Titre: Title:	Polymer flow under the influence of fluoroelastomers
Auteur: Author:	Ke Chang Xing
Date:	1996
Type:	Mémoire ou thèse / Dissertation or Thesis
Référence: Citation:	Xing, K. C. (1996). Polymer flow under the influence of fluoroelastomers [Thèse de doctorat, École Polytechnique de Montréal]. PolyPublie. https://publications.polymtl.ca/8944/

URL de PolyPublie: PolyPublie URL:	https://publications.polymtl.ca/8944/
Directeurs de recherche: Advisors:	Henri P. Schreiber
Programme: Program:	Non spécifié

UNIVERSITÉ DE MONTRÉAL

POLYMER FLOW UNDER THE INFLUENCE OF FLUOROELASTOMERS

KECHANG XING
DÉPARTEMENT DE GÉNIE CHIMIQUE
ÉCOLE POLYTECHNIQUE DE MONTRÉAL

THÈSE PRÉSENTÉE EN VUE DE L'OBTENTION
DU DIPLÔME DE PHILOSOPHIE DOCTEUR(Ph.D)
(GÉNIE CHIMIQUE)
AOÛT 1996

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cette thèse intitulée:

POLYMER FLOW UNDER THE INFLUENCE OF FLUOROELASTOMERS

présentée par: XING Ke Chang
en vue de l'obtention du diplôme de: Philosophie Docteur
a été dûment accepté par le jury d'examen constitué de:

M. LAFLEUR Pierre, Ph.D., Président
M. SCHREIBER Henri P., Ph.D., membre et directeur de recherche
M. FAVIS Basil, Ph.D., membre
M. RUDIN Alfred, Ph.D., membre

ACKNOWLEDGMENTS

It is my pleasure to sincerely thank my professors, colleagues and friends for their amicable and helpful nature. Without their helps through my Ph.D. program, I could not image to overcome endless difficulties from language barrier to very limited time available for my thesis while holding positions in industry.

Word can not be enough to express my indebtedness to my advisor, Professor Henry P. Schreiber. His initiation, guidance, encouragement, ways of research and financial assistance have been the most crucial support for me to reach my goals. No to mention knowledge itself, Prof. Schreiber's spirits of diligence and intelligence will certainly hold positive influences on my career and personal life for a long long time.

I owe many thanks to my friends for valuable discussion and cooperation for my degree program. My sincere appreciation goes to Mr. B. Zhang, Mr. G. Perron, Mr. R. Dielle, Ms. T. Gray, Drs. X. Zhang, I. Ulkem, R. Qin and W. Wang.

With special fondness, I must acknowledge my wife, Jing, and son, Paul, for their loves and caring I have received. Loves and encouragement form my parents are another driving force for me to overcome barriers in my life.

RÉSUMÉ

De nombreux polymères peu coûteux possèdent d'excellentes propriétés. Cependant, leur mise en oeuvre peut parfois s'avérer difficile et cet inconvénient limite leur usage. Afin de faciliter la mise en oeuvre, on doit souvent ajouter des additifs comme des fluoroélastomères (FE). L'amélioration de la mise en oeuvre lors de l'addition des FE est habituellement attribuée à la modification des interactions interfaciales entre le FE et le polymère de base. Dans la littérature, on trouve peu d'études quantitatives sur l'influence de l'ajout des additifs de type FE et aucun consensus n'existe sur les mécanismes en jeu.

L'objectif de ce travail est de mettre en évidence de façon quantitative le rôle joué par les FE lors de la mise en oeuvre et de proposer une interprétation décrivant les mécanismes impliqués. Ces travaux, basés sur des considérations expérimentales et théoriques, permettront d'optimiser les procédés de mise en oeuvre de plusieurs polymères lors de l'ajout d'additifs de type FE. D'un point de vue fondamental, l'étude vise à définir les mécanismes en jeu lors de l'ajout du FE et permettra de relier les interactions microscopiques entre les composants au comportement rhéologique (macroscopique).
Pour atteindre cet objectif, nous allons étudier de façon quantitative les effets d'un FE sur le comportement rhéologique de différents thermoplastiques et tenter de les relier aux interactions entre le polymère et l'additif.

La première étape vise à mettre en évidence le mécanisme de l'action du FE lors de la mise en oeuvre et d'étudier directement l'effet du FE à l'interface entre le polymère de base et l'additif. Un FE a été appliqué directement sur la paroi d'une filière (capillaire) lors de l'extrusion d'un polyéthylène linéaire de basse densité (LLDPE). Une comparaison des courbes d'écoulement a été faite pour l'extrusion du LLDPE fondu à travers un capillaire métallique propre et un capillaire enduit d'un FE. L'une des principales observations est la réduction de la résistance à l'écoulement, qui varie selon le taux de cisaillement, à cause de la présence de FE à la surface du moule. Le FE adhère de façon préférentielle à la surface du moule, qui possède une énergie de surface élevée, mais interagit faiblement avec le LLDPE fondu. Le FE agit donc comme un lubrifiant à l'interface polymère/additif et entraîne le glissement du LLDPE fondu. D'autres résultats montrent que le temps de glissement doit atteindre une valeur d'équilibre aux vitesses élevées d'extrusion. Les courbes d'écoulement pour l'extrusion à travers des moules enduits de FE sont divisées en régions distinctes et leurs pentes ont été normalisées à l'aide d'équations qui ont permis de relier des concepts de dynamique moléculaire et de décohésion à l'interface comme étant à l'origine du phénomène de l'écoulement glissement/adhésion

Il est important de vérifier la persistance de l'enduit de FE sur la filière pendant l'extrusion du LLDPE puisque l'effet interfacial du FE sur l'écoulement a déjà été démontré.

L'efficacité de l'enduit de FE a été quantifiée lors de nombreux essais d'extrusion du LLDPE. Les essais ont été effectués à différentes températures et vitesses d'extrusion. Une relation non-linéaire a été observée entre l'efficacité et le temps de vidange du LLDPE. Des températures élevées et des vitesses d'extrusion faibles favorisent le phénomène de purge du FE. Deux mécanismes ont été proposés pour expliquer l'enlèvement du FE déposé sur la paroi de la filière par l'extrusion du LLDPE: l'un est la migration du FE dans le courant principal et l'autre est l'enlèvement du FE dû au cisaillement généré par l'écoulement du polymère de base. Le mécanisme de migration est l'étape limitant la vitesse de purge.

Les observations sur les effets interfaciaux et les résultats du temps de purge du FE de la surface de la filière ont rendu possible l'étude de l'effet du FE dans les mélanges LLDPE/FE et du transfert du FE à l'interface. La présence d'une petite quantité de FE dans les mélanges LLDPE/FE peut réduire de façon significative leur résistance à l'écoulement. En analysant l'enregistrement détaillé des résultats expérimentaux, des effets de lubrification externe et interne du FE sur l'écoulement de LLDPE ont été observés. L'effet lubrifiant interne du FE a un rôle moins important que celui de la lubrification externe. L'effet externe s'intensifie avec le temps d'extrusion jusqu'à ce que l'équilibre soit atteint. Le fait que les effets externes varient dans le temps confirme que la migration du FE vers la paroi de la filière a lieu. La vitesse de migration vers la paroi est aussi dépendante du temps. Elle diminue avec le temps d'extrusion jusqu'à l'équilibre. Les facteurs favorables à la migration vers la paroi sont: les taux de cisaillement élevés, l'incompatibilité entre les polymères et les énergies de surface faibles. Le processus de migration à l'intérieur du courant principal est différent de celui près de la paroi. L'étape qui limite la migration du FE vers la paroi est la séparation de phase du FE du courant principal.

Le FE, qui facilite la mise en oeuvre des polyoléfines, peut aussi influencer l'écoulement d'autres types de polymères. Divers polymères ont été choisis selon leur caractère acide ou basique. La chromatographie inverse en phase gazeuse (IGC) et des méthodes rhéologiques ont été utilisées pour étudier les interactions entre les polymères de base (CPE, PS, PC, Surlyn) et la couche de FE enduite sur la surface du moule. Il a été observé que les interactions acide/base jouent un rôle important. L'enduit de FE peut affecter le procédé d'extrusion de ces polymères selon les propriétés acide/base des polymères. Les données rhéologiques ont indiqué que le FE influence la résistance à l'écoulement des polymères de base et joue un rôle dans le processus de relaxation du courant principal. Cette observation a permis de discuter de l'effet de frontière sur l'écoulement en fluage des polymères.

ABSTRACT

There are a number of polymers that are excellent in end-use properties and cost, but are difficult to be processed and shaped. This kind of drawback limits the applications of these materials. For this reason, the use of additives to modify the processing properties of polymers has been widely practiced. Adding a fluorocarbon elastomer (FE) or similar fluorinated polymer to improve processability of polymers is a particular case in point. The effects of this addition are usually attributed to the change in interfacial interaction between the host polymer and the stationary phase. Quantitative evaluations of the effects on processing due to the presence of FE-type additives are infrequent, nor is there broad agreement on the mechanism whereby the additive affects processability of polymers.

The present project intends to present a coherent, quantitative picture of the role played by FE in polymer processing, and to suggest possible mechanisms accounting for the effect. This objective is based on both applied and theoretical interests Practically, the study on the utility of FE in polymer processing will allow the effectiveness of FE additives to be optimized and the function of FE in various types of polymer to be sort out. From a fundamental viewpoint, the study of possible mechanisms for FE as a processing aid will benefit understanding the link between the microscopic interaction of components and macroscopic rheological behavior The route taken here is to study quantitatively the effect

of a fluorocarbon elastomer on the rheological behavior of thermoplastics, and relating the findings to concept of interaction between host and additive polymers.

The first step to reveal the mechanics of FE as a processing aid is to study directly the effect of FE at the interface between a flowing phase and the stationary phase. FE was directly applied to die lands of extrusion, allowing linear low density polyethylene (LLDPE) to flow through the coated die. A comparison was made of flow curves for the extrusion of a LLDPE melt through clean metal capillaries and when overcoated by a fluoropolymer (FE) processing aid. Characteristic differences between the flow traces include a shear rate-dependent reduction in flow resistance due to the presence of FE at the die surface. The FE preferentially adheres to high energy die surfaces, but interacts very weakly with LLDPE melts, thus acting as a lubricant at the interface of polymer/stationary phase, and promoting the slip of LLDPE melts. Arguments are presented showing that the fractional time of slippage must attain an equilibrium value at high extrusion rates. Flow curves for extrusion through FE-coated dies are divided into distinct regions and the slopes of these have been rationalized by equations which combine the concepts of molecular dynamics and of adhesive failure at the die wall/polymer interface as the origins of slip-stick flow.

Understanding the persistence of FE coatings on the die during extrusion of LLDPE

is of obvious importance since the interfacial effect of FE on the host polymer flow has been verified. The effectiveness of FE coatings followed repeated runs of LLDPE extrusion through an initially FE-coated die. Tests were carried out at various temperatures and extrusion rates. Non-linear relationships were observed between the effectiveness and flushing time or amount of purging LLDPE. High temperatures and low extrusion rates promoted the purging process. Two mechanisms have been postulated to account for the removal of FE deposited on a die land by the extrusion of LLDPE: One is the migration of FE into the mainstream, the other is the shear-dependent stripping of the FE by the flowing matrix polymer. Experimental data indicate that purging rates are relatively high at initial stages of the process, but very long flow times were required before LLDPE purging agent completely eliminated the FE effect. Arguments were favoring the purge to be the process of random stripping of FE from the die surface.

Knowledge of interfacial effects and of purging the FE from the die surface made it possible to use the behavior of LLDPE/FE blends to study the transfer of FE from LLDPE/FE bulk to the interface between the flowing phase and the stationary phase. The existence of a small amount of FE in LLDPE/FE blends can significantly reduce flow resistance of the entire material. The detailed record of experimental results showed the existence of external as well as internal lubrication effect of FE on LLDPE flow. The internal lubrication effect, however, was a minor factor when compared with the external

one. The external effect increased with time of extrusion to an equilibrium. The time-dependence of the external effect confirms an accumulation of FE at the die wall The rate of mass transfer toward the wall is also time-dependent It reduces with the time of extrusion to an equilibrium. The factors favorable to the mass transfer to the wall included strong shear field, incompatibility between polymers, and high surface energy of the die wall. The process of migration inside the mainstream is different from that leading to accumulation at the wall. The controlling step for FE to arrive at the wall is phase separation of FE from the mainstream.

Besides using FE as a processing aid for polyolefins, it is also possible to use FE to influence the flow of other polymers. According to their acidity/basicity, a variety of polymers were selected to explore the possibility Inverse gas chromatography (IGC) and rheological methods were used to investigate the interactions between FE coating layer and host polymers: Chlorinated Polyethylene (CPE), Polystyrene (PS), Polycarbonate (PC), an ionomer (Surlyn). It has been found that acid/base interactions play an important role. FE coating affects the extrusion process in accord with the acid/base properties of the polymers. IGC was shown to be a powerful tool to characterize the interactions between polymers. The rheological data indicated that FE not only influenced flow resistance of host polymers, but also played a role in the relaxation process of the mainstream. This observation was used in discussion on boundary effects on the creep flow of polymers.

CONDENSÉ EN FRANÇAIS

1. Introduction

De nombreux polymères peu coûteux possèdent d'excellentes propriétés. Cependant, leur mise en oeuvre peut parfois s'avérer difficile et cet inconvénient limite leur usage. Afin de faciliter la mise en oeuvre, on doit souvent ajouter des additifs comme des fluoroélastomères (FE). L'amélioration de la mise en oeuvre lors de l'addition des FE est habituellement attribuée à la modification des interactions interfaciales entre le FE et le polymère de base. Dans la littérature, on trouve peu d'études quantitatives sur l'influence de l'ajout des additifs de type FE et aucun consensus n'existe sur les mécanismes en jeu.

L'objectif de ce travail est de mettre en évidence de façon quantitative le rôle joué par les FE lors de la mise en oeuvre et de proposer une interprétation décrivant les mécanismes impliqués. Ces travaux, basés sur des considérations expérimentales et théoriques, permettront d'optimiser les procédés de mise en oeuvre de plusieurs polymères lors de l'ajout d'additifs de type FE. D'un point de vue fondamental, l'étude vise à définir les mécanismes en jeu lors de l'ajout du FE et permettra de relier les interactions microscopiques entre les composants au comportement rhéologique (macroscopique).

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2. Partie expérimentale

Les polymères de base et les fluoroélastomères utilisés dans ce travail sont présentés au tableau suivant. Les mélanges ont été préparés avec un mélangeur interne Brabender. Un mélange LLDPE/FE contenant 10% de FE a été effctué. Ce mélange a ensuite été dilué jusqu'à la concentration de FE désirée en le mélangeant dans le LLDPE vierge. Les extrusions ont été faites selon deux méthodes:

Méthode I: le polymère de base est extrudé à travers des capillaires propres de dimensions connues.

Méthode II:

a) Composants vierges: le polymère de base est extrudé à travers des capillaires similaires dont la paroi a été enduite de FE par extrusion. Dans ce procédé, les capillaires n'ont pas été nettoyés après l'étape d'extrusion du FE.

b) Mélanges: des mélanges de composition connue ont été extrudés de façon répétée à travers un capillaire ayant été nettoyé à la flamme avant le premier essai.

Afin de mieux évaluer l'efficacité des enduits de FE comme agent modifiant l'écoulement du LLDPE, nous introduisons le coefficient d'efficacité (Θ), défini ainsi:

$$\Theta = \frac{(F_I - F_{II})}{F_I} x100\%$$

où F_i est la force exercée sur le piston du rhéomètre lors de l'extrusion par les méthodes I et II respectivement. Le paramètre Θ a été utilisé pour comparer l'efficacité de FE-1 et de FE-2 à modifier l'écoulement des polymères de base choisis.

Les mesures rhéologiques ont été faites avec un rhéomètre à capillaire Instron, équipé de capillaires ayant des angles d'entrée de 90° et 180°, de diamètres de 1.27 et 1.75 mm respectivement et ayant des rapports L/D de 5, 10, 20 et 40. Le rhéomètre est relié à un ordinateur et l'acquisition se fait à toutes les demie-secondes. Le rhéomètre opère à vitesse contrôlée et permet d'étudier le comportement en écoulement sur plus de deux décades de taux de cisaillement. Les polymères ont reposé 10 minutes dans le baril du rhéomètre après la compaction. L'erreur sur les mesures ne dépasse pas 9%.

Tableau I: Polymères utilisés dans ce travail

Echantillon	Type	Spécification	Fournisseur
LLDPE	DOWLEX 2045	Indice de fusion =1.1	Dow Chemicals
PS	PS 204-00	$M_n=9.1\cdot10^4$, $M_w=1.9\times10^5$	Polysar Ltd.
PC	Lexan 130-111	Bisphénol-A	General Electric Inc.
Surlyn	Surlyn 9950	Indice de fusion =5.5, type de cation=Na	Dupont Inc.
CPE	Tyrin 4213	Cl%=42%	Dow Chemicals
FE-1	Dynamar L-11216	Viscosité de Mooney=48	3M Inc
FE-2	Viton Freeflow 20		Dupont Inc.

Les interactions polymère/polymère ont été étudiées par chromatographie inverse en phase gazeuse. Les polymères ont été préparés en solution sur un chromosorb G (60/80 mesh, traité avec du AW-DMCS) à 7% environ (massique). La phase enduite a ensuite été séchée dans un four sous vide à 80°C pendant 24 heures. Les colonnes ainsi remplies ont été placées sous hélium à 120°C pendant au moins 4 heures avant toute utilisation. Les sondes mobiles utilisées dans ce travail sont le n-hexane (n-C6), le n-heptane (n-C7), le n-octane (n-C8), le n-nonane (n-C9), le diéthyl éther (Ether), le tétrahydrofuranne (THF), l'acétate d'éthyle (EtAc), l'acétone et le chloroforme ($CHCL_3$). Tous ces produits, de grade analytique, sont utilisés sans traitement subséquent.

3. Résultats et discussions

Les travaux sont présentés en quatre chapitres ou articles scientifiques majeurs. Dans le premier article, intitulé "Fluoropolymères et leurs effets sur la mise en oeuvre du polyéthylène linéaire de basse densité", des comparaisons de courbes d'écoulement ont été faites pour l'extrusion d'un LLDPE fondu à travers des capillaires metalliques propres et des capillaires enduits de fluoropolymères. Une des différences observées au niveau de ces courbes est la réduction de la résistance à l'écoulement due à la présence du FE à la surface du filière. Le FE favorise le glissement du LLDPE fondu. L'efficacité du FE dépend de l'importance du champ de cisaillement et il existe un domaine optimal où le FE est le plus performant. Les courbes d'écoulement pour l'extrusion à travers des capillaires enduits de FE sont divisées en régions distinctes et leurs pentes ont été normalisées à l'aide d'équations qui ont permis de relier des concepts de dynamique moléculaire et de décohésion à l'interface comme étant à l'origine du phénomène de l'écoulement glissement/adhésion.

Les résultats mentionnes ci-haut ont mene a l'article suivant intitule "Purge de lubrifiants fluoroélastomères par l'extrusion du LLDPE". Le processus de purge du fluoropolymère de la surface des capillaires par l'extrusion en continu du LLDPE vierge a été analysé empiriquement et théoriquement. Les vitesses de purge dépendent de la température et des vitesses de cisaillement dans un processus qui semble impliquer la migration de l'additif dans le courant principal et son enlèvement mécanique de la paroi de la filière. Ces deux mécanismes ont été proposés afin d'expliquer l'enlèvement du FE déposé sur la paroi du capillaire par le LLDPE.

Le travail suivant, "Influence du FE sur l'écoulement des mélanges LLDPE/FE", se concentre sur les mécanismes par lesquels une petite quantité d'additif affecte fortement la résistance à l'écoulement des mélanges LLDPE/FE. Les observations des deux articles précédents ont permis de présenter une description détaillée de mécanismes qui expliquent l'efficacité du FE dans le LLDPE, un polymère ne pouvant qu'offrir des interactions de type dispersif. Les résultats obtenus montrent que le FE agit comme lubrifiant interne et externe lors de la mise en oeuvre du LLDPE. La lubrification externe est plus importante que l'interne. Les résultats expérimentaux sont expliqués à l'aide du concept de transfert de masse du FE a l'interface entre le courant principal et la phase stationnaire. Les différences entre le transfert de masse à l'intérieur des mélanges et celui à l'interface sont aussi discutées.

Le quatrième article, intitulé "Utilisation du FE lors de la mise en oeuvre de plastiques non-polyoléfiniques", combine une étude rhéologique à celle sur les interactions entre des polymères ayant différentes polarités par chromatographie inverse en phase gazeuse (IGC). Les polymères de base choisis pour ce travail sont: le polystyrène (PS), le polycarbonate (PC), le polyéthylène chloré (CPE) et un ionomère (Surlyn). Il a été observé que les enduits de FE peuvent affecter considérablement l'extrusion de ces polymères et que les résultats peuvent être expliqués à l'aide du concept des interactions acide/base entre le polymère et le FE. Cette étude porte sur les possibilités d'utilisation du FE en tant qu'additif modifiant l'écoulement de polymères capables d'interagir avec le FE via des forces non dispersives. Ce travail montre que l'IGC peut être un outil très utile permettant de relier certaines micro-propriétés à des phénomènes macroscopiques. Il est possible d'utiliser les relations établies dans ce travail entre les interactions polymère/polymère et les propriétés rhéologiques pour la sélection d'un additif approprié.

En somme, cette étude examine quantitativement les effets du FE sur l'écoulement de divers polymères ayant différentes polarités. Les applications et limitations du FE en tant qu'aide à la mise en oeuvre ont été évaluées en fonction des variations dans la résistance à l'écoulement. Des mécanismes qui relient les phénomènes rhéologiques aux interactions polymère/polymère ont été proposés.

4. Conclusions et recommendations

1) Conclusions:

- les enduits de FE appliqués aux filières d'extrusion ont favorisé le glissement du LLDPE à la paroi du filière, entraînant la réduction de la résistance à l'écoulement.
- l'efficacité des enduits de FE à réduire la viscosité dépend de la vitesse de cisaillement. Dans ce travail, l'efficacité optimale se situe dans un domaine de vitesses de cisaillement compris entre 100 et 200 s^{-1}.
- le glissement du LLDPE a lieu à l'interface FE/LLDPE et devient plus important avec la longueur du filière. L'efficacité du FE en tant qu'aide à la mise en oeuvre est donc aussi augmentée
- dans le phénomène de glissement/adhésion, la fraction du temps pour lequel il y a glissement augmente avec la vitesse de cisaillement jusqu'à un maximum caractéristique, qui n'atteint jamais la limite de 100%.
- les théories de la dynamique moléculaire et de décohésion, proposées comme étant à l'origine de l'écoulement sporadique dans le LLDPE, ont été reliées à l'aide d'équations basées sur ces concepts.
- la purge du FE, déposé sur la paroi du capillaire, par l'extrusion du LLDPE

est contrôlée par le phénomène de diffusion

- les résultats expérimentaux et le modèle mathématique proposés indiquent que les vitesses de purge sont plus élevées aux stades initiaux du processus. Des températures élevées et des vitesses d'extrusion faibles favorisent le processus de purge pour une même quantité de polymère de base. Le modèle prévoit que le temps requis pour vider complètement la paroi du capillaire du FE sera minimisé par des vitesses d'extrusion élevées, associées à des contraintes de cisaillement importantes.
- en mélangeant une petite quantité de FE avec le polymère de base, la résistance à l'écoulement est réduite et la mise en oeuvre est facilitée.
- le FE entraîne la lubrification interne et externe pendant l'écoulement de mélanges FE/LLDPE, mais l'effet externe est plus important. La lubrification externe augmente avec le temps d'extrusion jusqu'à l'équilibre.
- l'accumulation du FE sur la paroi du capillaire dépend aussi du temps. La vitesse d'accumulation diminue avec le temps d'extrusion jusqu'à l'équilibre. Les facteurs qui favorisent le processus d'accumulation sont les champs de cisaillement importants, l'incompatibilité entre le polymère de base et l'additif et une faible énergie de surface du FE. Le phénomène de transfert de masse à l'intérieur du courant principal est différent de celui d'accumulation à la paroi. L'étape limitante dans l'accumulation du FE à la

paroi est la séparation de phase du FE du courant principal.

