0.058
vsc@400	0.351	0.109	0.309	0.290	0.027	-0.124	0.327	0.462
vscm	0.249	-0.381	0.155	0.127	-0.185	0.101	-0.732	0.056
vscn	-0.337	0.292	-0.053	0.124	0.047	0.516	-0.154	-0.066
SR@10	0.395	-0.125	-0.179	0.180	0.098	-0.120	0.247	-0.714
SR@400	0.352	-0.178	0.032	-0.402	-0.040	0.459	-0.002	-0.186
YTS	0.211	0.336	0.306	0.282	0.255	-0.263	-0.413	-0.161
YTS %el	0.211	0.226	0.457	-0.140	0.259	0.482	0.150	0.010
UTS	0.416	0.101	-0.172	0.078	0.116	0.070	0.022	0.137
UTS %el	0.252	-0.282	-0.360	-0.234	0.244	-0.023	-0.026	0.422
kg/hr	0.201	0.166	-0.322	0.477	-0.570	0.307	0.078	0.090
kg/(hr rpm)	-0.152	-0.423	0.116	0.409	0.215	0.241	0.109	0.016
BP(MPa)	0.179	0.432	-0.082	-0.340	-0.279	-0.102	-0.140	0.005

Table B-15 Reference list of short forms and ANOVA summary for experiment set 2 statistical analysis

Short form	**Variable Description**	**ANOVA Signficance**		
		resin	source	pass
resin	- resin type: homopolymer/natural, copolymer/mixed colour (controllable factor)	-	-	-
vir/pcr	- source: virgin or post consumer (PCR) (controllable factor)	-	-	-
pass	- extrusion passes: 0 or 4 (controllable factor)	-	-	-
vsc1	- viscosity (dynamic) at 0.2 Hz (response)	not	not	10%
vsc400	- viscosity (capillary) at 400 s^{-1} (response)	10%	not	not
m vsc	- power law coeffiecient (response)	not	not	not
n vsc	- power law index (response)	not	not	not
elvsc5	- elongational viscosity at 5 s^{-1} (response)	not	not	10%
elvsc50	- elongational viscosity at 50 s^{-1} (response)	not	not	not
melt t	- DSC melt temperature (response)	1%	5%	10%
%cryst	- DSC percent crystallinity (response)	not	not	10%
max t	- DSC max. endothermic emp. (response)	5%	not	not
heat flo	- DSC heat flow at maxi. endothermic temp.(resp.)	not	not	10%
F50	- ESCR 50% failure point (repsonse)	not	not	not
PI	- Polydispersity Index from G' - G" (repsonse)	not	not	5%
sag	- maximum sag from horizontal (response)	10%	not	not
extprs	- extruder pressure (response)	not	not	not
SWRI	- normalized swell ratio index (response)	not	not	5%
KG/HR	- extruder output (response)	not	5%	10%
BGAVG	- average Bagley correction factor (response)	not	not	10%

Table B-16 Designed experiment and responses for experiment set 2

Experimental			Responses																
resin	source	pass	vsc1	vsc400	mvsc	nvsc	elvsc5	elvsc50	melt t	%cryst	max pk t	heat flo	F50	PI	sag	extr prs	SWRI	kg/hr	bgly avg
-1	-1	0	7885	411	15873	0.42	67743	5731	128.0	59.1	135.9	-2.6	7.25	3.3	216	10.9	-3.4	5.30	3.4
-1	-1	4	12400	365	21031	0.34	137175	13309	127.6	58.3	137.6	-2.1	5.75	9.1	178	11.4	-6.4	5.33	5.4
-1	1	0	7940	385	16431	0.41	59113	7736	126.8	60.8	135.5	-2.4	6	3.4	235	10.7	-3.4	5.37	3.3
-1	1	4	12500	351	21031	0.37	71090	13173	125.5	56.7	135.9	-2.4	6.75	7.7	165	11.2	-6.1	5.49	4.2
1	-1	0	13550	423	22915	0.38	73295	12946	125.2	65.6	134.7	-2.6	90	3.2	135	12.4	-4.1	5.17	3.9
1	-1	4	12900	381	17496	0.40	110941	6196	124.8	62.8	135.6	-2.2	19	4.5	267	11.9	-6.5	5.28	4.1
1	1	0	9900	439	19275	0.40	103903	5649	124.8	65.2	135.0	-2.3	10	3.5	203	11.2	-4.3	5.30	3.8
1	1	4	13900	452	14112	0.45	171381	9091	123.7	55.3	134.4	-2.0	8	7.3	210	11.2	-5.6	5.63	5.0

Factor	Code	
	-1	1
resin	homopolymer natural	copolymer mixed colour
source	virgin	PCR