- dans le cas des polymères non-oléfiniques, le FE peut faciliter la mise en oeuvre lorsque les interactions entre le FE et le polymère de base sont faibles; sinon, les fortes interactions entre l'enduit de FE et le polymère de base nuisent à la mise en oeuvre.

2) Recommendations pour études futures:

Les objectifs suivants devraient être poursuivis:

- une relation doit être établie entre les propriétés physiques (structure chimique, masse moléculaire, etc.) des FE et leurs effets sur la modification du comportement en écoulement des polymères de base (oléfiniques ou non). Cette étude permettrait d'améliorer la fabrication d'additifs de type FE dans le but de maximiser l'efficacité lors de l'écoulement.
- des polymères non-oléfiniques additionnels devraient être utilisés afin de mieux comprendre la relation entre l'efficacité du FE et les concepts d'interactions polymère/polymère.
- d'autres méthodes expérimentales devraient être mises au point afin de déterminer les conditions opératoires optimales requises pour l'utilisation du

FE. Parmi celles-ci, des efforts devraient être faits pour produire des enduits permanents de FE sur la surface de filières d'extrusion afin d'éviter le mélange du FE au polymère de base. De plus, l'efficacité devrait être étudiée en extrudant des polymères contenant une très faible quantité de FE à travers des capillaires enduits.

- des travaux exploratoires devraient être entrepris afin d'établir quelles sont les autres propriétés des polymères qui sont affectées par la localisation du FE en surface. Ces études pourraient porter sur les propriétés diélectriques et barrières, les procédés d'impression, l'adhésion des marqueurs et autres polymères à ces surfaces, etc.

TABLE OF CONTENTS

Page

ACKNOWLEDGMENT IV

RESUMÉ V

ABSTRACT X

CONDENSÉ EN FRANÇAIS XV

TABLE OF CONTENTS XXVII

LIST OF FIGURES XXVI

LIST OF TABLES XXXI

NOMENCLATURE XXXIII

1. INTRODUCTION 1

2. LITERATURE REVIEW 3

3. ORGANIZATION OF THE ARTICLES 18

4. FLUOROPOLYMERS AND THEIR EFFECT ON PROCESSING LINEAR LOW DENSITY POLYETHYLENE 20

5. PURGING FLUOROELASTOMER LUBRICANTS BY THE EXTRUSION OF LLDPE 48

6. INFLUENCE OF FE ON MELT FLOW OF LLDPE/FE BLENDS 78

7. USE OF A FLUOROELASTOMER PROCESSING AID WITH NON-OLEFINIC POLYMERS 113

8. CONCLUSIONS AND RECOMMENDATIONS 136

9. REFERENCES 139

10. APPENDIX 146

LIST OF FIGURES

Chapter 2. Literature Review

Figure 2.1. Melt viscosities of fluoroelastomer compounds at 160°C.

Figure 2.2. Torque transient curves for the LLDPE/Viton system

Figure 2.3. Theoretical flow curves of two ideal monodisperse polymers of molecular weights: $\overline{M}_w = 8.5 M_c$, and $\overline{M}_w = 19.3 M_c$.

Figure 2.4. Apparent flow curves for LDPE and HDPE resins. Capillary: flat entry die 1 mm diameter, and 20 L/D .

Chapter 4. styled for publication as Paper 1 . Polym. Eng. Sci.

Figure 4.1. Shear stress-shear rate relationships for LLDPE extrusion through clean dies (Type I) and FE-coated dies (Type II), die L/D=20, T=180°C. ○ Type I; ● Type II, first run; ∇ Type II, second run

Figure 4.2. Ratio of viscosities of FE to LLDPE as function of shear rate ☐ FE-1, ■ FE-2.

Figure 4.3. Shear rate dependence of viscosity reduction percentage (Θ), due to FE coating on die surface: T=180°C, die L/D=20. ○ FE-1; ● FE-2.

Figure 4.4. Plots of Bagley correction relating to LLDPE extrusion: 200°C, various L/D dies and shear rates.

Figure 4.5. Shear rate variation of FE coating effectiveness as flow resistance modifier, responsing to die length changes. Modifier is FE-1. T=180°C. L/D=5 (○), L/D=10 (●), L/D=20 (∇)

Figure 4.6. Efficiency of FE-1 flow modifier for LLDPE extrusion as function of processing time. T=160°C, shear rate=143 s^{-1}.

Figure 4.7 Comparison of corrected shear stress/shear rate plots for Type I and Type II extrusion of LLDPE at 180°C, showing definition of zone 1, 2 and 3 in Type II extrusion

Chapter 5. styled for publication as Paper 2 Intern. J. Polym. Processing.

Figure 5.1 Comparison of the viscosity of FE and LLDPE at various temperatures ○ 200°C, ▼ 180°C, □ 160°C

Figure 5.2. Typical details of Type I extrusion at 200°C and 143 s^{-1}.

Figure 5.3. Typical details of Type II extrusion (at same conditions as in Figure 2).

Figure 5.4. Regression of Θ vs. LLDPE mass at 180°C and various extrusion rates. ○ 14.8 mm^3/s, ● 27.9 mm^3/s, ∇ 59.4 mm^3/s

Figure 5.5 Regression of Θ vs. purging time (at same conditions as in Figure 4). □ 14.8

mm^3/s. ▼ 27.9 mm^3/s. ○ 59.4 mm^3/s

Figure 5.6 Influence of extrusion temperature on purging effect at 143 s^{-1} ○ 160°C. ● 180°C, ∇ 200°C.

Figure 75. Various possible mechanisms for the purging process.

Chapter 6. styled for eventual publication as Paper 3.

Figure 6.1. First extrusion of control LLDPE and its blends with FE at 143 s^{-1} and 200°C. 1: pure PE, 2: 0.1% FE, 3: 1.0% FE, 4: 3.3% FE.

Figure 6.2. Effect of shear rate on first extrusion of LLDPE/1% FE blend at 160°C. 1: LLDPE, 287 s^{-1}, 2: Blend, 287 s^{-1}, 3: LLDPE, 143 s^{-1}; 4: Blend, 143 s^{-1}

Figure 6.3. External efficiency of FE on flow of various blends at 143 s^{-1} and 200°C. ○: 0.1% FE; ●: 1.0% FE; ∇: 3.3% FE.

Figure 6.4. Influence of shear rate on efficiency of 1% FE additive in the flow of LLDPE at 160°C. ○ 143 s^{-1}; ● 287s^{-1}.

Figure 6.5. Influence of FE concentration on its maximum external efficiency and attainment of equilibrium extrusion force at 143 s^{-1} and 200°C. ○ maximum θ; ▼: equilibrium time.

Figure 6.6. Effect of extrusion conditions on the rate of efficiency increase of FE. 1 -3: FE was 0.1, 1.0 and 3.3%, respectively, at 200°C and 143 s^{-1} ; 4 and 5:

extrusion at 143 s^{-1} and 287 s^{-1}, respectively. All samples were LLDPE/1% FE blend at 160°C.

Figure 6.7 Relationship of the increasing rate and efficiency. ○: LLDPE/3.3% FE blend at 200°C and 143 s^{-1}; ●: LLDPE/1% FE blend at 200°C and 143 s^{-1}; ▽: LLDPE/0.1% FE blend at 200°C and 143 s^{-1}; □: LLDPE/1% FE blend at 160°C and 143 s^{-1}; ■: LLDPE/1% FE blend at 200°C and 287 s^{-1}.

Figure 6.8. Relationship of purging rate and flow modification efficiency of FE on LLDPE at various temperatures and shear rates. ○: at 160°C and 143 s^{-1}; ●: at 160°C and 287 s^{-1}; ▽: at 200°C and 143 s^{-1}

Figure 6.9. Estimation of mass transfer rate at various conditions. ○: LLDPE/1% FE blend at 160°C and 143 s^{-1}; ●: LLDPE/1% FE blend at 160°C and 287 s^{-1}; ▽: LLDPE/3.3% FE blend at 200°C and 143 s^{-1}; ▼: LLDPE/1% FE blend at 200°C and 143 s^{-1}; □: LLDPE/0.1% FE blend at 200°C and 143 s^{-1}

Chapter 4, styled for publication as paper 4. Polym. Eng. Sci.

Figure 7.1. Application of equation 1, with retention volume plotted against the product of probe dimension and dispersion surface free energy. Substrate is PS at 40°C

Figure 7.2. Illustrating graphical representation used to determine K_a and K_b parameters.

in accordance with equation 4. Upper portion is for PS, lower portion for FE

Figure 7.3 Extrusion force vs. extrusion time for CPE polymer

———— Type I, run 1

——·—— Type II, run 1, –·–·–·– Type II, run 2

–··–··–·· Type II, run 3, ·········· Type II, run 4

Figure 7.4 Initial effectiveness of FE, defined by coefficient (θ), as function of normalized acid-base pair interaction parameter.

Figure 7.5. Rate of change in FE effectiveness as function of normalized acid-base pair interaction parameter.

LIST OF TABLES

Chapter 2. Literature Review

Table 2.1. ESCA analyses of LLDPE/FE blends.

Chapter 4/Paper 1

Table 4.1. End Pressure Losses in Type I and Type II Processing of LLDPE A at 200°C. B At 180°C.
Table 4.2. Constants for Power-Law Equation Applying to Flow Curve Regions in Type II Processing. (Constants are for $\tau_w = Y\dot{\gamma}_a^x$).

Chapter 5/Paper 2

Table 5.1. Weight of FE in the Die.
Table 5.2. Dependence of FE Effectiveness on Extrusion Rate.
Table 5.3. Dependence of FE Persistence at die wall on Extrusion Rate.

Chapter 6/Paper 3

Table 6.1 Efficiency and Its Rate at Initial Stage and Subsequent Period

Table 6.2. Parameters of Regression for Blend Extrusion.

Table 6.3 Equilibrium Time (minutes) of FE Effect on Blend Flow.

Chapter 7 Paper 4

Table 7.1. Polymeric Materials Used in This Work.

Table 7.2. Characteristics of Molecule Probes Used in IGC.

Table 7.3 Surface Characteristics for Each Polymer at 70°C

Table 7.4 Specific Components ΔH_{sp} (kJ/mol) of the Enthalpy of Adsorption of Solutes.

Table 7.5. Summary of FE Effectiveness in Extrusion of Various Polymers:

1) CPE: Extrusion at 160°C, and shear rate = 71.4 s^{-1}

2) PC: Extrusion at 250°C, and shear rate = 143 s^{-1}

3) PS: Extrusion at 180°C, and shear rate = 143 s^{-1}

4) Ionomer: Extrusion at 180°C, and shear rate = 143 s^{-1}

NOMENCLATURE

English Letters

AN*	the dimensionless acceptor number of the vapor probe.
ac	accumulation process.
bd	blend.
d	density of polymer, g/m^3.
DN	the dimensionless donor number of the vapor probe.
ER	extrusion rate, m^3/s.
f_{ad}	force need to break adhesion per unit area of the stationary phase, Pa.
F	extrusion force, kg.
F_I	extrusion force during type I operation, kg.
F_{II}	extrusion force during type II operation, kg.
F_{ad}	the component of external force needed to break the adhesion between the polymer stream and the stationary phase, kg.
F_{st}	the component of extrusion force needed to establish laminar flow, kg.
k, k_i	coefficient of the rate of efficiency change to the rate of mass transfer (i=1, 2), g.
K_a	the dimensionless number of the ability of the solid to accept electrons.
K_b	the dimensionless number of the ability of the solid to donate electron.

I_{sp}	the dimensionless specific interaction parameter.
L	die length, m.
m	migration process.
M	the mass of LLDPE extruded over FE coating, g.
N	square root of the sum of squares of the residuals between calculated and experimental data (in chapter 5).
N	Avogadro's number, 6.02 x 10^{23} molecules g/mole.
pg	purge process.
R	radius of a die (except in Paper 4), m
R	gas constant (in paper 4), 8.314x10^3 kg m^2 s^{-2} kg-mol^{-1} $°K^{-1}$.
T	temperature, °C.
t	extrusion time, s.
t_e	equilibrium time. s.
t_s	average residence time for a flowing unit in the die. s
t_{sl}	fractional time for slip flow, s.
t_{st}	fractional time for stick flow, s.
V	velocity in the z-direction, m/s.
V_N^0	net retention volume, m^3.
w_i	dimensionless weight fraction of a component (i) in a blend.
W_T	total weight of FE remaining in the die at any time, g.

$W_{T,0}$	total weight of FE remaining in the die at beginning of purge, g.
x	dimensionless exponent coefficient in power-law equations (in paper I)
y	slope coefficient in power-law equations, Pa·s.

Greek Letters

θ	dimensionless effectiveness coefficient of FE on flow resistance of a host polymer.
θ_0	θ value at $t=0$, dimensionless.
λ	percentage of time during which slip occurs,dimensionless.
τ	local shear stress, Pa.
τ_n	nominal shear stress corrected for end effects, Pa.
γ_a	apparent shear rate, 1/s.
φ	the dimensionless ratio of a component in a binary blend at flow boundary.
ρ	density of polymer melt, kg/m^3.

1. INTRODUCTION

There are a number of polymers that have excellent end-use properties and attractive cost but are difficult to be processed and shaped. This kind of drawback limits the application of these materials, notable among which is linear low density polyethylene (LLDPE). For this reason, the use of additives to modify processing properties of polymers has been widely practiced. Adding a fluorocarbon elastomer (FE) or similar fluorinated polymer to improve processability of polymers is a particular case in point. The effects of this addition are usually attributed to the change in interfacial interaction between the host polymer and the stationary phase (Blatz, 1964, Shih, 1976, Rumamurthy, 1986; and Hatzikiriakos and Dealy, 1991). Quantitative evaluations of the effects on processing due to the presence of FE-type additives are infrequent, nor is there broad agreement on the mechanism whereby the additive affects processability of polymers.

The present project attempts to present a coherent, quantitative picture of the role played by FE in polymer processing, and to present a mechanism consistent with observations. This objective is interesting both to practical and theoretical workers. From the practical viewpoint, the study on the utility of FE in polymer processing should allow for the effectiveness of FE additives to be optimized. From the fundamental view, the study of mechanisms for the role of FE as a processing aid will further an understanding of the link between the microscopic interaction of components in a polymer system and its macroscopic rheological behavior The route taken here is to study quantitatively the effects of a fluorocarbon elastomer on the rheological behavior of thermoplastics, and relating the findings to concepts of interaction between host and additive polymers. The account of studies undertaken here is given in 4 major chapters: In the first paper (chapter 4), study is focused on interfacial effect of fluoropolymers on processing linear low-density polyethylene (LLDPE). The following chapter investigates the purging process of FE from die walls by the extrusion of a matrix polymer, such as LLDPE. In the next chapter, we present a detailed consideration of mechanisms accounting for the empirical observations of FE effectiveness on melt flow of LLDPE, a polymer able to exert only dispersion-force interactions. The last chapter is devoted to a consideration of wider applications for FE flow additives, involving matrix polymers able to interact with the FE through non-dispersion forces.

2. LITERATURE REVIEW

2.1. Fluoroelastomer as a Processing Aids

A fluoroelastomer (FE) was first used by Blatz (1964) as a processing aid in amounts of 100-20,000 ppm in polyolefins and their copolymers. He obtained smoother extrudate surfaces at higher rates than in the control. Shih (1976) found that FE and EPDM can mutually improve the flow of each polymer at additive concentration of less than 5% FE. He further observed that the improvement became less evident at shear rates above a critical value, as illustrated in figure 2.1. His work was confirmed by Kanu and Shaw (1984), who also noticed that there was no evident effect of FE additive on the rheological properties of host polymer when the measurement was carried out with a plate-plate

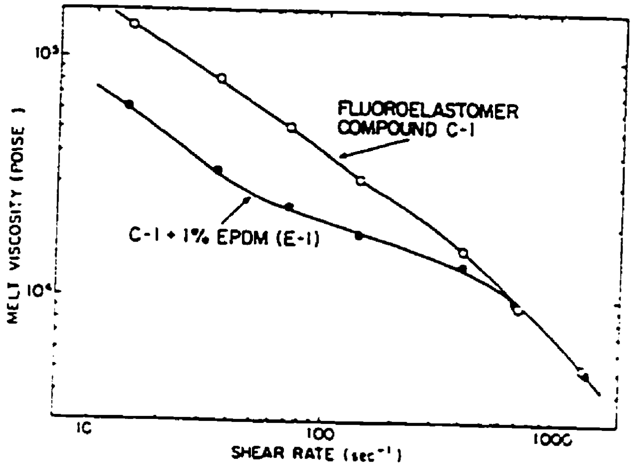


Figure 2. 1. Melt viscosities of fluoroelastomer compounds at 160°C

Improvements in the processability of polyolefins, especially linear low density polyethylene (LLDPE), due to the presence of FE have been extensively reported. Rudin et al (1985) indicated that minimum FE concentrations are needed to shift the onset of both surface defects and melt fracture to higher shear rates, and these requirements varied from one type of LLDPE to another. They found that 30-60 minutes of uninterrupted extrusion of FE/LLDPE blends was needed to build up a steady-state FE coating on the extrudates. Their data (1985, 1986) also showed that FE was more effective in delaying the onset of sharkskin than that of melt fracture. Athey et al (1986) reported that with a piston-driven capillary rheometer, 10–40% reductions in shear stress were obtained for blends of LLDPE (MI=1) with 400 ppm Viton (polyvinylidene fluoride) in the range of 100-700 s^{-1}, when compared with the control. Their data delineated less effect of FE on lower molecular weight LLDPE. More importantly, they also noticed that the effects of FE in the blend are time-dependent at the initial stage of extrusion, and that the induction time (or equilibrium time) was shorter at higher FE concentration in the blend. They reported the reappearance of melt fracture in the blend when processed above 1000 s^{-1} of shear rate. Valenza and La Mantia (1988) largely confirmed the dependence of effects of FE on the induction time and concentration, as shown in figure 2.2. They verified that not more than 1% of FE was needed to reach the greatest possible reduction of extrusion torque. In his comprehensive studies on the effects of wall material on the rheology of polyolefins, Ramamurthy (1986) claimed that FE additives eliminated extrudate defects in LLDPE after an induction time during screw extrusion operation. but were useless in the measurement with piston rheometer. More recently, Duchesne. Schreiber and Rudin (1990) discovered that higher levels of FE are needed to eliminate the extrudate defects in blends containing additives which acted as Lewis bases.

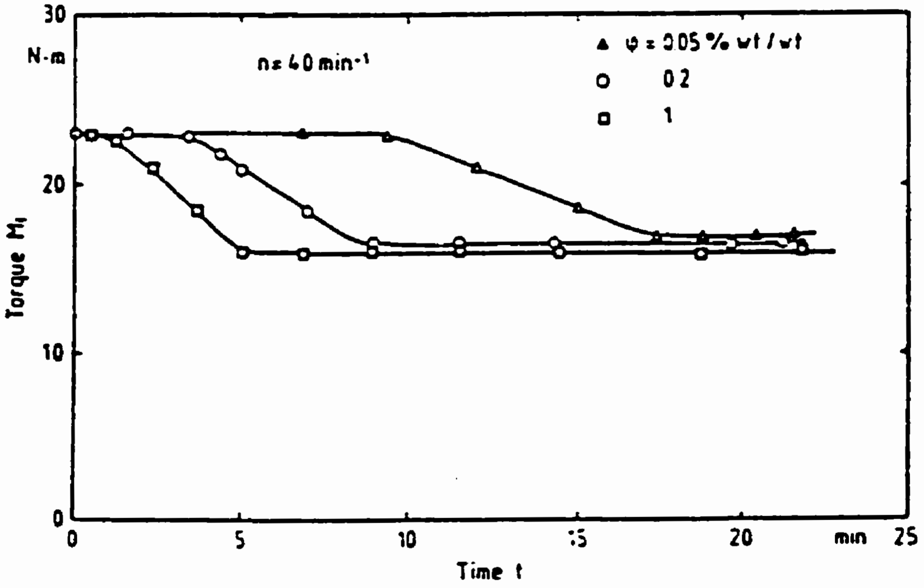


Fig. 2.2 Torque transient curves for the LLDPE/Viton system

In contrast to the general consistency in the reported improvement in extrusion of polyolefins by FE additives, studies on the mechanism of these effects have brought out very different explanations. Shih (1976) speculated that the significant reduction in flow resistance appeared to be the result of slippage of the host polymer over the die wall. Kanu and Shaw (1982) indicated the depression in viscosity of FE-containing polymers is not an intrinsic change of material property but a phenomenon of slippage peculiar to capillaries with sharp entrances. They stated that FE is forced to accumulate in regions of secondary flow near the entrance, followed by a spill over of discrete FE particles into the capillary along its wall. They suggested that the "slipping" may be more of a "rolling" action of the melt stream on the accumulated debris near the wall and thus it is not necessary for FE to coat the wall to form a solid layer on which the slip occurs. Kanu and Shaw's ideas were challenged by Athey et al (1986). In the latter's work, it was shown that time dependence of FE effects does not rely on the configuration of the die, since the reduction in viscosity gradually reached equilibrium with dies of different geometry. Athey et al also noticed that the FE was distributed evenly through the extruded LLDPE/FE film, although FE itself acted as a die lubricant. This is in contrast to the work of Duchesne et al (1986). These authors claimed that the FE concentration is high at the surface of extrudate and low inside the bulk, as table 2.1 shows.

Table 2.1. ESCA RESULTS

Sample	Approximate Atomic % Composition
Surface	Fluorine
250 ppm PPA 2231	1.2%
500 ppm PPA 2231	3.1%
1000 ppm PPA 2231	3.8%
Cross Section	
250 ppm PPA 2231	-
500 ppm PPA 2231	-
1000 ppm PPA 2231	-

Explanations of the effects of FE on the melt flow of polyolefins is an indistinct picture. What is certain, however, is that the polymer-wall interaction is critically involved in flow resistance and the extrudate irregularity noted in all of the above research reports. The main arguments put forth in the publications are the slippage of the polymer melt, a possible migration of additive polymer under flow conditions, and the adhesion between polymer melt and die land. It appears worth considering these issues, before turning to the objectives of the present work.

2.2. Origin of the Stick-slip Phenomenon

The intrinsic understanding of stick-slip phenomena is still wanting. We can, however, explore the origin during melt extrusion, along with chain motion and relaxation of polymer melt.

2.2.1. Theory of Molecular Dynamics (Lin, 1985)

From a viewpoint of chain dynamics slip-stick melt fracture can be viewed as a general phenomenon in non-crosslinked polymers. The dynamics are mainly characterized by reptational motion and chain tension relaxation. At low shear rate, the shear stress is mainly determined by reptational motion. At high shear rate, chain tension contributes to the total stress in addition to the inter-entanglement stress that is related to reptational motion. The processes of chain tension/relaxation and of reptational relaxation become increasingly distinct as the molecular weight increases. If the molecular weight is high enough (M_w > 10 Me, Me: average weight between 2 nodes of the entanglement network) chain tension relaxation is faster than reptational processes at a given shear rate, and then the polymer melt slips at the wall as shown in Figure 2.3

Following a slip event, the melt again adheres to the wall because of the decrease in chain tension and the fluctuation in the flow rate Fluctuations prevail with wide M_w distribution. Briefly, high molecular weight and narrow molecular weight distribution promote the slip-stick phenomenon.

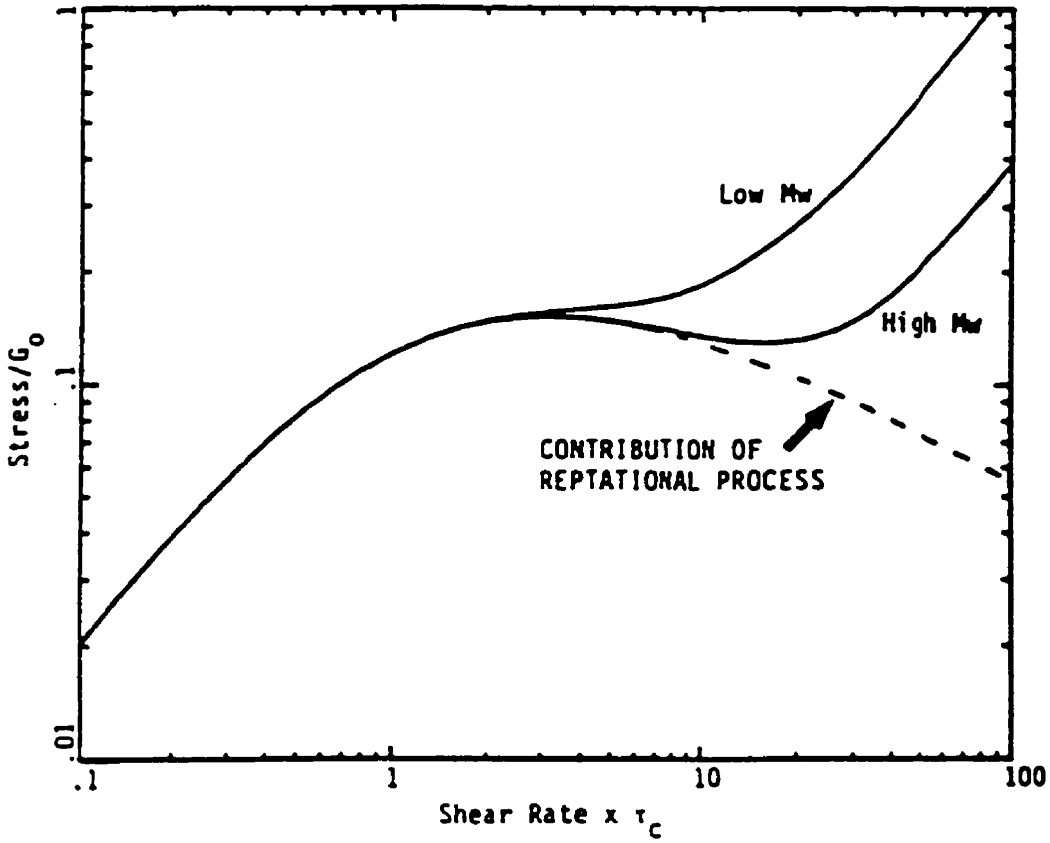


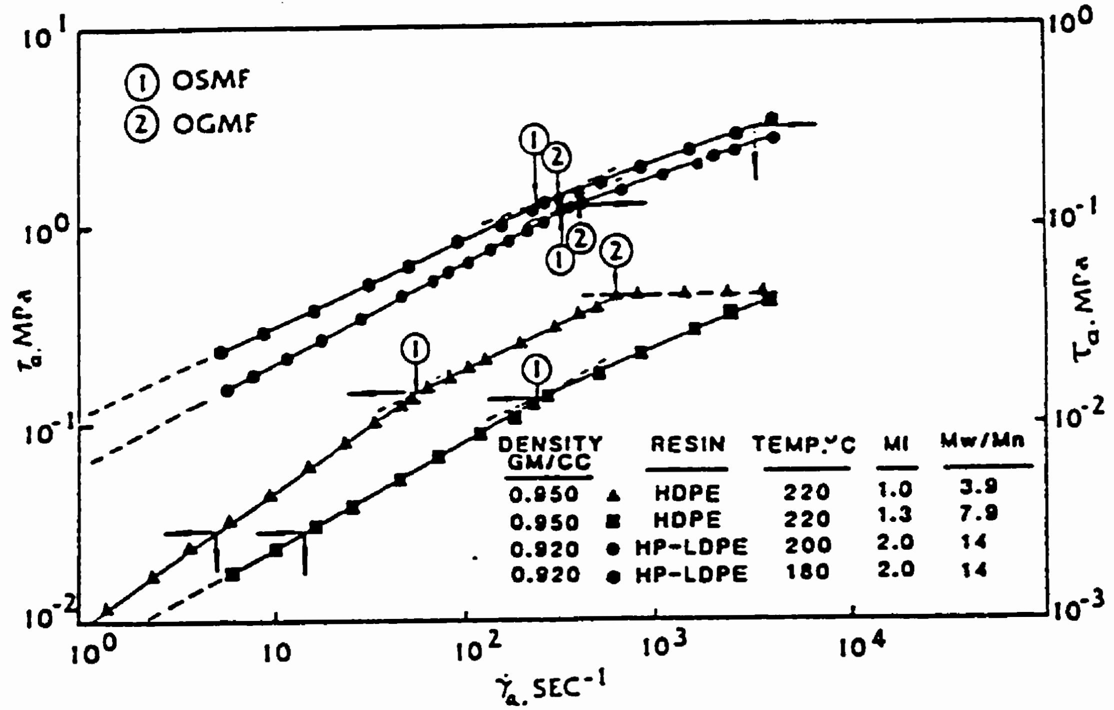
Figure 2.3. Theoretical flow curves of two ideal monodisperse molecular weights: $M_w = 8.5\ M_c$; and $M_w = 19.3\ M_c$

2.2.2. Theory of Adhesive Failure (Tordella, 1969; Petrie and Denn, 1977)

After the polymer melt has entered the die land from the reservoir, the flow at the die wall slows toward zero, independent of the speed of the mainstream. The greater the difference in speed between the mainstream and the boundary layer, the more intensive is the stress concentration at the flow boundary. As the shear rate increases, favoring rubber-like behavior in the polymer, the shear stresses in the mainstream and at the interface between polymer and the die wall rise. Slippage occurs at a shear stress exceeding the adhesive strength at the polymer stream/die wall interface. The polymer chains now relax and the high stress is reduced. The polymer returns to fluid-like behavior, adheres again to the wall, and the accumulation of high shear stress is repeated. Thus, a slip-stick cycle is created. At even higher shear rates, the melt behavior is closer to the elastomeric state. At this point "plug flow" becomes dominant. As plastic deformability is dramatically lower in the elastic state than in the fluid state, at sufficiently high shear rates the shear stress may become sufficiently high to result in a high frequency slip-stick transition.

2.2.3. Rheological Aspect (Ramamurthy, 1986; Dealy, 1992; Utracki, 1992).

There is general acceptance that slippage causes viscosity minima. The onset of slippage corresponds to a discontinuity in the slope of the apparent flow curve. A typical example with the discontinuity is shown in figure 2.4



DENSITY GM/CC		RESIN	TEMP.°C	MI	Mw/Mn
0.950	▲	HDPE	220	1.0	3.9
0.950	■	HDPE	220	1.3	7.9
0.920	●	HP-LDPE	200	2.0	14
0.920	●	HP-LDPE	180	2.0	14

Figure 2.4. Apparent flow curves for LDPE and HDPE resins.

Capillary: 1 mm diameter, and with abrupt entry

In the figure, points (1) and (2) identify slope changes corresponding to onset of surface melt fracture and gross melt fracture, respectively Both points were explained as due to slippage of the polymer melt on the die land (Ramamurthy, 1986), although proof of slippage was presented for point (1) only Figure 2.4 also shows the dependence of slippage on polymer molecular weight and molecular weight distribution. High molecular weight and narrow molecular weight distribution favor the occurrence of slippage at low shear rate. The explanation of these dependencies was given in the theory of molecular dynamics of polymer flow, above.

2.3. Migration of Polymeric Additives under Flow Conditions

A position-dependent concentration gradient can occur in polymer blends due to migration of the polymeric additive There are various theories which attempt to explain this phenomenon. Fluid kinetics, wall-exclusion mechanism, computer simulations, two-fluid theory and thermodynamic analyses are particularly noteworthy. (Agarwal, et al, 1994). Theoretical predictions are often in conflict with each other, even at qualitative levels, and there are few studies which provide direct experimental support for these theories. To date, there are no reports claiming to justify the mass transfer of fluoroelastomer additives in host polymers under flow. The migration concept nevertheless merits discussion because of the many factors which point to the existence of the effect.

For Poiseuille flow, for example, it is generally expected from kinetics theory that more viscous components of a multi-component system tend to migrate towards low shear regions (Ottinger, 1987; and Ravi Prakash 1992). However, Xia and Callaghan (1991) found that the polymer diffusion coefficient increases by as much as 5 times at the flow boundary (high shear region), modifying the probability that effective migration can occur in the course of typical flow times

According to the wall-exclusion mechanism, high viscous components under flow deplete near the wall due to steric effects generated at the wall. (Shidara and Denn, 1993). Inadequacies of this type of analysis, however, were noted by Brunn (1985)

Application of Mont Carlo simulations for Poiseuille flow of polymer solutions indicated a decrease of the thickness of the depletion layer with shear rate. (Duering and Rabin, 1991), but contrary results were reported by Ausserre and co-workers (1991) for rigid polymer

The two-fluid theory (Doi and Onuki, 1992) has been used to analyze Poiseuille flow of polymer solutions in straight channels by Ianniruberto et al (1994). Their work suggests migration of the viscous component from the walls of the channel to the center of the flow stream They also found that effects of the migration phenomenon are manifested much sooner close to the wall than within the flow stream.

Schreiber et al (1965, 1966) have attributed the migration phenomenon to thermodynamic drives, namely, the changes in entropy arising out of the deformation of macromolecules. Ausserre et al (1991) among others reported experiments in agreement with the above suggestions.

2.4. Adhesion of Polymer Melt on the Die Land

The occurrence of slip corresponds to adhesion breakdown at the interface of polymer and stationary phase (die wall). Unfortunately, the adhesive process in the melt and the influence on the conformation of the polymer near the wall has received limited attention (Kalika and Denn, 1987). We can only explore the influence of component properties on the interfacial properties in terms of currently available adhesion theory.

The work of adhesion (W_a) between phase 1 and phase 2 is given by (Wu, 1982)

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12} \qquad (1)$$

where γ_{12} is the interfacial tension between phase 1 and phase 2, γ_1 and γ_2 are surface tensions of phase 1 and phase 2, respectively. The surface tension, according to Fowkes

(1987) . is the sum of dispersive and polar contributions The interfacial tension may be established by many means For polymer-polymer interaction. the harmonic-mean equation is preferred (Wu, 1979). Accordingly,

$$\gamma=\gamma^{d}+\gamma^{p} \quad (2)$$

and

$$\gamma_{12}=\gamma_{1}+\gamma_{2}-\frac{4\gamma_{1}^{d}\gamma_{2}^{d}}{\gamma_{1}^{d}+\gamma_{2}^{d}}-\frac{4\gamma_{1}^{p}\gamma_{2}^{p}}{\gamma_{1}^{p}+\gamma_{2}^{p}} \quad (3)$$

where d and p are the dispersion and polar components. respectively.

For the interface between a polymer and a high-energy material (metal. metal oxide. glass, etc), a geometric-mean equation is better suited (Lee, 1973):

$$\gamma_{12}=\gamma_{1}+\gamma_{2}-2\left(\gamma_{1}^{d}\gamma_{2}^{d}\right)^{0.5}-2\left(\gamma_{1}^{p}\gamma_{2}^{p}\right)^{0.5} \quad (4)$$

Both equations (3) and (4) state that γ_{12} diminishes when the surface tensions and polarities match well between the two phases Under these considerations the work of adhesion is maximized, as is the interaction between the phases.

Since data for the surface properties of FE are not yet available, we have to take another fluorine-containing polymer, e.g. polytetrafluoroethylene (PTFE), as our model to predict the interfacial interaction. The surface tension of PTFE lies between 11.1-14.6 mJ/cm^2 at 180°C, that for PE is 20.4-26.5 mJ/cm^2 (Wu, 1982). Since PE and PTFE are non-polar polymers, the wetting-contact theory of adhesion applies to this couple. The theory states that it is easy for a material of low surface tension to wet one with higher surface tension; the reverse is difficult. Thus, an explanation may be provided for the effects of FE on the flow of polyolefins; namely that FE wets and adheres to the high surface energy metal of the die wall more readily than does LLDPE. The FE thus causes slippage of the host polymer on its surface and reduces the overall flow resistance of the melt. If this inference is correct, then, given that the surface tension of FE is likely to be lower than that of most host polymers: FE may be a universal processing aid for non-polar polymers. For polar polymers, however, the above analyses may not be correct as the wetting theory only takes in account the dispersion force acting between the two phases.

The discrepancies between expectations of theory and the findings of experiments on the effect of FE on polymer processability lead to the formulation of questions which remain to be settled by future research. These are listed in the expectation that they will also help clarify the objectives and the organization of this thesis.

2.5. Remaining Questions

Question directly arising from literature:

Are the effects of FE on processing properties of polyolefins due to the slip of host polymer or not?

Associated Questions:

1) What are the quantitative effects of FE on the processing property of polymers?
2) Under what processing conditions does FE perform best as a polymer processing aid?
3) How does FE affect the processing in detail?
4) Where and what are the microscopic sites of FE that affect the macroscopic flow properties?
5) Is FE useful to the processing of polymers other than polyolefins?

It is the above questions that lead us to the goals of this research: to investigate polymer flow under influence of FE, and to connect rheological observations with polymer-polymer interaction, and possible mechanisms.

3. ORGANIZATION OF THE ARTICLES

In the first paper 'Fluoropolymers and their effects on processing linear low density polyethylene', comparisons are made of flow curves for the extrusion of a LLDPE melt through clean metal capillaries and when overcoated by fluoropolymer process aids. Characteristic differences between the flow traces include a shear rate-dependent reduction in flow resistance due to the presence of FE at the die surface. The FE promoted the slip of LLDPE melts. Flow curves for extrusion through FE-coated dies are divided into distinct regions and the slopes of these have been rationalized by equations which combine the concepts of molecular dynamics and of adhesive failure at the die wall/polymer interface as the origins of slip-stick flow.

The above findings led to the formulation of the next article entitled 'Purging Fluoroelastomer Lubricants By The Extrusion of LLDPE'. There a descriptive account was given of the purging process. Two mechanisms have been postulated to account for the removal of FE deposited on a die land by the extrusion of LLDPE. Experimental data indicate that purging rates are higher at initial stages of the process than at subsequent period.

The third article, 'Influence of FE on Melt Flow of LLDPE/FE Blends' focuses on mechanisms whereby small quantities of flow modifier strongly affect the flow resistance of LLDPE/FE blends. Along with observations from the above two papers. experimental findings are rationalized with the concept of FE mass transfer at the flow boundary.

The fourth paper named 'Use of A Fluoroelastomer Processing Aid with Non-olefinic Polymers', combines a rheological study with an Inverse Gas Chromatography study of interactions between polymers with various polarity It has been found that FE coatings can variously affect extrusion of these polymers, and that the observations may be rationalized by concepts of acid/base interaction between host polymer and FE.

In brief, this work essentially examines effect of FE on flow of various polymers with different polarities, but not to consider the origins of extrusion flaws such as shark-skin or melt fracture. Applications and limitations of FE as a processing aid were observed in terms of changes in flow resistance. Mechanisms were explored by linking rheological phenomena with polymer-polymer interactions.

4. Fluoropolymers and Their Effect on Processing Linear Low Density Polyethylene

K C Xing and H P Schreiber
Department of Chemical Engineering. Ecole Polytechnique
P.0. Box 6079, Station Centre Ville
Montreal, H3C 3A7, QC. Canada

A comparison is made of flow curves for the extrusion of a LLDPE melt through clean metal capillaries and when overcoated by fluoropolymer (FE) process aids. Characteristic differences between the flow traces include a shear rate-dependent reduction in flow resistance due to the presence of FE at the die surface. The FE preferentially adheres to high energy die surfaces, but interacts very weakly with LLDPE melts, thus acting as a lubricant at the interface of polymer/stationary phase. and promoting the slip of LLDPE melts Arguments are presented showing that the percent slippage time must attain an equilibrium value at high extrusion rates Flow curves for extrusion through FE-coated dies are divided into distinct regions and the slopes of these have been rationalized by equations which combine the concepts of molecular dynamics and of adhesive failure at the interface of die wall/polymer as the origins of slip-stick flow

Polym. Eng. Sci . **36**. 387 (1996)

Introduction

There is wide interest in the use of additives to improve the processing properties of polymers. A particular case in point concerns linear low-density polyethylene (LLDPE), a widely applied commodity polymer but one known for its difficult melt processability. At shear rates suited for extrusion, flow defects are observed which severely limit the economics of processing. These are generally identified as shark-skin and cyclic or slip-stick melt fracture. Remedial measures are required and the use of fluoroelastomer (FE) or related fluoropolymer additives has proven to be effective in suppressing both the surface defects (shark-skin) and the unstable extrusion (slip-stick) problems referred to above. Numerous studies have considered the role played by FE additives in LLDPE extrusion. While much progress has been made towards understanding that role, a complete picture is still wanting. This report is intended to further that understanding by presenting some quantitative analyses of the effects on LLDPE processing due to the presence of FE flow modifiers. In so doing it complements our earlier discussions of the topic (1,2). The use of FE additives as processing aids for olefinic polymers and copolymers was reported by Blatz (3) some 30 years ago. Subsequently, many authors (4-12) have elaborated on the subject. There is consensus that FE polymers blended into LLDPE improve the appearance of extrudates at high output rates and reduce the polymer melt viscosity. Athey (5) and Rudin (6), among others, found that the benefits of FE additives are not immediately evident but become so after finite periods of extrusion, the time needed to establish steady-state conditions depending on the FE concentration. Implied is a need for the additive to migrate to the die wall in order to exert its effect. In his extensive studies. Ramamurthy (7,8) also noted the existence of an induction time for the benefits of FE addition to be felt. and suggested that FE effectiveness depended on the materials used to construct extrusion dies. As a result. the suggestion was made that the additive acted as an adhesion promoter between flowing melt and die wall. delaying the onset of discontinuities. He also noted that the additive seemed more effective in screw extrusion than in extrusion with a piston driven rheometer

The concurrent view on the mechanism for the changes in processing due to the presence of FE considers the additive to act as a die lubricant, allowing the host polymer to slip along the die wall. This view has been expressed most recently by Hatzikiriakos and Dealy (10-12). but also by Kanu and Shaw (4). Shih (13). and by Denn and coworkers (14,15). Since in normal practice the FE is finely dispersed in the polymer matrix. this view accounts for the observed time delay in flow improvements, that delay being set by the kinetics of the migration needed to accumulate a critical amount of the additive at the die/polymer interface. The evidence presented in references 10-12 persuasively argues in favor of the melt slip option. showing that the FE reduced the critical shear stress for slippage from 0 09 MPa for a control high density polyethylene to 0 02 MPa Also favoring the slippage and migration concepts are earlier results from our laboratories (6), concerned with the effectiveness of FE processing aids in pigmented LLDPE. Acid-base interactions between additive and pigment were reported to lead to the adsorption of the FE, thus hindering the additive's migration. As a result, excess amounts of FE were required to attain expected processing benefits.

A start point for the present investigation is the presumed action of the FE additive at the boundary between die wall and flowing melt. To focus on this interface, the flow comparisons made here involve a LLDPE melt without FE additive, extruding through uncoated metal dies and through dies with similar dimensions, previously coated by selected FE flow modifiers

Experimental Section

The host polymer in this work was a LLDPE (Dowlex 2045) supplied by Dow Chemical Co. The polymer had a melt flow index of 1.1. GPC measurements in trichloro benzene solutions gave values of Mn = 36,000 and Mw = 91,000, respectively. FE-1 was a Dynamar product, supplied by the 3M Company, FE-2 was DuPont's Viton Freeflow 20.

As implied above, two extrusion procedures were followed:

Type I: Extrusion through clean dies of specified dimensions.

Type II: Extrusion of the host polymer through similar dies previously coated by first extruding the pure FE melt. In this procedure, dies were not cleaned following the FE extrusion step.

Measurements were made with an Instron capillary rheometer, fitted with 90 degree-entry dies, 1.27 mm. in diameter and with L/D of 5.0, 10.0 and 20.0. Controlled piston speeds allowed scanning the flow behavior of the LLDPE over more than 2 decades of shear. The polyethylene was conditioned in the rheometer for 10 minutes prior to determinations and carry an uncertainty not exceeding 9%. Type I experiments were performed on dies freshly cleaned by firing at >600 °C. In Type II runs, the mass of FE on coated dies was evaluated by weight comparisons of initially clean dies and coated dies. Gravimetric analyses of dies at the end of Type II runs indicated the amount of FE retained on die walls.

Results and Discussion

1 FE effectiveness in LLDPE extrusion:

The effect of FE at the die wall/polymer interface is evident in a comparison of

Type I and Type II extrusion, as given in Figure 4.1. The LLDPE is processed at 180 °C through a die with L/D = 20, and FE-1 is the fluoropolymer in Type II runs. Data for 2 successive runs are shown for Type II extrusion. At very low shear rates there is no measurable difference between Type I and Type II results, but when γ exceeds about 10 s^{-1} there is an appreciable lowering of the apparent viscosity under Type II conditions. The lowering of flow resistance is clearly shear-rate dependent, and appears to reach a maximum at shear rates in the $10^2 s^{-1}$ range. At higher shear rates the trend in Figure 4.1 points to an approach of data for the different extrusion modes, an extrapolation indicating that near 1000 s^{-1} the flow resistances will again be indistinguishable. Flow data with FE-2 at the die wall were analogous to those in Figure 4.1, and both sets are in general agreement with earlier reports (5,13) which limited improved processability of polyolefins due to the presence of FE additives to shear rates below 700 1/s. A noteworthy feature in the Figure is the contrast between the smoothness of the Type I flow curve and the apparent segmented nature of Type II curves. Further discussion of this will follow later in the article.