Coding table for factors

Table B-17 Correlation matrix for experimental set 2

	resin	vir/pcr	pass	vsc1	vsc400	mvsc	nvsc	elvsc5	elvsc50	melt t	%cryst	max t	heat flo	F50	PI
resin	1.00														
vir/pcr	0.00	1.00													
pass	0.00	0.00	1.00												
vsc1	0.52	-0.14	0.68	1.00											
vsc400	0.68	0.17	-0.40	0.03	1.00										
mvsc	-0.03	-0.29	-0.04	0.34	-0.38	1.00									
nvsc	0.36	0.36	-0.20	-0.20	0.69	-0.86	1.00								
elvsc5	0.42	0.06	0.63	0.58	0.34	-0.30	0.18	1.00							
elvsc50	-0.24	-0.10	0.38	0.58	-0.41	0.68	-0.66	0.06	1.00						
melt t	-0.83	-0.43	-0.28	-0.63	-0.48	0.09	-0.39	-0.44	0.05	1.00					
%cryst	0.49	-0.27	-0.62	-0.13	0.24	0.43	-0.16	-0.38	-0.26	-0.12	1.00				
max pk t	-0.71	-0.41	0.33	-0.14	-0.75	0.29	-0.73	-0.02	0.31	0.74	-0.27	1.00			
heat flow	0.24	0.24	0.73	0.46	0.06	-0.32	0.08	0.90	0.03	-0.40	-0.43	0.13	1.00		
F50	0.47	-0.42	-0.34	0.40	0.25	0.57	-0.17	-0.24	0.37	-0.23	0.60	-0.39	-0.48	1.00	
PI	-0.28	0.10	0.85	0.54	-0.40	0.12	-0.39	0.60	0.62	-0.02	-0.73	0.51	0.67	-0.38	1.00
sag	0.07	0.06	0.10	-0.36	0.00	-0.75	0.50	0.13	-0.80	-0.03	-0.04	-0.03	0.32	-0.56	-0.24
extprs	0.61	-0.56	0.12	0.71	0.08	0.59	-0.33	0.09	0.38	-0.38	0.52	-0.18	-0.09	0.83	-0.08
SWRI	-0.12	0.10	-0.95	-0.74	0.43	-0.19	0.38	-0.60	-0.40	0.32	0.37	-0.36	-0.70	0.21	-0.78
KG/HR	-0.10	0.67	0.56	0.22	0.08	-0.53	0.43	0.51	0.09	-0.35	-0.84	-0.16	0.59	-0.58	0.59
BGAVG	0.09	-0.09	0.78	0.71	-0.09	0.13	-0.31	0.84	0.54	-0.19	-0.49	0.35	0.78	-0.14	0.89

Table B-17 (cont.) Correlation matrix for experimental set 2

	sag	extprs	SWRI	KG/HR	BGAVG
sag	1.00				
extrpress	-0.37	1.00			
SWRI	-0.03	-0.31	1.00		
KG/HR	0.12	-0.51	-0.33	1.00	
BGAVG	-0.24	0.21	-0.78	0.42	1.00

Table B-18 Eigenvalue analysis for experimental set 2 principal components

	I1	I2	I3	I4	I5	I6	I7
Eigenvalue	5.786	4.821	3.543	1.454	0.809	0.448	0.139
Proportion	0.340	0.284	0.208	0.086	0.048	0.026	0.008
Cumulative	0.340	0.624	0.832	0.918	0.965	0.992	1.000

Table B-19 Loadings for experimental set 2 principal components

Experimental run	Z1	Z2	Z3	Z4	Z5	Z6	Z7
hopoly, 0 pass	2.740	1.227	-1.695	-0.472	0.578	-0.765	0.505
hopoly, 4 pass	-3.528	-1.634	-2.095	0.637	1.195	-0.035	-0.137
natural hdpe, 0 pass	2.300	1.329	-1.565	-0.290	-0.364	0.126	-0.737
natural hdpe, 4 pass	-1.776	-1.123	-1.275	-1.273	-1.509	0.410	0.278
copoly, 0 pass	1.608	-3.946	2.413	-0.671	0.222	-0.370	-0.134
copoly, 4 pass	-0.267	0.355	0.811	2.442	-1.004	-0.485	0.064
mixed colour, 0 pass	1.566	0.544	0.934	0.639	0.592	1.386	0.233
mixed colour, 4 pass	-2.644	3.248	2.472	-1.012	0.290	-0.267	-0.071

Table B-20 Principal components for experimental set 2

Variable	PC1	PC2	PC3	PC4	PC5	PC6	PC7
vsc1	-0.292	-0.151	0.314	0.025	-0.176	-0.209	0.094
vsc400	0.118	0.163	0.387	-0.137	0.521	0.104	0.253
m vsc	-0.042	-0.436	-0.015	-0.008	-0.023	0.400	0.132
n vsc	0.132	0.365	0.229	-0.146	-0.045	-0.289	0.054
elvsc5	-0.307	0.166	0.207	0.156	0.405	-0.022	0.021
elvsc50	-0.236	-0.307	-0.029	-0.354	-0.044	-0.081	-0.491
melt t	0.095	-0.077	-0.456	-0.023	0.372	-0.394	-0.016
%cryst	0.259	-0.211	0.180	0.373	0.106	0.379	-0.203
max t	-0.156	-0.122	-0.435	0.221	0.223	-0.119	0.104
heat flo	-0.325	0.200	0.087	0.255	0.139	0.221	-0.505
F50	0.116	-0.324	0.305	-0.087	0.048	-0.363	-0.310
PI	-0.400	-0.004	-0.120	-0.117	0.022	0.037	0.088
sag	0.072	0.326	-0.064	0.502	-0.230	-0.219	-0.284
extrprss	-0.042	-0.316	0.319	0.237	-0.061	-0.364	0.137
SWRI	0.365	0.044	-0.023	-0.292	0.305	0.024	-0.384
KG/HR	-0.237	0.295	0.020	-0.374	-0.236	0.125	-0.074
BGAVG	-0.394	-0.025	0.058	0.040	0.320	-0.066	-0.030