The close similarity between data for successive Type II processing indicates that FE is not fully removed from the die wall during initial extrusion. The inference is toward the function of FE as a true die lubricant, and one not readily miscible with the bulk polymer. We have already remarked in an earlier publication (2) on the need for the FE additive to be no more than sparingly miscible with the host polymer if it is to function effectively. Present results also argue against a reduction in the flow resistance of polyolefins containing FE additives as being due, partly, to the viscous properties of the additive itself (7,8). The data in Figure 4.2 are the source for the statement. Shown is the ratio of apparent viscosities of the two FE additives to that of the host polymer, over a wide shear rate range. The apparent viscosities of the flow additives are always substantially greater than that of the LLDPE, so that a large reduction of the blend viscosity is unlikely.

In order better to evaluate the effectiveness of FE coatings as flow modifiers in LLDPE extrusion, we introduce the effectiveness coefficient (θ), defined as follows

$$\theta = \frac{F_I - F_{II}}{F_I} x100\% \qquad (1)$$

where F is the force exerted on the rheometer piston by the melt in Type I and II extrusion. The θ parameter has been used to compare the effectiveness of FE I and FE II as flow modifiers for the present LLDPE, as shown in Figure 4.3. Both of the modifiers reduce the flow resistance, and the corresponding θ values follow analogous paths as shear rate varies. That path leads to well defined maxima in the shear rate region of 100 s^{-1}, as already noted above. Quantitatively, in the present case FE-I is the more effective modifier, reducing the flow resistance by about 45%, as compared with a maximum θ of about 25%

for FE-2. Repeat extrusion through the same coated dies led to similar curves as those in Figure 4.3, with relatively little reduction in the maximum θ values. This again points to limited loss of the FE polymer during the initial extrusion run and supports the notion of slippage of the flowing polymer over the coated die, similar to concepts advanced by Hatzlkiriakos and Dealy (10-12). Inferred is very weak bonding at the FE/LLDPE interface, but significant bond strength at the FE/metal wall boundary. The general shape of curves in this figure is the result of differences in the shape of flow curves for Type I and Type II extrusion, noted during consideration of Figure 4.1. The slope changes in the segments of curves for Type II processing are directly related to the appearance of θ vs. γ plots.

2. End effects and slippage sites in FE-coated dies

There is wide recognition of the ability of FE additives to eliminate or reduce the severity of flow defects such as cyclic melt fracture and surface roughness, frequently associated with the processing of LLDPE melts. Attention is drawn to the initiation sites of these flow instabilities. One source of origin for flow instabilities in capillary extrusion is the die entry region(16,17). A calculation of die entry corrections, and their response to the presence of FE on the die wall therefore is appropriate. Bagley's method (17) was applied to data for Type I and Type II extrusion, and an example is given in Figure 4.4 for Type II extrusion at 200 °C, using dies coated with FE-1. While at lower temperatures excellent linear plots were obtained. the curvature displayed here was typical of results at higher extrusion temperatures. Following the example of Hatzikiriakos and Dealy (11) .who have reported similar findings, second order polynomial fitting of these lines led to extrapolations to L/D =0 and thus to the definition of end pressure losses (Pe) at each shear rate The end pressure loss is often used as a descriptor of Bagley corrections to flow data (11,18), and we have followed the practice.

A summary of Pe values for both types of extrusion is given in the two parts of Table 4.1; part A. applies to extrusion at 200 °C. and compares results for Type I and Type II procedures. with FE-1 as the flow modifier Part B. relating to 180 °C extrusion. also compares Pe values for Type II extrusion involving both FE-1 and FE-2. Clearly. the presence of FE at the die wall results in greater end pressure losses, more particularly with the use of FE-1. This would be inconsistent with concepts that identify the die-entry region as the primary source of flow instabilities known to be palliated by FE polymers Consequently the data of Table 4 1 point to the die land and the die exit as loci for surface defects and cyclic melt fracture in the extrusion of LLDPE. The relationship between the FE effectiveness factor θ and die dimensions, shown in Figure 4.5, supports this view. The effectiveness of FE coatings in reducing the flow resistance of LLDPE increases systematically with increasing die L/D. just as the influence of die entry events. of course. decreases with rising die L/D The pressure loss data also are relevant to the sporadic slip-stick flow. widely associated with the flow instabilities of concern here (2,7,10,11,14,15) The significant decrease in the slope of flow curves in Type II extrusion. illustrated in Figure 4.1, may be associated with the onset of slippage along the die land. Precedents for such an association are found in contemporary literature (7,10,14,19). It has been noted by Nielsen (20) that when polymer slips at the die wall, greater elongational deformation takes place in the die entry region. with the consequence of increased end pressure loss. Recently Fujiyama and Kawasaki (21) have reported a sharp increase in Pe when slip occurred during the extrusion of high density polyethylene. in confirmation of the concept. The data in Table 4.1 therefore further establish the die land as the locus of cyclic flow instabilities, and the role of FE as a lubricant at that boundary.

The role of lubricant noted above may. of course. be manifested by the slip of the FE polymer over the die land, or by slip of the LLDPE over an adhering FE layer. If the bond strength of that layer to the die wall is sufficient, then for any stated condition of extrusion. the efficiency factor θ should remain constant. In fact. however. when LLDPE is continuously extruded. the θ value decreases along paths illustrated by the example in Figure 4.6. An extrapolation of the function shows that θ =O after about 10 hours of extrusion. Gravimetric analyses show that 18±4 %, of the initial mass of FE remains on die walls following 4 hours of isothermal processing, regardless of the die L/D. Thus. finite amounts of FE are removed from the die wall during extrusion, either by the modifier diffusing into the polymer melt, or by the FE itself flowing along the die wall and exiting with the extruding melt. Increased permanence of FE layer effectiveness would in the one case require a greater degree of immiscibility with the host polymer In the other case the effectiveness level and its durability would vary with the selection of die construction material, as was indeed reported by Ramamurthy (7,8)

3. Further analysis of flow characteristics

The effect of FE on LLDPE flow characteristics may be analyzed in more detail using statistics and principles of transport phenomena. Accepting the occurrence of slip during extrusion under appropriate conditions, the total external force (F) for extrusion may be written

$$F = F_{ad} + F_{st} \qquad (2)$$

where F_{ad} is the component of external force needed to break the adhesion between the polymer stream and the stationary phase, and F_{st} is the force component needed to establish laminar flow. We now introduce λ , the percent of time during which slip occurs. This is equated to the percentage of total flow boundary in which slip occurs and is determined by

$$\lambda = \frac{t_{ad}}{t_{ad} - t_{st}} \tag{3}$$

where t represents the respective times for slip and stick flow. F_{ad} can then be expressed as the force (f_{ad}) need to break adhesion per unit area of the stationary phase.

For a circular die.

$$F_{ad} = 2\pi RLf_{ad}\lambda \tag{4}$$

F_{st} at r = R in turn is given by the local shear stress (τ) and time friction(λ) from

$$F_{st} = 2\pi RL(1-\lambda)\tau \tag{5}$$

The total extrusion force F over the die land is then stated as

$$F = 2\pi RL\tau_n \tag{6}$$

where τ_n is the nominal shear stress corrected for end effects.

$$\tau_n = \lambda f_{ad} - (1-\lambda)\tau \tag{7}$$

Combining equations 2 and 4 - 6, it follows that equation 3 shows λ to be a function of slippage time, and thus also of the apparent shear rate (γ_a) Differentiating equation 7 with respect to $\dot{\gamma}_a$ provides an expression for the slope of the flow curve during slip

$$\frac{d\tau_n}{d\dot{\gamma}_a} = (f_{ad} - \tau)\frac{d\lambda}{d\dot{\gamma}_a} + (1 - \lambda)\frac{d\tau}{d\dot{\gamma}_a} \tag{8}$$

A requisite for adhesive failure is an inequality between the local adhesive bond strength and the local shear stress, thus

$$\tau_n > f_{ad} \tag{9}$$

Equation 8 and the above inequality predict that at low shear, where no slip occurs, $f_{ad} > \tau_n$, and $\lambda = 0$ When eventually τ_n exceeds f_{ad}, λ becomes finite, indicative of slip From equation 8 it follows that a reduction in the flow curve slope will be a consequence of the event. Since a finite external force is a prerequisite for melt flow, λ cannot attain unity and therefore the polymer cannot slip over the entire die land . Rather, the parameter reaches a limiting value at high shear rate and remains constant beyond this rate of extrusion At this point, the slope of the flow curve must again increase These consequences of the proposed model may be tested by analysis of experimental data

The flow data shown in Figure 4.7 relate to the point. As in Figure 4.1 a comparison is made between data for Type I and Type II extrusion at 180 °C, two dies being represented in each processing mode The curves for Type I extrusion are smooth, with the most evident changes in slope located in the range of 100-120 kPa, similar to observations reported by Ramamurthy (7). The Type II curve is distinctly segmented and conveniently separated into 3 sections, as illustrated. A significant reduction in the slope is noted near 45 kPa, and the slope then increases at about 90 kPa. The pattern in Fig.7 is followed exactly at higher extrusion temperatures, and is in keeping with the predictions stated above. Extrusion data of this kind can be represented by a power law statement such as:

$$\tau_w = Y\dot{\gamma}_a{}^x \qquad (10)$$

Values of the y and x parameters, for extrusion at 180 and 200 °C, are summarized in Table 4.2. The exponent quantifies the apparent changes in flow curve slopes. The decrease in slope in the transition from zone 1 to zone 2 is usual, since generally with rising shear rate the degree of shear-thinning also rises, as in Type I extrusion.

Various rationalizations may be offered for the effects of FE on the flow behavior of LLDPE melts. One of these is based on the motion of segmented chain molecules. Reptation or segmental creep is proposed at the boundaries of a flow stream. According to Silberzan and Leger (24) segmental creep is favored and the total flow resistance is lowered when the interaction between polymer and die wall is lowered. In this context, FE with a lower surface energy than LLDPE, would wet preferentially the high surface energy walls of metallic extrusion dies, thereby lowering the adhesion between LLDPE and die walls. This would account for the lower slopes and reduced flow resistance in Type II extrusion, even at very low shear rates.

The slope changes in zones 2 and 3 of Type II extrusion are linked to the slip-stick flow of LLDPE melts. Earlier literature on the subject either considers the slip of polymer melts to be a general phenomenon of uncross-linked fluids (25), or to be the result of a sporadic adhesive failure at the melt/stationary phase interface(10,14,15,16). In this view, the prerequisite for adhesive bond strength. During slip, the melt is separated from the is reduced to zero. The frequency of occurrence of the event will increase with increasing shear rate, calling for a reduction with shear rate of the flow curve slope. As already noted, at higher shear rates, the per-cent time of slip flow (λ) associated with the extrusion of a given volume element of melt increases to a constant value but cannot attain 100%. While λ is increasing, flow resistance is reduced, and FE effectiveness, as stated by θ, increases substantially. Since for slip to occur, there must be an accumulation of chain tension at the polymer/boundary interface, the flow mode at high shear reflects the fluctuation between stress accumulation during the adhesion phase, and slip during the failure phase. When the cycle attains a steady-state, represented by the limiting value of λ, then further reductions in the flow resistance due to increasing applied stress can only be met by chain orientation and disentanglement. Since now the internal friction between segments is no longer dissipated by increased slippage, the flow curve slope in this shear rate region will tend to rise. Earlier mention of the peculiarity was made by Athey (5), and more recently by Clan (22) and by Valenza and La Manitia (23).

Equation 8 of this paper seems to bridge the opposing view on the origins of cyclic melt fracture, as represented by reference 25 on the one hand, and 2, 10, 14, 15, 16 on the other. The stress at the flow boundary (τ_n) is proportional to the polymer viscosity during laminar flow, and the factor (f_{ad}) introduced in the expression correlates an interfacial property with the viscosity characteristic of the polymer bulk. Turning next to the various forms of equation 10, these are rooted in the theory of adhesive failure at the interface as the cause of slip-stick flow. However, because melt viscosity is critically dependent on polymer molecular weight, weight distribution and shear rate, these equations also show the dependence of slip-stick flow on these factors. In this respect the equations incorporate the concept of molecular dynamics as the origin of slippage at sufficiently high rates of shear.

Conclusion

The investigation has led to the following conclusions

* FE coatings on extrusion dies have promoted the slip of LLDPE polymer at the die boundary , with a resulting reduction in the flow resistance.

* The effectiveness of FE coatings to reduce process viscosity is a function of the shear rate. In this work, optimum effectiveness was associated with a shear rate range of 100-200 s^{-1}.

* Slippage of LLDPE occurs at the FE/LLDPE interface, and its extent increases with increasing die length. FE effectiveness as a flow modifier therefore also rises with increasing die length.

* In slip-stick flow of LLDPE, the percent time during which the melt slips increases with shear rate to a characteristic maximum, but cannot attain the limit of 100%.

* Theories of molecular dynamics and of adhesive failure, alternatively proposed as the origins of sporadic flow in LLDPE, have been linked by equations based on concepts drawn from both approaches.

Acknowledgments

This work was supported by research grants from the Natural Sciences and Engineering Research Council, Canada. Our thanks go to staff members of the research department, 3M Canada, for useful discussions and for the supply of some research materials.

References

1. AJJI, A., VARENNES, S., SCHREIBER, H.P and D DUCHESNE, Polym Eng. Sci., **33**, 1524 (1993)
2. VARENNES, S. and SCHREIBER, H.P. J. Adhesion, **46**, 3 (1994)
3. BLATZ, P.S., US Patent, 3,125,547 (1964).
4. KANU, R.C. and SHAW, M.T., Polym. Eng. Sci., **22**, 507 (1982).
5. THEY,B.J., THAM, R.C., SOUFFIE, R.D. and CHAPMAN,G.R., SPE. ANTEC, Conf. Proc. **44**, 1149 (1986)
6. RUDIN, A., WORM, A.T andBLACKLOK, J E .SPE ANTEC Conf. Proc., **43**, 987 (1985).
8. RAMAMURTHY, A.V., Adv. Polym. Technol., **6**, 489 (1986).
9. RUDIN, A., SCHREIBER, H.P. and DUCHESNE, D., Polym. Plast. Technol. Eng., **29**, 199 (1990)
10. HATZIKIRIAKOS, S G , and DEALY, J M , J Rheology, **35**, 497 (1991)
11. HATZIKIRIAKOS, S G , and DEALY, J M , J Rheology, **36**, 845 (1992)
12. HATZIKIRIAKOS, S.G., and DEALY, J.M., J. Rheology, **36**, 703 (1992)
13. SHIH, C.K., Polym. Eng. Sci., **16**, 742 (1976).
14. KALIKA, D.S. and DENN, M.M., J. Rheology, **31**, 815 (1987).
15. HILL, D.A.,HASEGAWA, T. , and DENN, M.M., J. Rheology, **34**, 891 (1990).
16. TORDELLA, J P , Rheology, Vol 5, Ch **2**, Academic Press, New York (1969)
17. BAGLEY,E.B , J. Appl. Phys., **28**, 624 (1957)
18. LAUN, H.M., Rheol. Acta., **22**, 171 (1983).
19. UTRACKI, L.A. , Polymer Alloys and Blends, Ch. **2**, Hanser Publishers, New York,

(1992).

20. NIELSEN, L.E., Polymer Rheology, Ch. 6, Marcel Dekker, New York (1977).
21. FUJIYAMA, M. and KAWASAKI, Y., J. Appl. Polym. Sci., **42**, 467 (1991).
22. KLEIN, D.F., SPE RETEC: Polyolefins V: Proc. **5**, Internat. Conf. on Polyolefins, 285 (1987)
23. VALENZA, A. and LA MANITIA, F.P., Intern. Polym. Proc. J. **2**, 220 (1988)
24. SILBERZAN, P. and LEGER, L., Macromolecules, **25**, 1267 (1992)
25. LIN, Y.H., J. Rheology, **29**, 605 (1985).

Table 4.1. End Pressure Losses in Type I and Type II Processing of LLDPE

A. At 200°C

$\dot{\gamma}_a$ (sec^{-1})	End P Loss (kPa) Type I Extrusion	End P Loss (kPa) Type II Extrusion
2.86	3.55	2.30
7.14	14.1	19.1
14.3	26.7	45.0
28.6	42.0	102
71.4	70.2	179
142	128	217
285	214	305
572	366	490

B. At 180 °C

$\dot{\gamma}_a$ (sec^{-1})	End P Loss (kPa), Type I	End P Loss (kPa), Type II Extrusion & FE-1	End P Loss (kPa), Type II Extrusion & FE-2
2.86	14.1	14.1	20.1
7.14	28.3	33.7	30.1
14.3	49.4	64.2	52.2
28.6	52.2	121	84.3
71.4	95.3	225	169
142	166	319	229
285	279	446	265
572	577	652	289

Table 4.2. Constants for Power-Law Equation Applying to Flow Curve Regions in Type II Processing. (Constants are for $\tau_w = Y\,\dot{\gamma}_a^{X}$)

Curve Region*	1		2		3	
T(°C)	180	200	180	200	180	200
Y	12.3	11.5	22.4	14.8	11.2	8.9
X	0.61	0.60	0.38	0.43	0.54	0.59

* For identification of flow curve regions, see Fig 7

Figure Captions

Figure 4.1. Shear stress-shear rate relationships for LLDPE extrusion through clean dies (Type I) and FE-coated dies (Type II), die L/D=20, T= 180°C. ○ Type I; ● Type II, first run; ∇ Type II, second run.

Figure 4.2. Ratio of viscosities of FE to LLDPE as function of shear rate: □ FE-1; ■ FE-2.

Figure 4.3. Shear rate dependence of viscosity reduction percentage (Θ), due to FE coating on die surface; T= 180°C, die L/D=20: ○ FE-1, ● FE-2.

Figure 4.4. Plot of Bagley correction relating to LLDPE extrusion; 200°C, various L/D dies and shear rates.

Figure 4.5. Shear rate variation of FE coating effectiveness as flow resistance modifier: response to die length changes. Modifier is FE-1; T= 180°C, L/D=5 (○), L/D=10 (●), L/D=20 (∇).

Figure 4.6. Efficiency of FE-1 flow modifier for LLDPE extrusion as function of processing time. T=160°C, shear rate=143 s^{-1}

Figure 4.7. Comparison of corrected shear stress/shear rate plots for Type I and Type II extrusion of LLDPE at 180°C, showing definition of zone 1,2 and 3 in Type II extrusion.

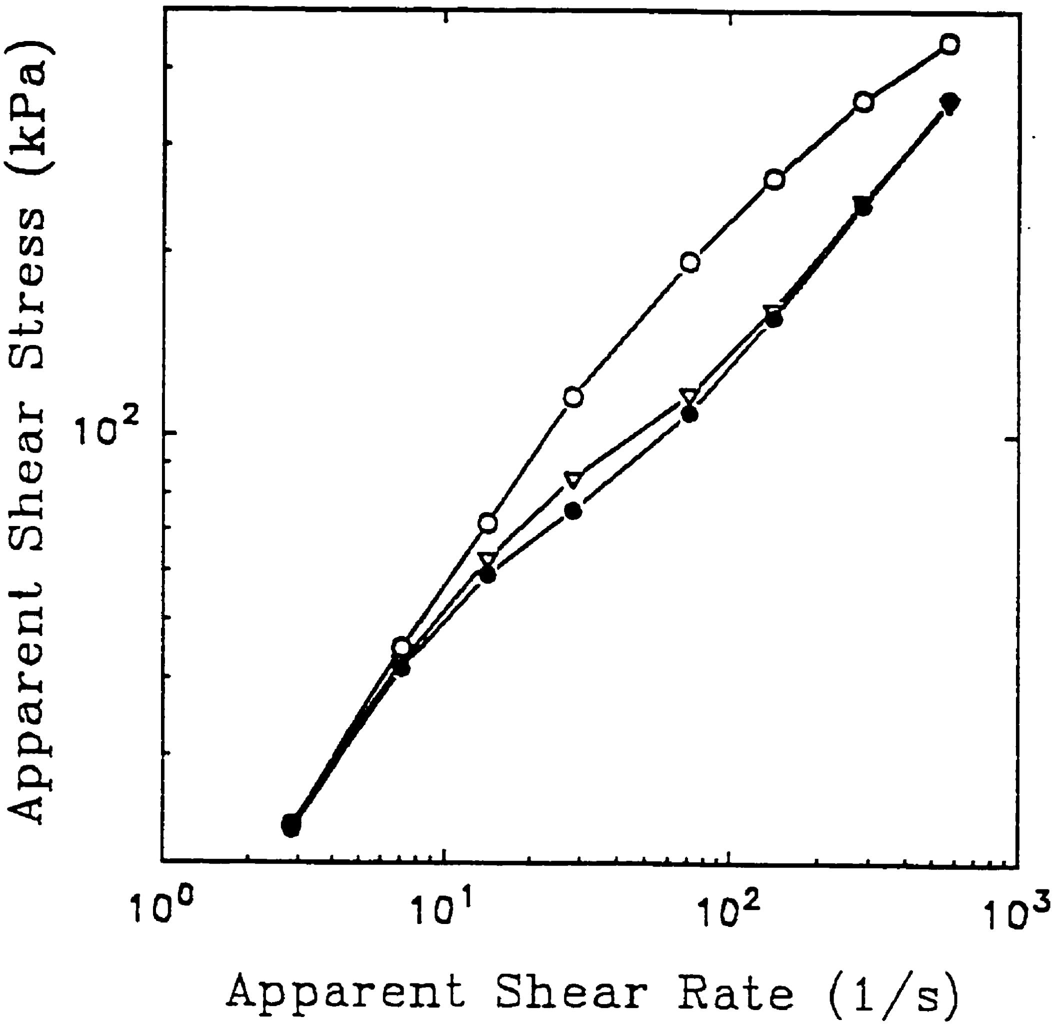


Figure 4.1. Shear stress-shear rate relationships for LLDPE extrusion through clean dies (Type I) and FE-coated dies (Type II), die L/D=20, T= 180°C ○ Type I, ● Type II, first run; ∇ Type II, second run.

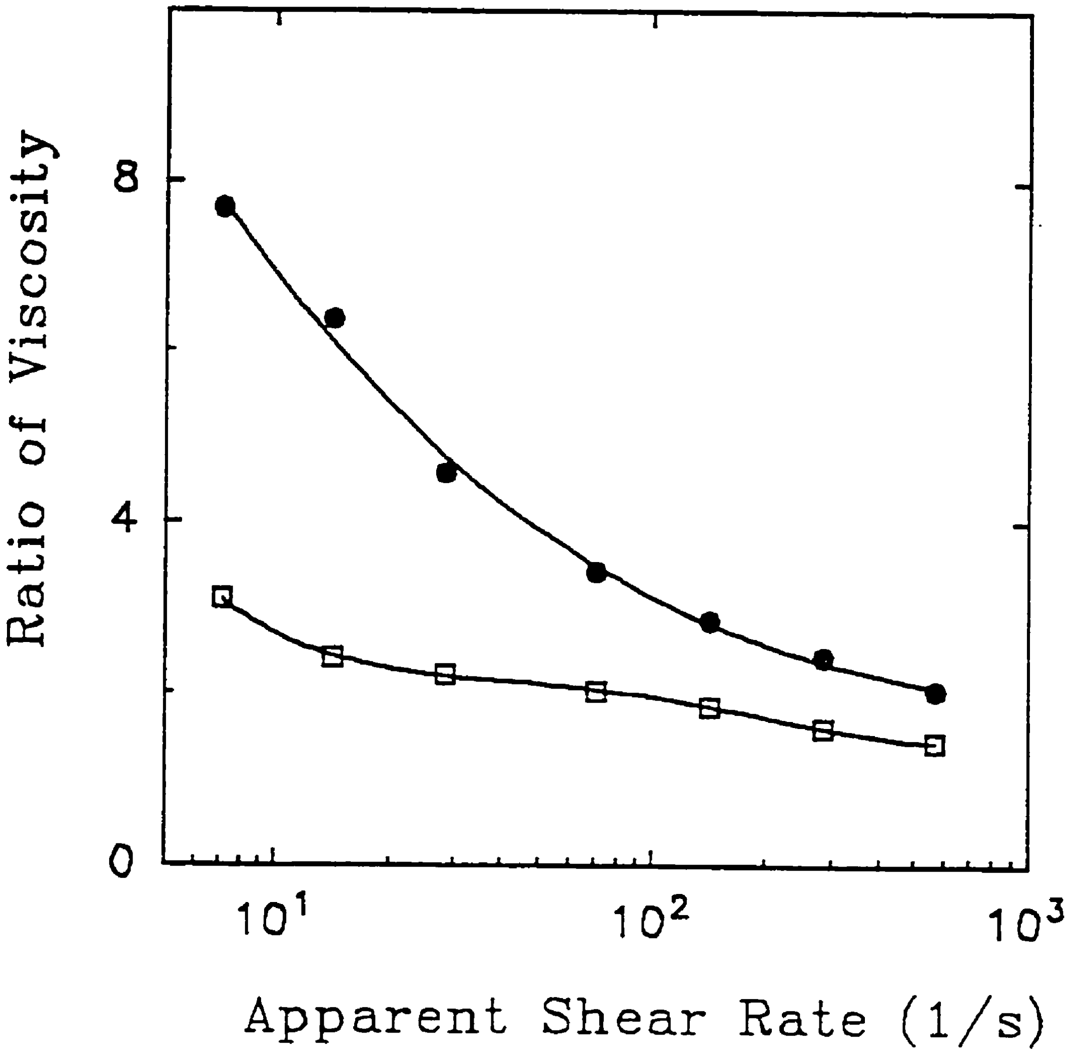


Figure 4.2. Ratio of viscosities of FE to LLDPE as function of shear rate ☐ FE-1 ■ FE-2

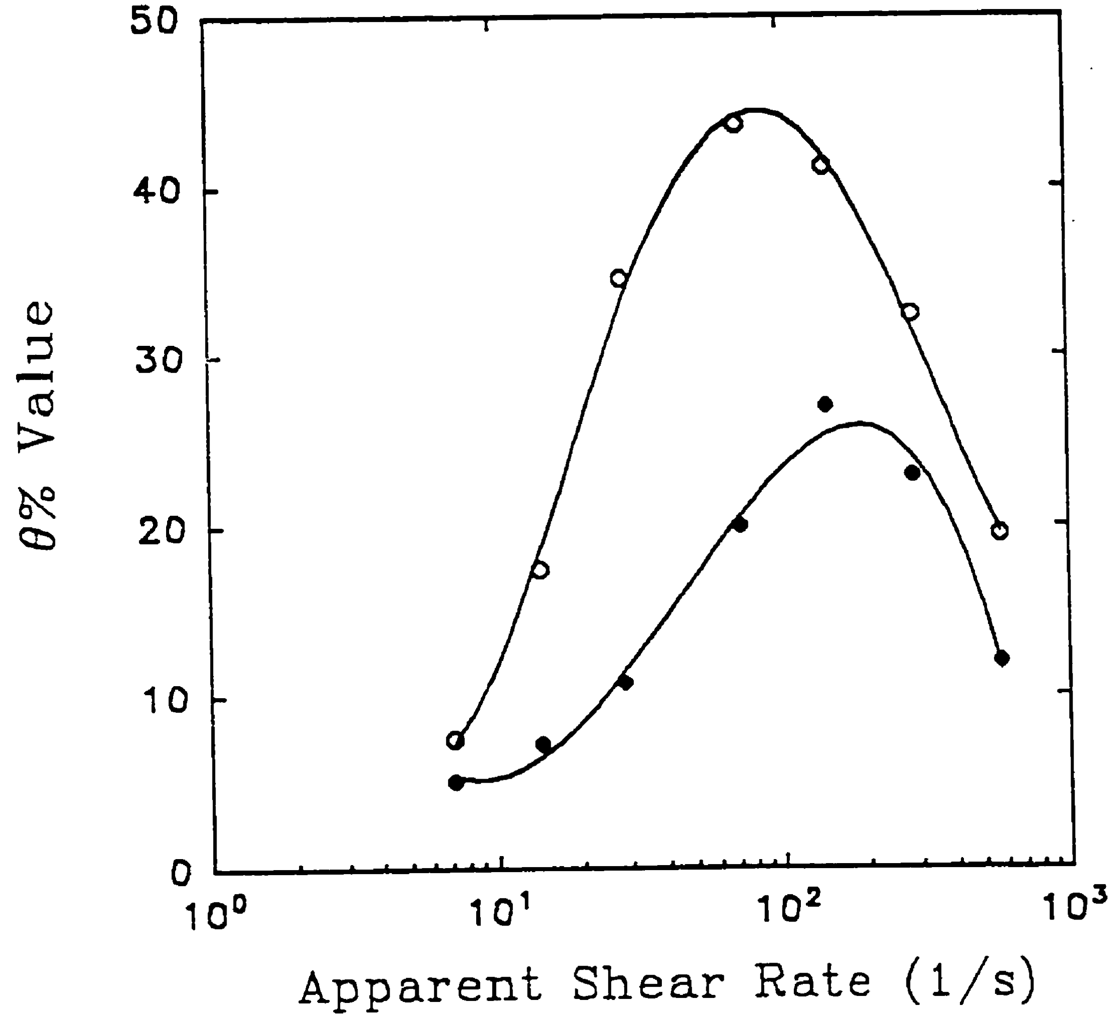


Figure 4.3. Shear rate dependence of viscosity reduction percentage (Θ), due to FE coating on die surface; T= 180°C, die L/D=20. ○ FE-1; ● FE-2.

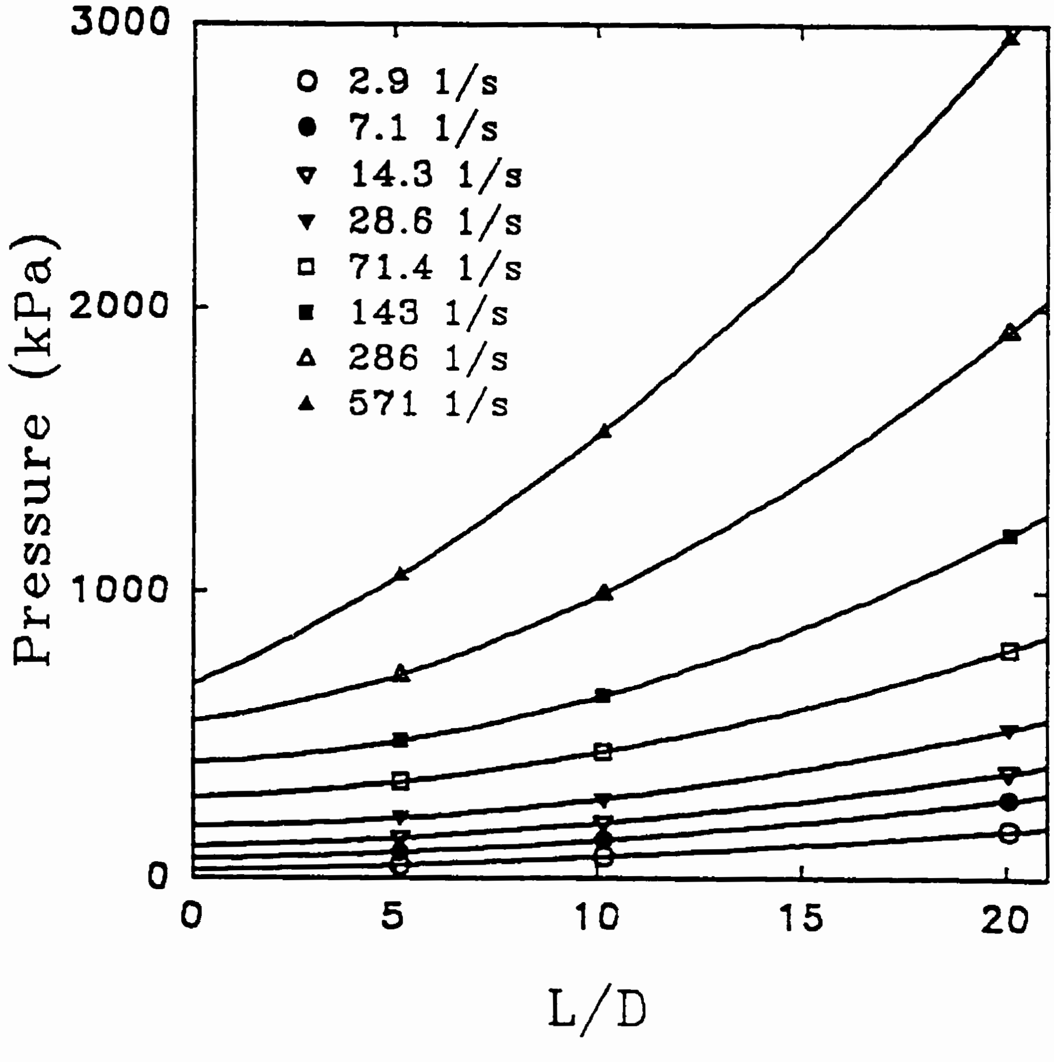


Figure 4.4. Plot of Bagley correction relating to LLDPE extrusion; 200°C, various L/D dies and shear rates.

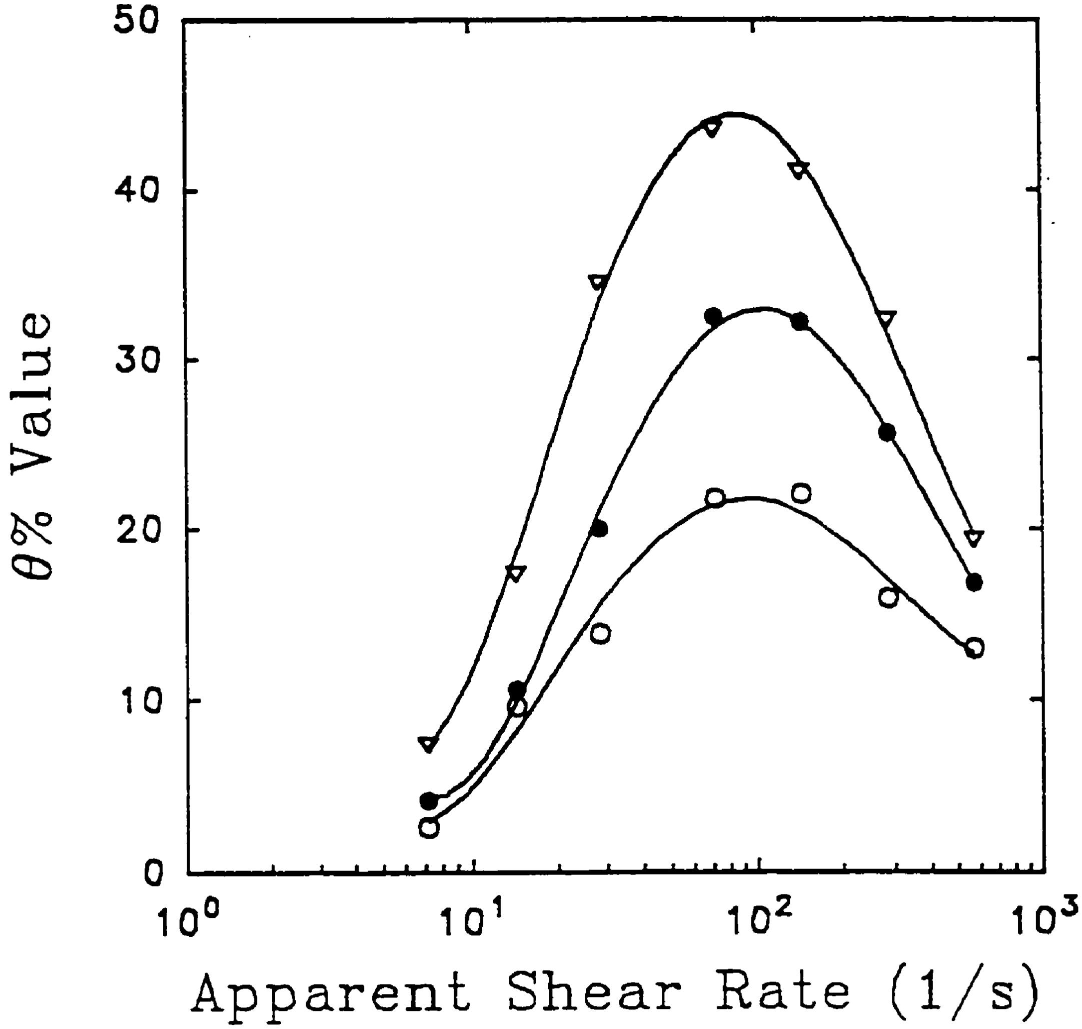


Figure 4 5 Shear rate variation of FE coating effectiveness as flow resistance modifier: response to die length changes Modifier is FE-1. T= 180°C. L/D=5 (○), L/D=10 (●), L/D=20 (∇)

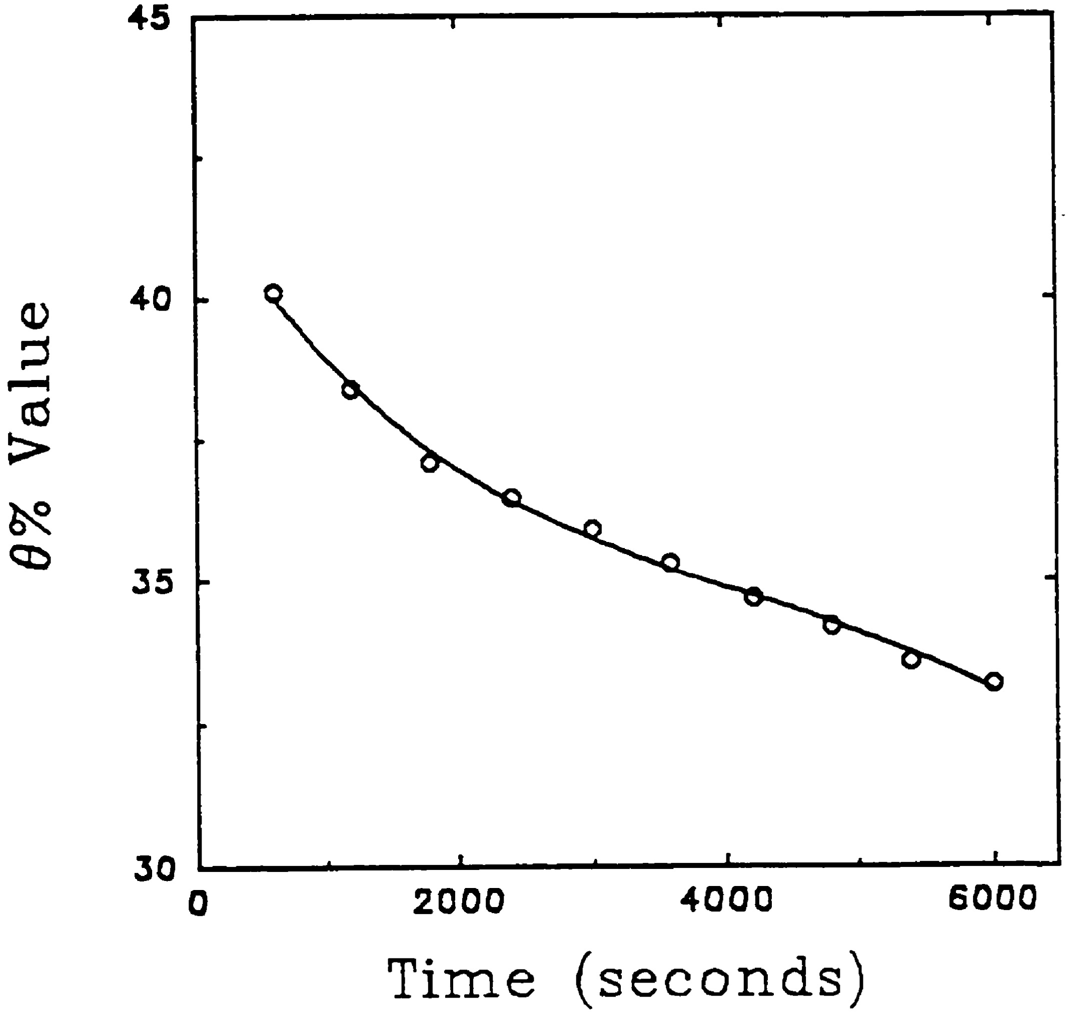


Figure 4.6 Efficiency of FE-1 flow modifier for LLDPE extrusion as function of processing time. T=160°C. shear rate=143 s^{-1}

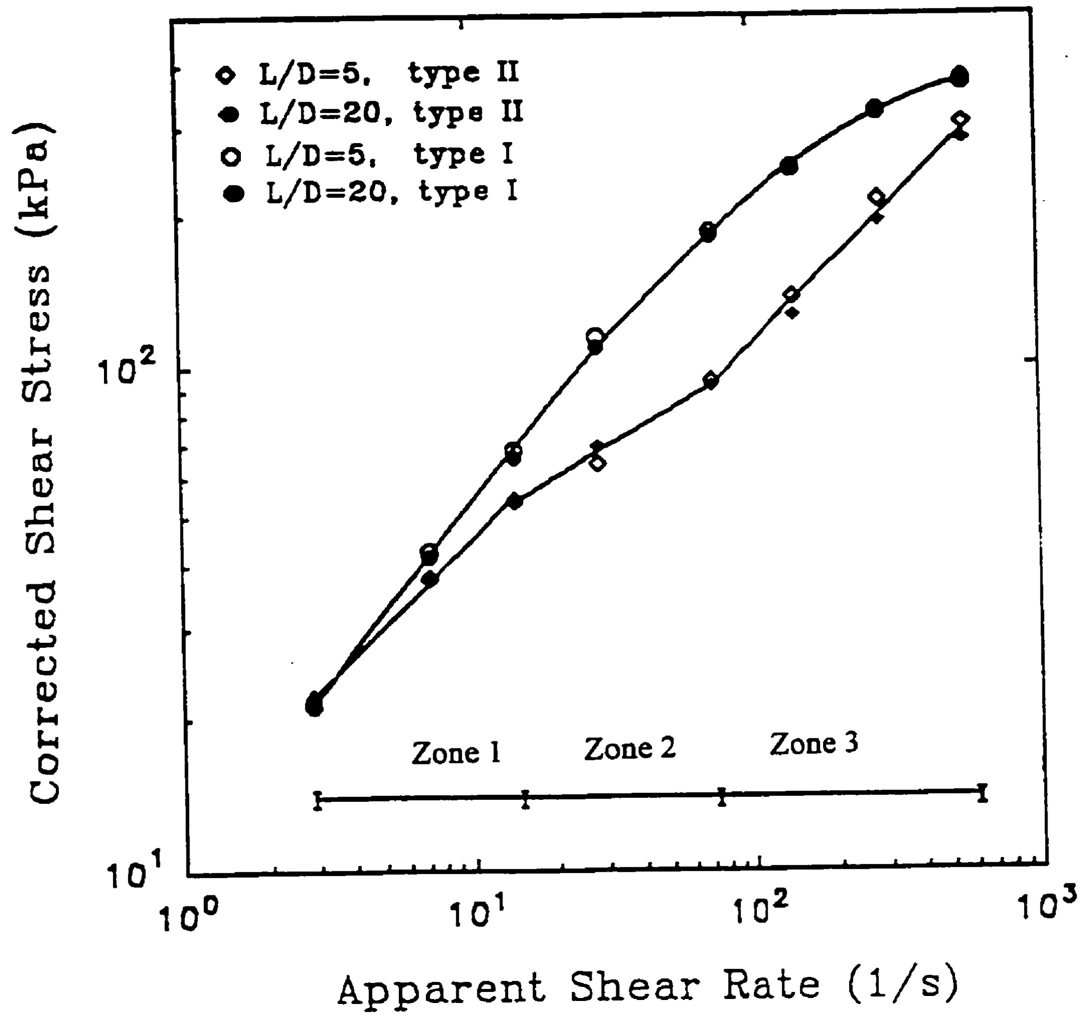


Figure 4 7 Comparison of corrected shear stress/shear rate plots for Type I and Type II extrusion of LLDPE at 180°C, showing definition of zone 1,2 and 3 in Type II extrusion

5. PURGING FLUOROELASTOMER LUBRICANTS BY THE EXTRUSION OF LLDPE

K C Xing and H.P Schreiber*

Ecole Polytechnique, Montreal, Quebec, Canada

The process of purging fluoropolymer processing aids from extrusion dies by the continuous extrusion of LLDPE has been analyzed quantitatively Purging rates are dependent on melt temperature and on shearing rates in a process that appears to involve both the penetration of processing aid into the melt stream and its mechanical stripping from the die surface. A statistical analysis has been carried out which accounts for the dependence of purging rates on temperature, shearing rate and extrusion time. The procedure should find use on designing purging operations for industrial-scale equipment

* Mail address Prof H.P Schreiber, Department of Chemical Engineering, Ecole Polytechnique, P O Box 6079, Stn Centre-Ville, Montreal, QC H3C 3A7, Canada

1. Introduction

Fluoroelastomers (FE) have been widely used as polymeric lubricants for processing linear, low-density polyethylene (LLDPE). It is generally recognized that small amounts of FE can significantly reduce the flow resistance of LLDPE [1-6] Ramamurthy et al[1-3] have shown that the effect is due to changes in the properties of die surfaces, as the fluoropolymer additive forms a contiguous coating. The coating layer can be formed by the long extrusion of a LLDPE/FE blend [1-3], or by directly applying FE onto die surfaces[4-7]. In either case a subsequent need may arise to purge the die of residual FE. In general, purging one polymer melt from extrusion dies with another is an important facet of polymer processing technology. To date, however, the topic has received limited attention in the literature [7-8]

The objective of this paper is to consider purging practices in sufficient detail so as to identify factors which affect the process. The purging of FE from extrusion dies by the processing of LLDPE is considered from an analytic viewpoint.

2. Experimental

The polymer matrix of this work was a thermally stabilized LLDPE, Dowlex 2045, supplied by Dow Chemical, with M_w = 91,000 as determined by size exclusion chromatography in trichlorobenzene at 130°C. The fluoroelastomer (FE) was Dynamar L-11216 supplied by 3M Canada. This is a copolymer of vinylidene fluoride and hexafluoropropylene, with a Mooney viscosity reported by the supplier to be 48.

An Instron rheometer was used as extrusion device, with melt temperatures controlled in the interval 160 - 200°C. The rheometer was connected with a computer to record extrusion force at half second intervals. Experimental data were processed with the "Sigmaploter Graphics System", Version 5.0, made by Jandel Corporation. The die used was 1.75 mm in diameter and the length/diameter ratio was 40.0. The flat-entry die was made of mild steel.

In a typical experimental sequence, pure FE was extruded first to fill the initially clean die. Thereupon the rheometer was cleaned, but not the die. The total weight of die and residual FE was measured and recorded (W_{BF}), after removing the die from the Instron device. The die was then reinstalled in the device and purged by extruding pure LLDPE under controlled conditions of extrusion temperature and extrusion rate. Due to poor compatibility between FE and LLDPE, most of the FE was ejected as a plug by the flowing LLDPE at the beginning of purging process. Because of the weak interaction between these two polymers, there is no effective bonding between the FE plug and extruded LLDPE. At room temperature, FE is a soft, grey elastomer, and LLDPE a white rigid plastic. Because of significant color and modulus differences between FE and LLDPE, it was easy to identify and separate the ejected FE from the LLDPE. The weight of the recovered FE plug is recorded as W_{PG}. The difference between W_{BF} and W_{PG} thus defines the amount of FE remaining in the die. For each purging run, the rheometer was filled with about 16 grams of LLDPE; extrusion was started following a 10 minute allowance for establishing thermal equilibrium. At the conclusion of a run, the cylinder was refilled and the process repeated. As many as 8 repetitions were carried out, with purge times therefore exceeding 130 minutes in some cases. We refer to this procedure as Type II extrusion. In control runs, identified as Type I extrusion, unmodified LLDPE was extruded under the same conditions through a freshly cleaned die. The persistence of FE in the die was determined from observed differences between the flow behavior in Type I and Type II extrusion sequences.

3. Results and Discussion

Previous literature suggests that a key factor in purging polymer from a die is that the viscosity of the purging polymer should exceed that of the polymer being removed [8] In practice, of course, this condition cannot always be met, nor was it the case here. In this work, the LLDPE used as purging polymer had a lower melt viscosity than the FE to be purged from the die. Figure 5.1 compares the melt viscosities of LLDPE and FE over more than 2 decades of shear, at 160 - 200°C In this shear rate interval the viscosity of FE varies from more than 3 times that of LLDPE at low shears, to about 1.5 times that of the matrix polymer at high shear rate.

3.1 Analysis of Type II, purging extrusion

The start point for this section is a view of the flow behavior of LLDPE through a reference, clean die. As shown in Figure 5.2 for extrusion at constant piston speed, the extrusion force increased sharply at first and then gradually attained a nearly constant force at extrusion times exceeding about 100 seconds. On repeat extrusion through the same die, the shape of the flow curves closely resembled that of the initial run, but at somewhat lower extrusion forces . By run 3, noted in the figure, there is indication that extrusion has attained a steady state.

Type II extrusion through the FE-coated die produced very different patterns, as illustrated in Figure 5.3. Knowing the mass of remained FE, its density (ca. 1.84 g/cm^3 at room temperature) and the die size, the initial thickness of the FE coating is estimated as shown in Table 5.1. A sharp stress peak at the onset of the first extrusion sequence is followed by a sharp reduction to a stress level well below any observed in the entire series of Type I runs. A subsequent slow increase in stress is also observed. In succeeding extrusion runs, the average extrusion force is greater than in the first run. Indeed, the increase in extrusion force is systematic. but even in run 8 the extrusion force was still appreciably lower than the corresponding level in Type I runs. This signal of the ability of FE coatings to reduce the flow resistance of LLDPE was still visible well beyond the 8th extrusion.

Table 5.1. Weight of FE in the Die

	Extrusion Rate (RE)=27.9 mm/sec			Temp = 180°C	
	160°C	180°C	200°C	E=14.4	E=56.7
W_{BF}	0.28	0.26	0.27	0.28	0.29
W_{PG}	0.24	0.23	0.25	0.24	0.27
W_{RM}	0.04	0.03	0.02	0.04	0.02
L(μm)	56	42	28	56	28

NOTES: W is weight of FE in grams. BF before starting purge. PG plug of FE purged out at outset. and RM remaining FE in the die at the beginning of purge. W_{RM} values bear average error of 30% from 3 observations. L is the calculated average thickness of FE coating; it may be smaller than actual value as FE density is lower at extrusion temperature than at room temperature.

Comparison of Figures 5.2 and 5.3 also shows marked differences in the fluctuation of extrusion force in Type I and Type II procedures. In Type I extrusion. some force fluctuation is noted at the apparent shear rate of 143 s^{-1}. The difference between peaks and valleys of extrusion force was generally less then 5 kg, at a frequency greater than 250 seconds. In contrast. Type II processing at the same extrusion rate produced fluctuation amplitudes of 5-10 kg., and more importantly, at frequencies that were often less than 150 seconds. Instability in extrusion force is usually considered to be an indication of slippage of the host polymer mainstream over the die surface [9] This slippage contributes to the reduction of extrusion force when LLDPE flows through a FE-coated die

3.2 Quantitative characterization of purging processes

With the on-line computer recording system noted in the experimental section, the course of changes in extrusion force could be followed throughout the extrusion run, as shown in Figures 5.2 and 5.3. The differences in extrusion force under identical processing conditions were used to quantitatively study the course of purging processes.

Previous studies[1-7] have verified that integral layers of FE on the die surface are effective in reducing the flow resistance of LLDPE. The effect vanishes as FE is stripped off from the die surface. Mathematically, this leads to the definition of a parameter (Θ), which expresses the effectiveness of FE as a means of reducing the flow resistance of LLDPE. Thus,

$$\Theta\% = \frac{F_I - F_{II}}{F_I} x 100 \tag{1}$$

where F_I is the extrusion force of LLDPE over a clean die surface and F_{II} is the force when flowing over a FE-coated die surface. Obviously, Θ will be zero when the FE has been fully purged from the die surface.

The recording system used in this work registered fluctuations occurring at intervals of 0.5 second. However, in order to minimize the influence of random variations due to instrumental or sample purity factors, we have used the average extrusion force over an entire run to characterize differences between the two extrusion protocols. The average force for each run was calculated from the value at the initially stable point to the end of the run. In turn, the initial stable point, following the initial stress peak, was defined by the point following which at least 3 identical, consecutive force readings were recorded. Differences between average force readings for Type I and II extrusion were then used to interpret the purging process in the present system. In the following sections we consider the dependence of purging on variables of the extrusion process.

3.2.i) Dependence on extrusion rate and time of flow

In the following, the experimental uncertainty in θ was established by repeat investigations, to be less than ± 9 %. The dependence of purging on extrusion rate is indicated in Figure 5.4. At an extrusion rate of 14.8 mm^3/second, in the first run the efficiency factor θ was more than 34%. Following the extrusion of 90 grams of LLDPE, the efficiency factor fell to only 11%. Hence, the mean reduction effectiveness of the FE coating was 0.25 percentage points per gram of LLDPE. In detail, Θ decreased sharply at the beginning of extrusion, but the decrease became much less evident following the extrusion of about 24 grams of LLDPE. At the extrusion rate of 29.7 mm^3/second, the path followed by Θ was quite different from that noted above. At the onset of extrusion, the average efficiency was less than 32%. After more than 100 grams of LLDPE had been processed through the coated die, the Θ value remained essentially unchanged, near 26%. Thus, the mean loss of effectiveness of the FE coating was only 0.06% per gram of LLDPE. As was the case at the lower rate of extrusion, the drop in Θ was most pronounced in the first run, then became less marked and roughly constant in following extrusion runs. The same trend continued at the extrusion rate of 59.4 mm^3/sec. Here there was a reduction in Θ from 32 % at the beginning to somewhat more than 29 % the end of extrusion. In this case, for a constant quantity of LLDPE extruded, the average loss rate of FE effectiveness is less than 0.04% per gram of LLDPE.

The relationships between Θ and the mass (M), in grams of LLDPE extruded under isothermal conditions through the coated die can be expressed by regression analyses as follows.

1) At 14.8 mm^3/second.

$$\theta = 44.47 - 1.10M + 1.29x10^{2}M^{2} - 5.44x10^{5}M^{3} \qquad (2)$$

2) At 29.7 mm^3/second ,

$$\theta = 35.21 - 0.337M + 4.51x10^{3}M^{2} - 2.06x10^{5}M^{3} \qquad (3)$$

3) At 59.4 mm^3/second ,

$$\theta = 32.91 - 5.39x10^{-2}M + 1.93x10^{-4}M^{2} - 1.08x10^{-6}M^{3} \qquad (4)$$

The time dependence of θ at various extrusion rates is fully analogous with the trends shown in Figure 5.5. Thus, at 14.8 mm^3/second extrusion rate, the average efficiency loss following 1000 seconds of extrusion is in excess of 12%. In the same period of extrusion, the efficiency loss at 28.9 mm^3/second was about 4 percentage points and decreased further to about 2.6 percentage points at an extrusion rate of 59.4 mm^3/second.

As before, regression analyses of relationships between extrusion time (t), in seconds and θ may be formulated:

1) At 14.8 mm^3/second ,

$$\theta = 44.35 - 1.19x10^{2}t + 1.52x10^{6}t^{2} - 6.96x10^{11}t^{3} \qquad (5)$$

2) At 29.7 mm^3/second ,

$$\theta=35.79-8.57x10^{-3}t-2.73x10^{-6}t^2-2.06x10^{-10}t^3 \tag{6}$$

3) At 59.4 mm^3/second .

$$\theta=32.91-2.45x10^{-3}t+4.00x10^{-7}t^2-1.01x10^{-10}t^3 \tag{7}$$

With equations 2-7, we can calculate the extrusion time and the mass of LLDPE needed to reduce the flow modifying effect of FE to zero. Results of the calculation are given in Table 5.2. Clearly, shorter extrusion times but larger masses of LLDPE appear needed to nullify FE effectiveness at higher rates of flow. A more detailed analysis modifies this view. Roughly doubling the flow rate from 14.8 to 27.9 mm^3/s, reduces the time requirement by about 38 %, while a nearly 4-fold rise in the extrusion rate only incurs an additional extrusion time reduction of some 7%. Similarly, while the purging potential of LLDPE increases with the extrusion rate, the increase fails to match the variations in flow rate. Thus, the mass of LLDPE needed at 27.9 mm^3/s is only about 38% greater than at the lowest extrusion rate (14.8), and about 150 % greater when extrusion rate rises by about 400 % to 59.4 mm^3/s. This suggests that purging is an interfacial phenomenon, and one that is abetted by the migration or penetration of FE into the LLDPE matrix. If this penetration rate were only temperature-dependent, then the amount of LLDPE needed to completely strip off the FE should be 4 times greater for extrusion at 59.4 mm^3/s than that at 14.8 mm^3/s, an expectation not met in fact. A possible reason may be a dependence of migration kinetics on the extrusion rate. At the lower and more closely matched melt viscosities in effect at high extrusion rates, these rates may be expected to accelerate thereby accounting for observations.

Table 5.2. Dependence of FE Persistence on Extrusion Rate at 180°C

EXTRUSION RATE (mm³/s)	TOTAL TIME (s)	LLDPE MASS (g)	R_t	R_m
14.8	1.2×10^4	1.3×10^2	0.98	0.98
27.9	7.5×10^3	1.8×10^2	0.98	0.97
59.4	7.0×10^3	3.2×10^2	0.99	0.99

Notes: R is the relative coefficient of regression. Subscripts t and m stand for time and mass.

3.2.ii) Dependence on extrusion temperature

The effectiveness of purging is a function of melt temperature, as documented in Figure 5.6. This shows the purging characteristics at 160, 180 and 200°C and constant extrusion rate. Higher temperatures increase the time-dependent variation of θ, in a manner consistent with the speculation noted above. Thus, at 160°C, Θ decreases from above 30% in the first extrusion run, to about 27% after more than 4800 seconds of purge. The reduction proceeds at a nearly constant rate. At 180°C, the effectiveness in the same extrusion period drops from an initial 31.7 to 26.1%. Moreover, the path of the θ vs time curve is quite different. Simple linearity occurs only after several extrusion runs, the reduction in effectiveness being non-linear earlier in the extrusion process. At 200°C, the Θ value has its greatest decrease (in the present context), falling from more than 33 to 16.0% after 4800 seconds of purge. The average rate of reduction therefore is more than 5 times greater than the corresponding rate at 160°C. Once again, a more complex relationship is evident between θ and extrusion time.

The results again lead to regression analyses, stated as

1) at 160°C,

$$\theta=31.34-2.38x10^{-3}t+4.99x10^{-7}t^{2}-3.96x10^{-11}t^{3} \qquad (8)$$

2) at 200°C,

$$\theta=45.02-2.41x10^{2}t+7.44x10^{6}t^{2}-2.94x10^{10}t^{3} \qquad (9)$$

The relationship at 180°C is stated in equation 6.

Equations 6, 8 and 9 may be used to calculate the time needed fully to remove the FE from the die. Results of the calculation are given in Table 5.3. The persistence of FE on the die wall is highly dependent on the extrusion temperature, the residence time being reduced by 50% over the 40°C range involved.

Table 5.3. Dependence of FE Persistence on Extrusion Temperature

TEMPERATURE (^{0}C)	160	200
TIME (sec)	1.3×10^3	5.9×10^2
R	0.98	0.99

The persistence of FE effectiveness as a modifier of LLDPE flow can also be considered from the viewpoint of time-temperature equivalence. The contact time between elements of FE and LLDPE is raised at low extrusion rates and higher temperatures. Both factors tend to accelerate the depletion of the FE layer. In contrast, that depletion is retarded at shorter contact times, favored by raising the extrusion rate. Implied in the rationalization is the dependence of purging effectiveness on the degree of interpenetration of the molecular species in contact at the interface.

3.3. i) Purging viewed as a microprocess

Experimental findings elaborated in Table 5.1 indicate that only a very small amount of FE is left in a die immediately following a purge experiment. In terms of residual layer thickness, this corresponds to a few tens µm. Considering that a very much greater amount of LLDPE is swept out in a cycle, it follows that the purge is basically a microprocess in which the material of the stationary phase is removed by the flowing host material. Implied is a transfer of the stationary material to the mainstream due either to interpenetration at contact points and/or to mechanical detachment . due to the drag exerted by the mobile material on the stationary phase

In the above mechanisms interpenetration would be the result of thermal motion, driven by concentration differences and promoted by high temperatures in the extrusion experiment. The drag process is more complex The flowing LLDPE will cause a gradual depletion of the FE layer when the force at the interface between the polymers is greater than the cohesive strength of the stationary phase, and/or the bond strength at the FE/ die land interface. In the former case, a gradual depletion of the FE layer is indicated, while a more massive and relatively rapid loss of the FE would be manifested in the latter case. Thus, three microprocess mechanisms may be postulated to account for the removal of FE from the die

a) FE is removed gradually, layer by layer, from the FE/LLDPE interface to the FE/die wall boundary.

b) FE is swept more rapidly along the die land from the die entry to its outlet;

c) FE is stripped off randomly from the die land.

The consequences of these postulates on the variation of θ may be illustrated for convenience, as in Figure 5.7

There is broad agreement in the literature[1-6], that the effect of FE on LLDPE flow follows from a change in the interfacial properties within the extrusion system. If mechanism a) above is accepted, then the effect of FE on LLDPE flow should remain constant until nearly all of the FE had been stripped from the die. The efficiency should then drop very sharply as the purge process comes to an end. The Θ vs. time relationship should be in the shape of curve (a) of Figure 5.7. Since experimental data do not follow this pattern the mechanism cannot be dominant.

In terms of mechanism b) converging flow would describe the behavior of LLDPE in the FE channel. Under these conditions the stationary phase closer to the exit of the channel would be subject to greater stress than portions near the die entry[10]. Since the cohesive strength of the FE is independent of its position in the die, the depletion of the polymer would be most pronounced at the die exit. The θ vs Time plot should be similar to line b in figure 5.7. Again, this is contrary to experimental findings.

The third mechanism, implying the random removal of FE into the mainstream, is consistent with the high molecular weights of both the FE and the host polymer. Assuming that the molecular weight of FE is above the polymer's critical weight for chain entanglement, a network structure may be attributed to the FE layer. Because of this, the FE surface is likely to be uneven, particularly at the beginning of an extrusion run when the coating is relatively thick The uneven or "lumpy" surface would promote the random interdigitation between FE and LLDPE over the entire length of the coating At the interlocked interface, interpenetration and mechanical detachment would tend to occur simultaneously. The postulate of entanglements would favor the chances of FE being removed directly from the FE/metal interface, and argues against the layer-by-layer removal of the flow modifier First to be removed would be FE from areas where the adhesive bond with the metal wall is flawed. The flaws, originating from metal impurities, or from cohesively weak boundary layers formed by low molecular weight chains [11], etc., may be assumed to distribute randomly along the die land. Accordingly, random stripping of the FE from the die wall may be postulated as a consequence The proposed mechanism also suggests that the relative contributions of interpenetration and mechanical loss to the purging of FE will change in the course of the process. The drag effect should be dominant at the beginning of purging , because of the coating roughness which will favor the removal of FE micro-droplets by the flowing host polymer. As the process goes on, the coating would become smoother and thinner, reducing the importance of mechanical losses and shifting emphasis to the interpenetration of FE, thus reducing the rate at which FE is introduced into the flowing polymer. The resulting relationship of Θ vs. time should then be in the shape of curve (c), Figure 5.7 This conforms with experimental data, as reported in Figures 5.4 to 5.6.

In summary, experimental evidence favors the combination of interpenetration and mechanical losses, occurring randomly along the entire die land, as the microprocess steps involved in the purge of FE into host polymers such as the present LLDPE. The mechanism must also be consistent with independent variables of the extrusion process, as noted below

3.3.i.i) Effects of process variables

The purging process should be a function of any variable affecting the cohesive or bond strength of the stationary phase or the flow of the mainstream The degree of thermodynamic interaction between purged and purging materials may be foreseen as one such variable; details of processing conditions represent another. In practical terms, processing conditions represent choices of extrusion rate or force, and of melt temperature. In the case of defined polymers, processed under stated rates and temperatures, the extrusion force becomes a dependent variable Discussion therefore focuses on the influence of extrusion temperature and rate.

(a) Extrusion temperature

At given extrusion rate an inverse relationship can be postulated between melt temperature and extrusion force (shear stress). High extrusion force promotes the drag action on the deposited FE and therefore the purging rate should be reduced at higher temperatures. In fact, however, the reverse is true. The reason is given in Figure 5.1, which shows that at higher temperature the melt viscosity ratio between FE and LLDPE is reduced, a factor favoring the purging process[8]. The effect is more pronounced at shear rates consistent with practical extrusion operations. The experimental data in Fig.6 confirm the direct link between purging rate and melt temperature. At 160°C Θ decreased from an initial reading near 30% to about 28% in a process period of 5000 sec., corresponding to 8 extrusion runs. This equates to an efficiency reduction of less than 0.75% per run. The reduction at 180°C followed a roughly similar path, but the total drop in θ (32 to about 26%) was greater. At 200°C the reduction of efficiency became significantly greater. The principal reduction in Θ, of almost 9 % per run, occurred in the initial stage of extrusion, while near the end the reduction slowed to about 0.8% per run. Since the extrusion rate was constant in these trials, we can attribute the observed effects to changes in the loss of FE to the LLDPE mainstream. At first, this will tend to augment the dimension of the interphase between bulk LLDPE and FE and further promote the mass transfer, particularly in strongly interdigitated regions. The ensuing rapid loss of FE will lead to thinner and smoother FE layers, decreasing the interconnectivity between the FE and LLDPE phases. Overall mass transfer across the interface will be reduced, and with this also the purging rate. The rationalization accounts for the empirical observations presented herein

(b) Extrusion rate

Since, at constant temperature, a direct functionality exists between extrusion rate and extrusion force, it seems reasonable to suggest that the purge of stagnant polymer melt from the die should proceed more rapidly at increasing extrusion rates The facts of the matter are more complex, as shown in Figure 5.4. At 180°C the purging rate variation in the initial stages of extrusion is anomalous; expectations are followed only in the latter stages of extrusion. The seemingly anomalous initial trends invite speculation as to cause. In order to purge FE from the die, the mass transfer must be initiated and/ or drag loss must occur at points of contact between the FE and the host polymer Now, as noted in literature reports[4,13], these polymers are not miscible, so that little rapid, spontaneous transfer can be expected to occur, particularly when the contact surface between the polymers is irregular, as postulated. Some minimum time of contact will be required if elements of the FE are to transfer into the flowing mass of LLDPE The time of contact between segments of the two polymers varies inversely with the extrusion rate, so that the pattern established by initial purging rates may be accounted for. Only in later stages of extrusion, when smoother interfaces and a well-developed interphase have been established, will the purging rate vary with output rate in the expected manner.

4. Conclusions

1) Two mechanisms have been postulated to account for the removal of FE deposited on a die land by the extrusion of LLDPE One is the mass transfer of FE into the mainstream. the other is the shear-dependent stripping of the FE by the flowing matrix polymer.

2) Both experiment and the proposed mechanisms indicate that purging rates are higher at initial stages of the process. Higher temperatures and lower extrusion rates promote the purging process.

Acknowledgement

This work was financed by grant from the National Sciences and Engineering Research Council. Canada. We thank 3M Canada Inc. for supplying materials and for useful discussion.

5. References

1. BLATZ, P.S., US Patent, 3,125,547 (1964).
2. KANU, R.C. and M.T. SHAW, Polym. Eng. Sci., **22**, 507 (1982).
3. RAMAMURTHY, A.V., J. Rheol., **30**, 337(1986).
4. VALENZA, A. and LA MANITIA, F.P., Inter. Polym. Proc., **II**(3/4), 220 (1988)
5. HATZIKIRIAKOS, S.G., and DEALY, J.M., J. Rheol., **36**, 845 (1992)
6. AJJI,A., VARENNES, S., and SCHREIBER, H.P., Polym. Eng. Sci., **33**, 1524 (1993).
7. XING, K.C. and SCHREIBER, H.P., Polym. Eng. Sci., **36**, 387, (1996).
8. GLASSES, S., Polymer Melt Rheology, Chap. **2**, Cambridge Press, London, 1982
9. EL KISSI, N. and PIAU, J., J. Non-Newtonian Fluid Mech., **37**, 55 (1990)
10. WU, S., Polymer Interface and Adhesion, Chap. **6**, Marcel Dekker Inc., New York, 1990.
11. HAN, C.D., Rheology in Polymer Processing, Chap. **3**, Academic Press, 1976.
12. VARENNES, S., and SCHREIBER, J. Adhesion, **46**, 3 (1994)

Figure Captions

Figure 5.1. Comparing the Viscosity of FE and LLDPE at various Temperatures. ○ 200°C, ▼ 180°C, □ 160°C

Figure 5.2. Typical Details of Type I extrusion at 200°C and 143 s^{-1}

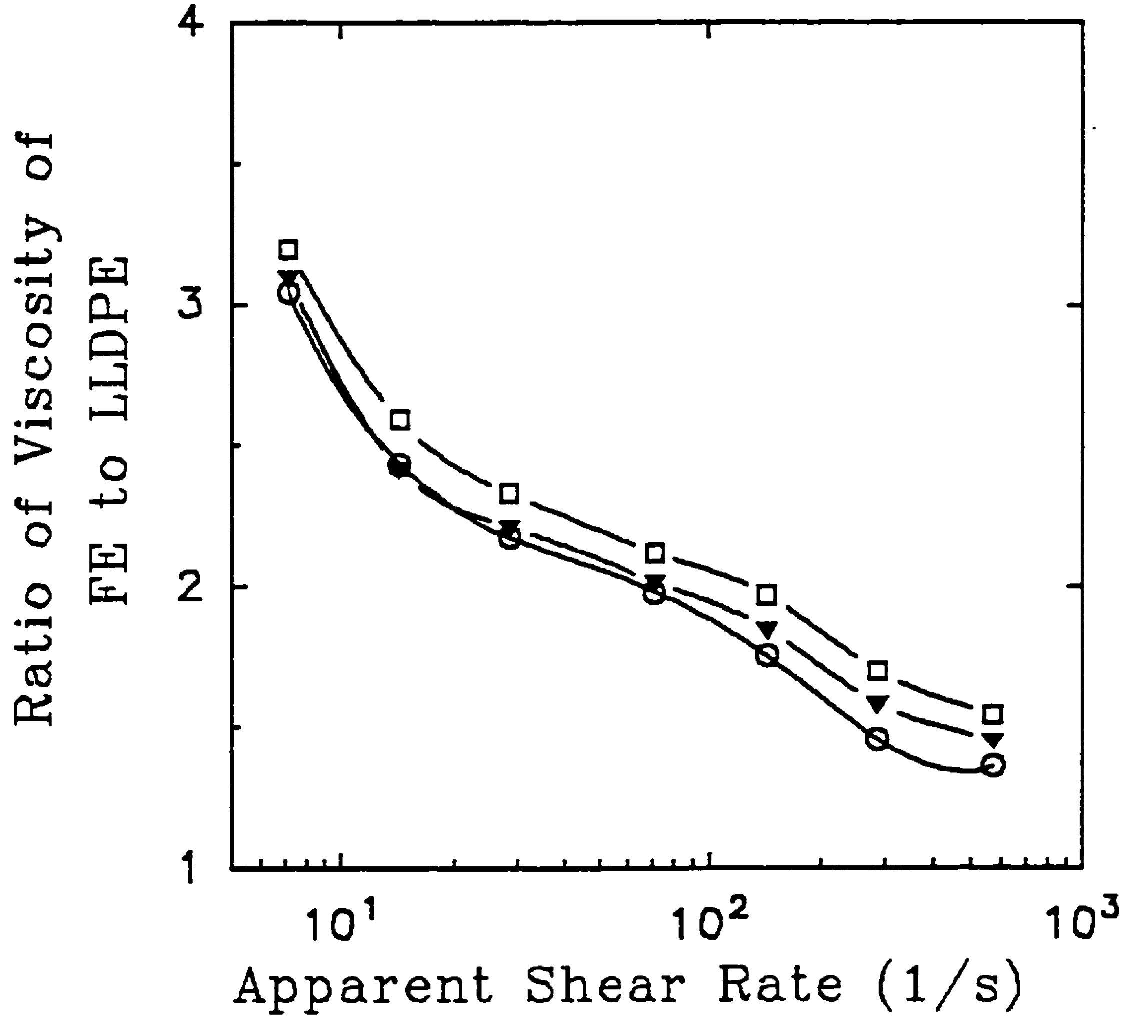
Figure 5.3. Typical Details of Type II extrusion (at same conditions as in Figure 5.2)

Figure 5.4. Regression of Θ vs. LLDPE Mass at 180°C and various extrusion rates. ○ 14.8 mm^3/s, ● 27.9 mm^3/s, ∇ 59.4 mm^3/s.

Figure 5.5. Regression of Θ vs. Purging Time (at same conditions as in Figure 4). □ 14.8 mm^3/s, ▼ 27.9 mm^3/s, ○ 59.4 mm^3/s

Figure 5.6. Influence of Extrusion Temperature on Purging Effect at 143 s^{-1} ○ 160°C, ● 180 °C, ∇ 200°C.

Figure 5.7. Various Possible Mechanisms for the Purging Process.



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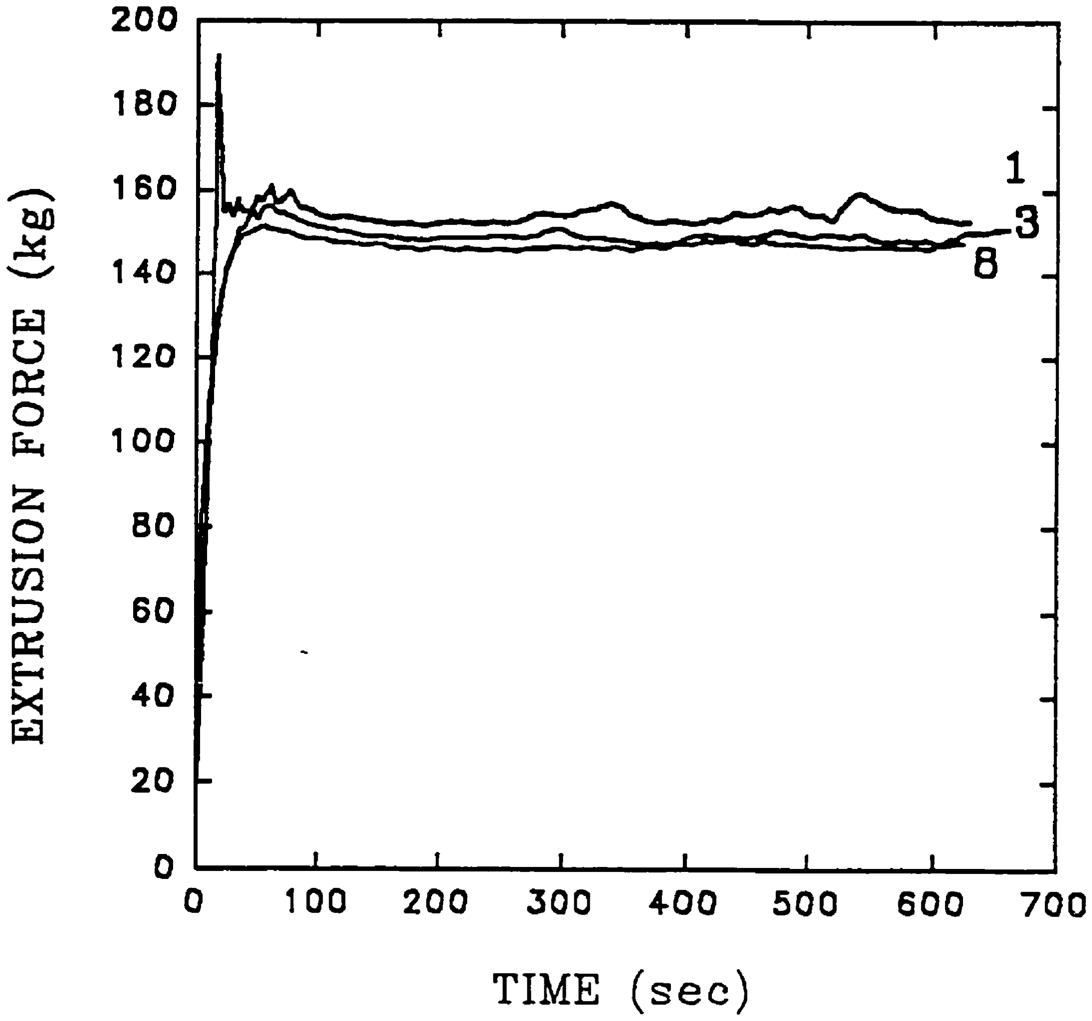


Figure 5.2 Typical Details of Type I extrusion at 200°C and 143 s⁻¹

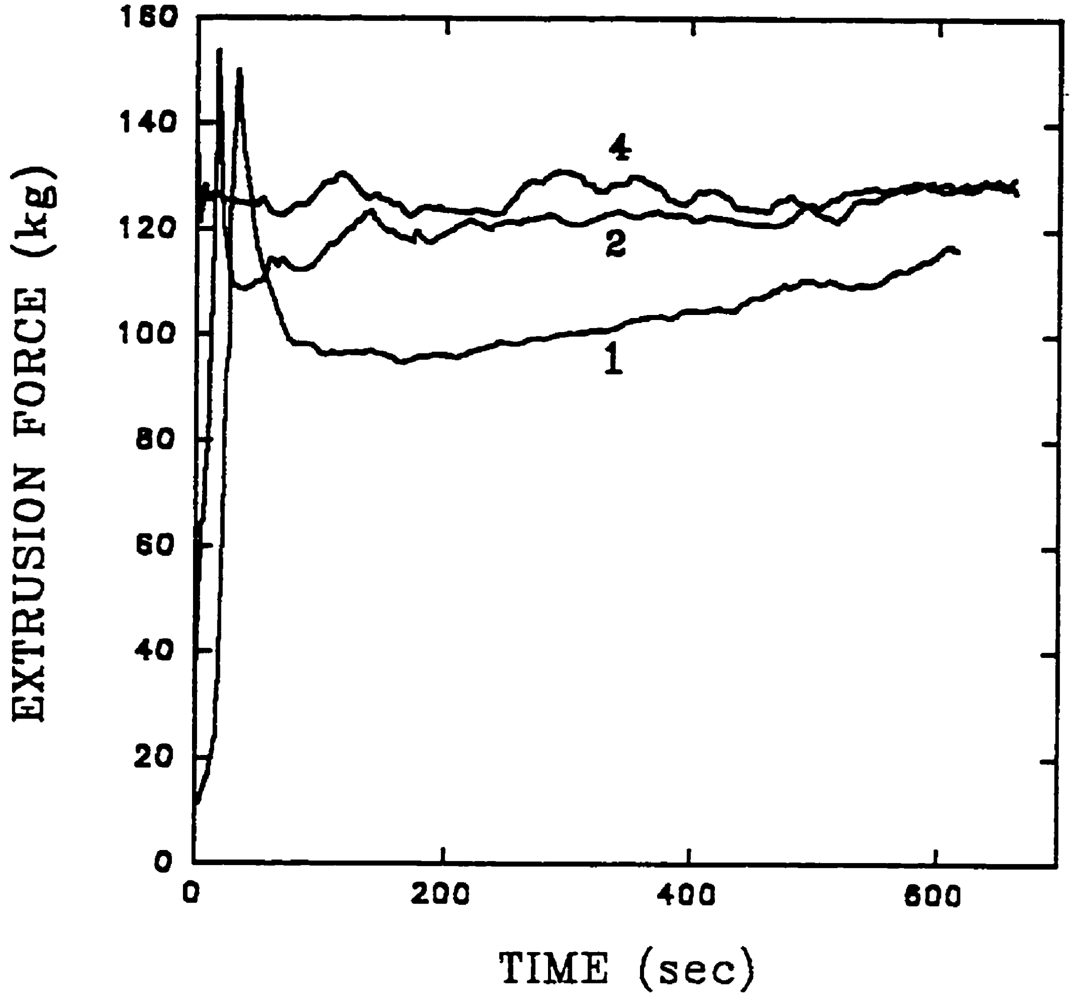


Figure 5.3. Typical Details of Type II extrusion (at same conditions as in Figure 5.2)

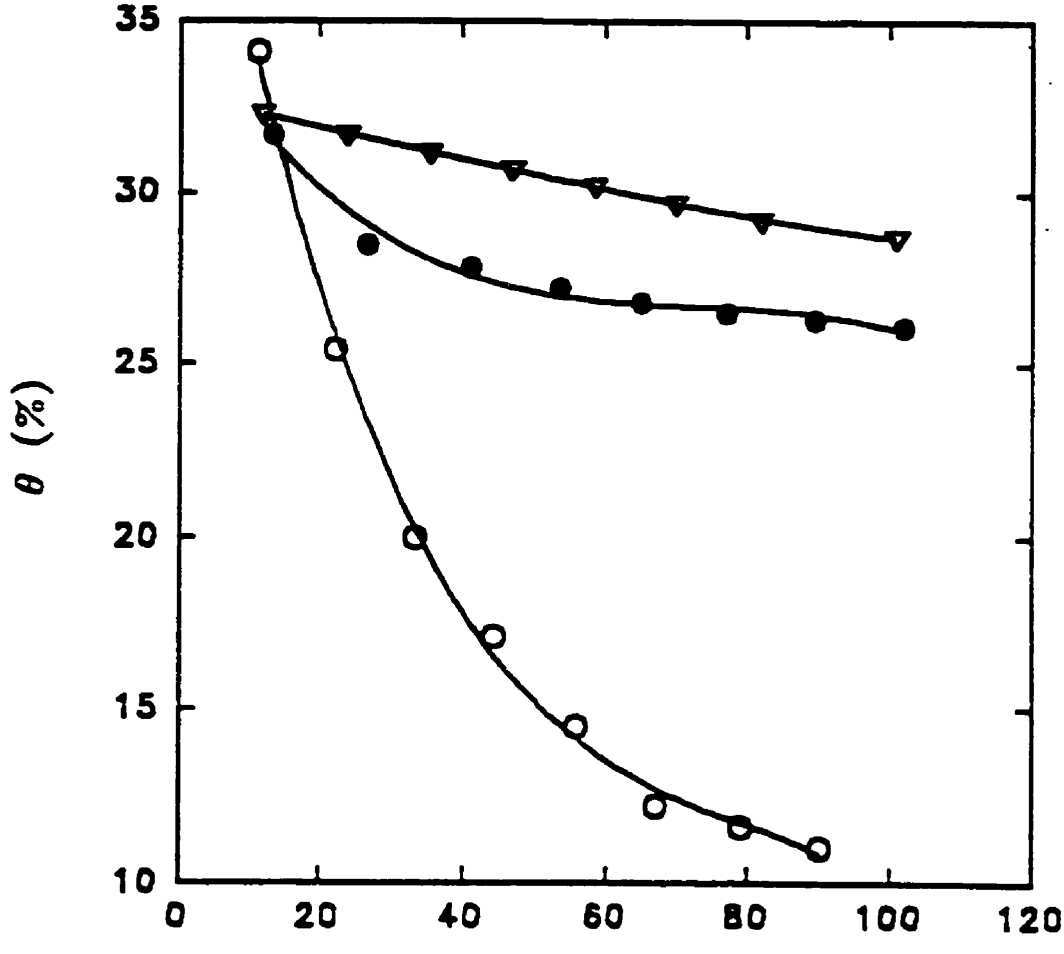


Figure 5.4 Regression of θ vs. LLDPE Mass at 180°C and various extrusion rates. ○ 14.8 mm³/s. ● 27.9 mm³/s. ∇ 59.4 mm³/s.

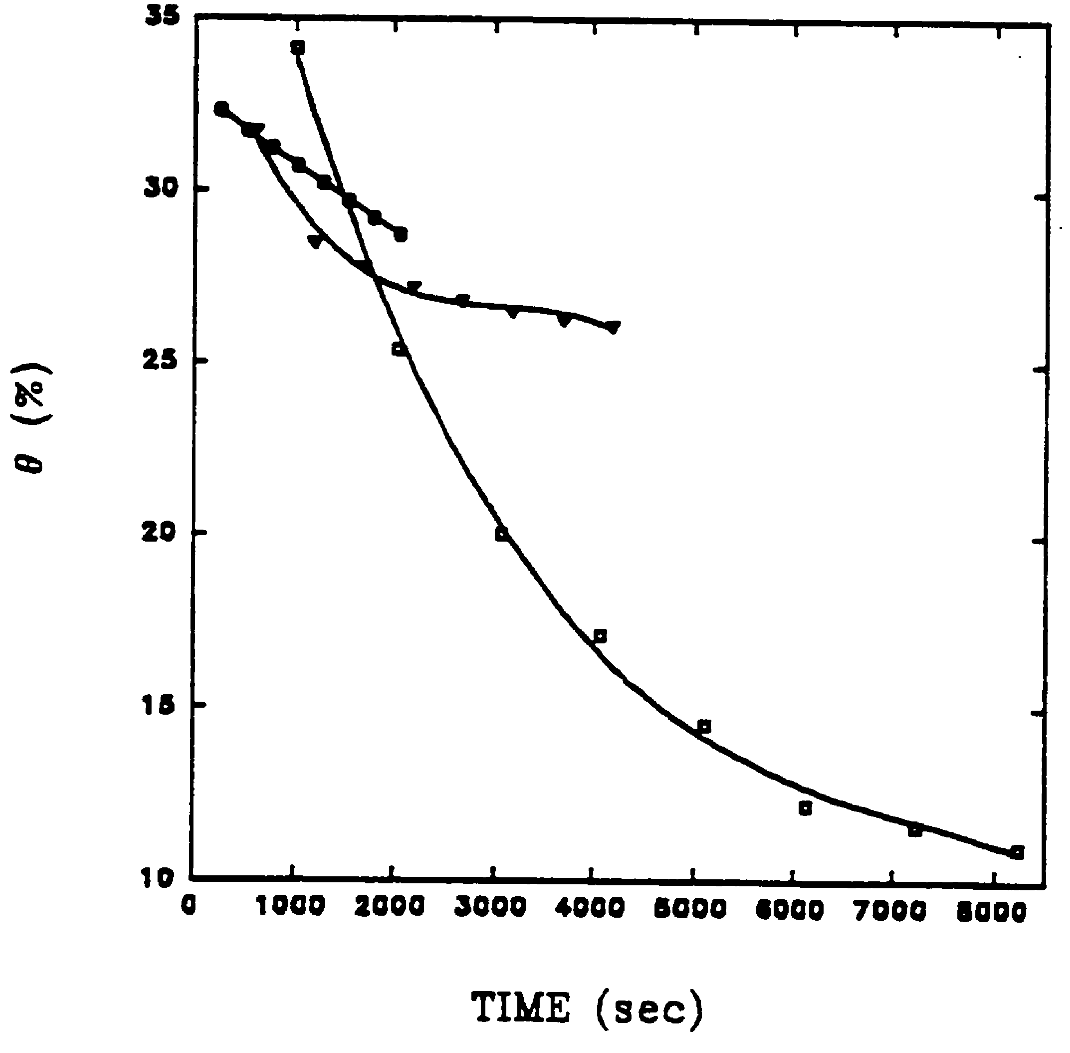


Figure 5.5. Regression of θ vs. Purging Time (at same conditions as in Figure 4), □ 14.8 mm^3/s, ▼ 27.9 mm^3/s, ○ 59.4 mm^3/s.

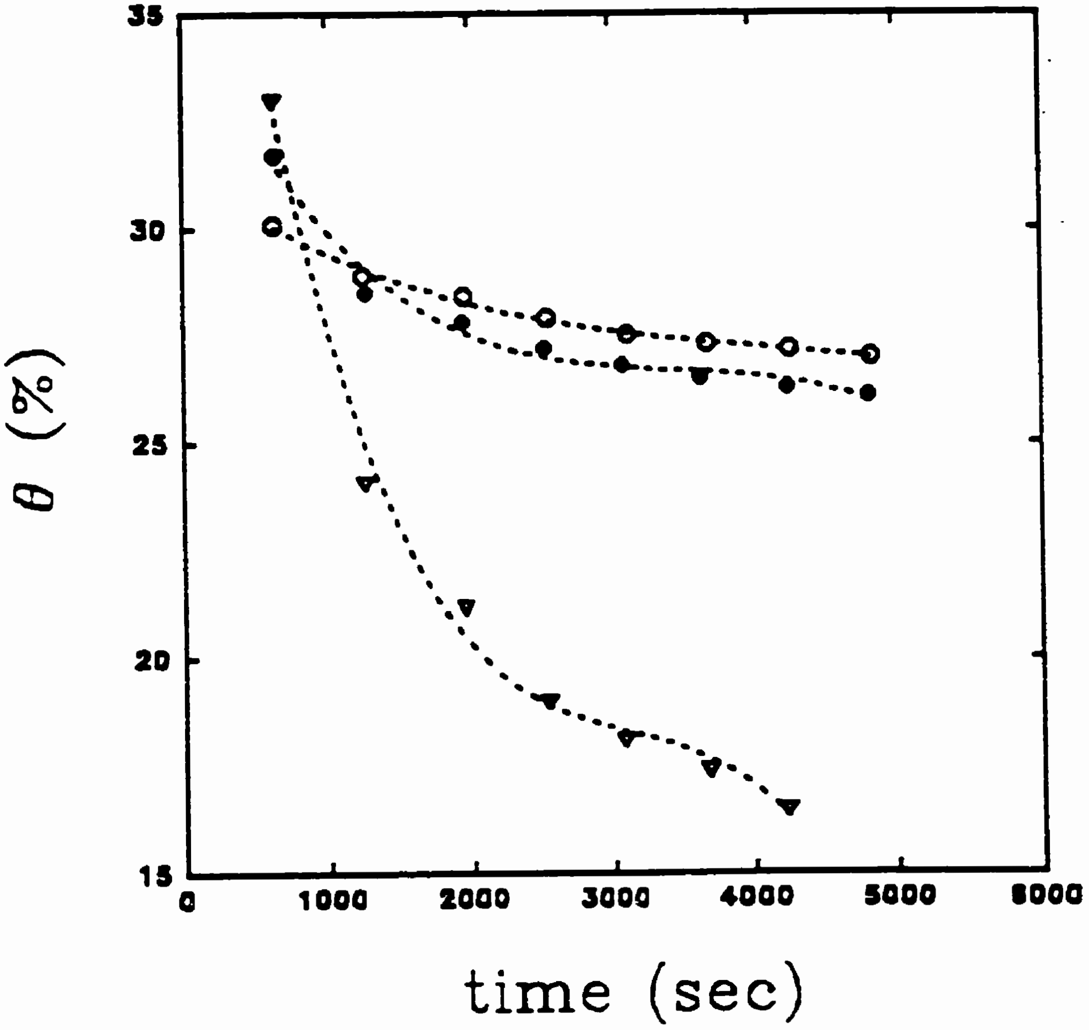


Figure 5.6. Influence of Extrusion Temperature on Purging Effect at 143 s^{-1}. ○ 160°C, ● 180 °C, ∇ 200°C.

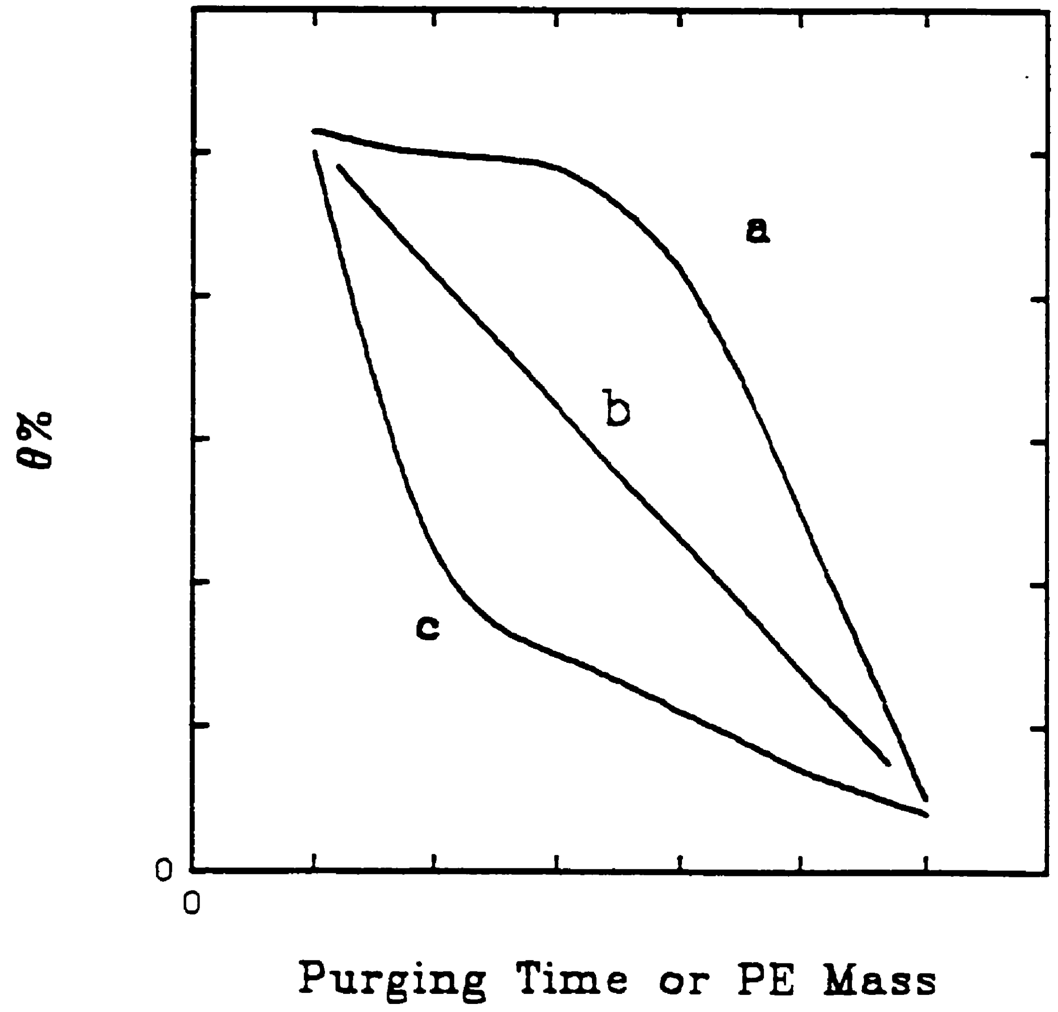


Figure 5.7 Various Possible Mechanisms for the Purging Process

6. INFLUENCE OF FE ON MELT FLOW OF LLDPE/FE BLENDS

K.C. Xing and H.P. Schreiber

Department of Chemical Engineering, Ecole Polytechnique

P.O. Box 6079, Stn. Centre Ville

Montreal, H3C 3A7, QC. Canada

I. Introduction

This paper (chapter) continues the qualitative and quantitative analysis of beneficial flow modifications of processing linear low density polyethylene (LLDPE), by the addition of a fluoroelastomer (FE). FE additives are well-known for their ability to reduce flow defects such as shark-skin and slip-stick cycling, and to improve processing rates (Blatz, 1964; Ramamurthy, 1986, Rudin, 1986, and Xing and Schreiber, 1996). Blatz (1964) was among the first to use FE for the reduction of surface flaws in polyolefin extrudates. Other researchers used polyolefin/FE blends to reduce extrusion force and raise extrusion rate (Valenza and La Matina, 1987; Rudin, et al. 1986; Johnson, et al. 1988). A widely reported observation in processing these blends was the existence of an induction time before the additive's effects became significant (Shih, 1976; Kanu and Shaw, 1982, Athey, et al. 1986). Implied was a need for the minor additive to be redistributed in order to produce the desired effect. In other cases, FE was used to directly coat the extrusion die (Valenza and La Matina, 1987; Hatzikiriakos, et al 1995, Xing and Schreiber 1995). In these reports, the benefits were observed instantly. The observations justify the well-known notion that FE additives improve LLDPE processing by changing the interfacial property between the mainstream and the die surface (Valenza and La Matina, 1987; Hatzikiriakos and Dealy, 1991; Xing and Schreiber, 1995). The most frequent industrial use of FE flow modifiers is in the form of well-dispersed minor phases in polymer blends. It is thus important, from a practical point of view, to understand the factors and mechanisms which influence the apparent need of FE to accumulate at the die wall. The question of mass transfer during viscous flow also has much basic interest. It involves transport phenomena, rheology, morphology, thermodynamics and other aspects of basic science, as documented in the literature (Schreiber et al, 1966; Brunn and Chi, 1984, Khan, et al, 1994, and Agarwal, et al, 1994). Curiously, however, these concepts have not been applied to the LLDPE/FE system, in spite of its obvious importance to both science and technology, and the implied relevance of transport phenomena to the flow effects associated with the presence of FE additives. The present work is directed toward this question

II. Experimental

The materials used in this work were those described previously (Xing and Schreiber, 1995 & 1996a) Blends were prepared with a Brabender Plasti-corder. A masterbatch of LLDPE/FE, with 10% wt FE, was first made by compounding at 160°C and 120 rpm for 5 minutes. The masterbatch was then diluted to the desired FE concentrations by blending in pure LLDPE , under the same operating conditions. Compounded blends were compression molded while still hot and plates were then comminuted to fine pellets suitable for extrusion

Extrusion and rheological measurements were carried out with an Instron Rheometer connected to a computer for on-line recording Details of the Rheometer and the extrusion die were given in our recent paper (Xing and Schreiber, 1996a). After carefully filling the Rheometer barrel and allowing 10 minutes for establishing thermal equilibrium, extrusion was run under controlled output rates. In "continuous" extrusion, the barrel was refilled repeatedly with LLDPE/FE blends of known composition In these runs the die was cleaned by fire-flashing prior to the first run, but not thereafter For comparison, pure LLDPE was extruded under the same conditions as the blends.

The effects of FE on the flow resistance of the mainstream were quantified by the efficiency parameter (Θ) Following our earlier report (Xing & Schreiber, 1995), this was calculated from

$$\theta=(1-\frac{F_{II}}{F_{I}})x100\% \qquad (1)$$

where F stands for the force applied to the polymer melt during extrusion of a blend (II) or of the control LLDPE (I) Again as in previous work, values of F were averaged over the time of the extrusion run at given rate

III. Results and Discussion

A. Extrusion Phenomena

A.1 Initial Extrusion Forces

Shown in Figure 6.1 are extrusion details of the first run of LLDPE, and of LLDPE/FE blends at different FE concentrations, at 200°C and 143 s^{-1}. Identical extrusion conditions were imposed on each system. In line with other reports (Valenza and La Matina, 1987; and Hatzikiriakos and Dealy, 1991), the plot shows an inverse variation of extrusion force and extrusion time, attributable to the noted effect of external lubrication The data also indicate systematic reductions of maximum extrusion forces with increasing FE concentrations in the blends. The maximum force for pure LLDPE was 150.1 kg., while corresponding maxima were 148.9, 140.8 and 136.2 kg for blends at FE levels of 0.1%, 1% and 3.3%, respectively The maxima were reached within 30 seconds of the start of extrusion. For discussion of initial effectiveness of FE on the extrusions, the following definitions of time intervals are used:

1) initial stage: from start of extrusion to attainment of maximum extrusion force reach its peak;
2) subsequent stage: from the maximum force to the end of extrusion

For external lubrication effect. FE functions only when it is at the die surface Its effectiveness depends on the area of die wall it covers. which is in proportion to the total amount of FE accumulated at the die surface. This amount in turn should be in proportion to that of the blend flowing over the surface, being a function of the extrusion rate and time. The extrusion rate increases with increasing extrusion force. from zero to the full rate at the end of initial stage. Since the extrusion force increased almost linearly during this period. the extrusion rate should increase even faster due to pseudo plasticity of polymers and lubrication effect. This means that in the initial stage the average flow rate of a blend over the die wall would be less than 50% of the rate during the subsequent period. Assuming the loss due to purge to be negligible, the average rates ($\Delta\Theta/\Delta t$) of the effectiveness increase in the initial stages should thus be less than 50% of the rates during the subsequent periods. if the external lubrication effect had been the sole cause of the initial effectiveness This assumption, however. does not apply to the present work.

Comparisons of the average rate of the efficiency change in initial stages of extrusion and during the subsequent period are shown in Table 1 The data indicate that none of the initial rates of effectiveness increase were less than 50% of the average rates during the subsequent periods. In fact. the rates in the initial stages were often significantly greater than those in subsequent stages. Thus, external lubrication is unlikely to be the sole mechanism for the reduction of flow resistance.

Table 1. Effectiveness and Its Rates, 200°C and 143 s^{-1}

	Initial Stage		Subsequent Period	
FE level	Θ_0	$\Delta\Theta/\Delta t$	$\Theta-\Theta_0$	$\Delta\Theta/\Delta t$
0.1%	0.8	0.026	15.3	0.033
1.0%	6.2	0.21	21.2	0.045
3.3%	9.3	0.30	24.0	0.051

Other plausible reasons may be proposed to account for the high initial reductions in extrusion force. Plasticization of the host polymer is one possibility. In these investigations, however, this is not the case. The FE used for this work had a higher apparent viscosity than the LLDPE (Xing and Schreiber, 1996a). If FE had plasticized the LLDPE, the flow resistance may have been expected to increase. Further, FE can not be considered a plasticizer for LLDPE because of the poor miscibility between these substances.

We may argue that the initial reduction of extrusion force resulted from reduced friction between chains of the major component and chains of the minor, incompatible component. This phenomenon may be termed internal lubrication. Without internal lubrication, the high viscosity of FE would tend to increase the flow resistance of the blends in the initial stage of extrusion. This would be increasingly evident regarding to the initial effectiveness at various temperatures and extrusion rates

At 160°C, reductions of initial extrusion force were observed at different extrusion rates, as shown in Figure 6.2. At the shear rate of 143 1/s, the maxim extrusion force was 234.7 kg for pure LLDPE, and 228.9 kg for the blends with 1% FE. This reduction converted to an efficiency of 2.5% during the first 40 seconds of processing. In the more than 550 seconds of subsequent extrusion, the efficiency factor(Θ), rose by another 8.9%. At 287 1/s, the maximum force was 325.7 kg for LLDPE, and 315.9 kg for the 1% FE/LLDPE blend. This translates to a 3% reduction of extrusion force in the first 38 seconds, followed by about 10.2% of additional reduction in the subsequent 280 seconds of extrusion.

Considering that LLDPE is able to purge FE from dies more rapidly at higher temperature (Xing and Schreiber, 1996b), it seems possible that the compatibility between FE and LLDPE improves at higher temperature. Note that the initial reduction of extrusion force at 160°C was less than that at 200 °C , the inference is that the internal lubrication of LLDPE by FE is lower at the lower temperature.

A.2. Maximum Efficiency, Equilibrium Time and Increasing Rate of Efficiency

Relationships between external lubrication efficiency and extrusion time under the influence of FE level and extrusion rate are illustrated in Figures 6.3 and 6.4, respectively.

The maximum efficiency at various circumstances can be figured out by regressing data in these figures. Curve fitting leads to the following equation to satisfy the data:

$$\theta - \theta_0 = [1 - \exp(-at)] \cdot b \qquad (2)$$

Here Θ_0 is the initial effectiveness, and t the time from start of subsequent stage The parameters a and b are listed in Table 2 for blends at various FE levels and processed under a variety of conditions.

Table 2. Parameters of Regression for Blend Extrusion

	200°C, 143 1/s			1% FE, 160°C	
% FE	0.1%	1.0%	3.3%	143 1/s	287 1/s
$a \times 10^3$	0.7038	1.193	1.444	0.9397	2.048
b	15.28	21.23	23.98	26.52	23.68

The above equation is also useful for calculation of equilibrium time, which is defined as the moment when the efficiency reaches 95% of the ceiling value

Figure 6.5 shows calculated maximum efficiency and equilibrium time for various blends at 200°C Evidently, there are no simple, linear relationships between the FE concentration and maximum effectiveness or equilibrium time, which is in line with other literature (Duchesne et al, 1990).

Applying equation 2 to extrusion of LLDPE/1% FE blend at 160°C and different rates, the calculated maximum efficiency is greater at lower extrusion rates. The θ are 26.5% at 143 1/s, and 23.7% at 287%. The equilibrium time, in contrast, is significantly greater at the slower rate, being more than 3900 seconds at 143 1/s, but only 1710 seconds at 287 1/s. Doubling the extrusion rate reduced the equilibrium time by more than 60%.

By differentiating equation 2, we can calculate the rate of efficiency increase in subsequent stage.

$$\frac{d\theta}{dt} = a * b * \exp(-at) \tag{3}$$

The calculated rates are shown in figure 6.6. The rates increased with FE concentration as expected, but the increases became less pronounced at longer extrusion time. Since longer extrusion time resulted in the FE covering a larger area of the die, this follows the inference that the rate of FE accumulation on the die surface may be assumed to depend on the detailed conditions of the flow boundary.

Figure 6.6 also indicates that temperature influences the rate of efficiency increase. In general, the efficiency increment was reduced at high temperature. Thus, the FE accumulates more slowly at the die surface at higher temperatures. This is consistent with our previous findings showing that purging rates increased at higher temperatures (Xing and Schreiber, 1996b).

Another important trend in figure 6.6 is the strong effect of shear field on dΘ/dt. Doubling the extrusion rate resulted in the highest rise in the efficiency rate observed in this study. Apparently, extrusion rate has a stronger influence on the accumulation of FE at the wall than does the FE concentration and the process temperature. As the FE used in this work had a higher viscosity than the host LLDPE, and therefore possible a higher molecular weight, this result appears at odds with some accounts of polymer migration during flow (Brunn and Chi, 1984, Khan, 1994, and Agarwal, et al. 1994). In those reports, the high molecular weight components of a polymer blend are stated to migrate towards the center of a shear field where the shear force is minimum.

A.3 Mass Transfer Rate of FE from the Blends to the Die Surface

It is impossible to directly measure the transfer rate with our experimental system, but the rate can be estimated by applying equation of mass conservation. The mass balance of FE on the die wall is:

$$(\frac{dm}{dt})_{tr} = (\frac{dm}{dt})_{ac} - (\frac{dm}{dt})_{pg} \qquad (4)$$

where tr, ac and pg stand for transfer, accumulation and purge

The external efficiency of FE is in proportion to the area of the die coating, regardless of the origin of the FE coating Because the die wall is impermeable, the accumulation rate of FE on the die surface must be in proportion to the rate of efficiency increase:

$$\left(\frac{dm}{dt}\right)_{ac} = k_1 \left(\frac{d\theta}{dt}\right)_{bd} \qquad (5)$$

For the same reason, the purging rate is a function of reducing efficiency

$$\left(\frac{dm}{dt}\right)_{pg} = k_2 \left(\frac{d\theta}{dt}\right)_{pg} \qquad (6)$$

For a given LLDPE/FE system extruded under stated conditions.

$$k_1 = k_2 = k \qquad (7)$$

k value can be found at initial stage of purging process:

$$k = \frac{m_{\max}}{\theta_{\max}} \qquad (8)$$

where the maximum value of Θ and m for any LLDPE - FE pair can be estimated by precoating the die and extruding pure LLDPE under the same extrusion conditions (Xing and Schreiber, 1996b).

With the above equations, the mass transfer rate of FE to the wall from the bulk blend is readily obtained, if $(d\Theta/dt)_{bd}$ and $(d\Theta/dt)_{pg}$ are known. Because the time axes of the purging process and the process of the blend extrusion are dissimilar, we need to calculate $(d\Theta/dt)_{bd}$ and $(d\Theta/dt)_{pg}$, at the same efficiency instead of the same time, but under fixed extrusion conditions This can be done by combining equations 2 and 3 for $(d\Theta/dt)_{bd}$, and using results from purging processes under the same extrusion conditions for $(d\Theta/dt)_{pg}$ Taken into account here is that even in the extrusion of LLDPE/FE blends, the purging agent is still LLDPE component, as is the case in purging a FE-precoated die with pure LLDPE. Calculated $(d\Theta/dt)_{bd}$ and $(d\Theta/dt)_{pg}$ are shown in Figures 6.7 and 6.8, respectively

Shown in Figure 6.9 are the estimated mass transfer rates of FE to the die surface from the blends at various situations, by combining data from Figures 6.7 and 6.8 along with k values calculated from equation 8. The plots in Figure 6.9 show some interesting features.

For a given blend processed under fixed extrusion conditions, the transfer rate seems to be a constant, independent of extrusion time. The plots in this figure indicate, however, that the rate gradually decreases as the external efficiency Θ increases.

The data in Figure 6.9 also reveal relationships between the mass transfer rate, extrusion conditions and FE concentrations in the blends. It follows that high extrusion rates promote the FE transfer from the mainstream to the stationary phase. As expected, the transfer rate also rises with increasing FE concentration. Higher temperature does not appear to favor the transfer, but complications arise at longer flow times. The observations parallel to those on the rate of effectiveness increase under influence of various factors. Based on the findings, raising the extrusion rate is the most effective way among these factors to speed up the FE transfer. In order to account for the relationships in Figure 6.9, an analysis of the mechanism of mass transfer is called for.

B. Mechanism of FE Transfer to the Die Surface

Few reports have addressed the phenomena of FE moving from LLDPE/FE blends to the die wall. Those who have noted the process (Valenza et al. 1987, Duchesne et al. 1990) confirmed the existence of an induction period for FE to improve the flow of LLDPE, as shown in Figure 2.2 in Section of "Literature Review". One reason for neglecting the consideration of processes of transfer is the apparent discrepancy between experimental observations and expectations based on theories of polymer migration.

Leading theories of polymer migration include thermodynamic analyses (Schreiber et al, 1965; Busse, 1967; Metzner, et al 1979; and Aubert and Tirrel, 1980), the consideration on flow of suspension particles (Briscoe, 1990), theory of collision rates (Lighton, 1987), and the principle of minimum viscous dissipation (Han, 1990). According to all of these theories, LLDPE but not FE should be located preferentially at the die wall, because FE is more viscous and denser than LLDPE. Along with data of other researchers, this work reveals that an induction period does exist for FE to function as a processing aid in polymer blend during extrusion. Our previously findings (Xing and Schreiber, 1995) also indicate that an immediate reduction in flow resistance of LLDPE is obtained when the polymer flows through a die precoated by FE. All facts strongly suggest the gradual accumulation of FE on the die surface when a LLDPE/FE blend is flowing over it. The blend is the sole source of FE accumulation. Therefore, a mass transfer of FE must occur from the bulk blend to the die surface during extrusion. It is this gradual accumulation that accounts for experimental findings. The experimental observations thus argue in favor of the mass transfer effect of FE to the die wall, although they are inconsistent with the cited theories.

The contravention, however, is not confined to LLDPE/FE blends. Similar observations were reported for a FE/EPDM system (Kanu and Shaw, 1982). In that work, it was found that less than 5% of FE additive in the pertinent matrix resulted in a reduction of up to 40% in the total extrusion force in capillary flow, again following an induction period. When the measurements for the same system were carried out with plate-plate rheometers, however, no effect of FE additive on the flow of the blends was found.

All of the above findings confirm that the mass transfer of FE from the mainstream of a blend to the die wall does exist. As the transfer rate changes in the induction stage, the transfer is more likely to be driven by differences in surface and interfacial energy.

At room temperature, the surface tension of LLDPE is about 32 mJ m^{2} greater than that of FE, in the range of 22 mJ/m^{2} (Wu, 1990) The difference in surface tension may be broader at the extrusion temperature since the temperature coefficients of surface tensions of FE is slightly greater than LLDPE (Wu, 1990). On the other side of the flow boundary, the surface tension of metal or metal oxides is much higher than that of polymer melts at extrusion temperatures (Murarka, 1971) The two polymers will compete to wet the metal surface of the die. Since wet ability tends to increase with greater differences between wetting agent and wetted surface, the FE will wet the die surface preferentially. Interaction between FE/metal wall is relatively strong in comparison with the Van der Waals force between LLDPE/FE, resulting in a separation of FE from the mainstream. For the same reason, there will be a tendency for FE to adhere to the wall rather than be purged away by LLDPE. As more LLDPE/FE is extruded there is a systematic increase in the die area coated by the FE. This of course reduces the surface energy of the die surface dramatically, decreasing the drive for the further accumulation of FE. In terms of a mass transfer hypothesis, the transfer rate would consequently decrease. The rate at which FE is purged from the die wall, on the other hand, would increase as the coated area grows. Eventually, a dynamic equilibrium may be postulated between accumulation and purge of FE, thus accounting for the slight flatness at high Θ end of curves in Figure 6.9

Entropic considerations (Aubert 1983, Brunn and Grisafi, 1985; and Ausserre, 1986) also favor the selective accumulation of FE on the die surface: The structure of LLDPE makes it one of the most flexible macromolecules. Attachment to the die wall therefore will reduce the configurational entropy of LLDPE more than that of the more rigid FE The entropy loss and surface energy considerations, clearly show FE to be the preferred component to localize at the die wall. On the other hand, the reduction in configurational entropy of FE chains sticking to the wall will counteract the tendency for phase separation at this locus, and thus limit the thickness of the retained layer. This may explain the reduction of mass transfer after long extrusion and at high temperature

The transfer of FE to the die wall can be further analyzed statistically. In a polymer blend, each component has some probability to appear at the flow boundary, depending on its concentration. When any one of the components appears at the flow boundary, it may either remain in the mainstream or become attached to the stationary phase. Given the component with low surface tension moving out of the melt stream due to weak polymer-

polymer interaction, the mass transfer may be considered a stochastic process and is developed further as such.

For random distribution in a binary blend, the ratio (φ) of a component at the flow boundary can be expressed as:

$$\varphi = \frac{w_A/d_A}{w_A/d_A - w_B/d_B} \qquad (9)$$

where w and d are weight percentage and density, respectively, and A and B represent the two components. Since the density of FE is roughly double that of LLDPE (Duchesne et al, 1990), the φ value of FE should be about 50% of its weight fraction in the blends.

Due to poor compatibility between host LLDPE and FE, low surface tension of FE and high concentration of LLDPE in the mainstream, any LLDPE deposited at the wall will tend to be purged away by the mainstream. If FE and the host polymer are assumed to be totally immiscible, the minimum time needed to equilibrate the effect of FE on the flow of the blend is:

$$t_e = \frac{t_s}{\varphi} \qquad (10)$$

where t_s is the average residence time for a flowing unit in the die, which is determined by

$$t_e = \frac{L}{V} \tag{11}$$

Here L and V are the die length, and the average velocity of the melt in the die.

Applying equations 9 - 11 to our experimental data leads to results listed in Table 3. The calculated equilibrium times are not the same as actual ones, but the differences are well within one order of magnitude. This suggests that the stochastic process is implicated in the gradual accumulation of FE at the die wall.

Another interesting finding is that in most cases the actual equilibrium time was longer than the calculated. This suggests that the mass transfer rate was not as fast as it should be if phase separation between LLDPE and FE had occurred instantly. This hints that phase separation is the controlling step in the process of FE attaining the die wall. The concept is supported by the observation that the mass transfer slowed down as the die area coated by the FE increased

Table 3. Equilibrium Time (minutes) of Effect of FE

	200°C, 143 1/s			160°C, 1% FE	
	0.1%	1.0%	3.3%	143 1/s	287 1/s
Calc.	185.8	18.5	6.4	18.5	9.2
Actual	69.5	41.8	34.6	53.1	24.3

Before ending this section, it is worthwhile to note differences in mass transfer of FE inside the mainstream of the blends and at the die wall during extrusion. Inside the mainstream, the transfer should be time-independent for the following reasons. For a given system, the interaction between the polymers is independent of time under fixed extrusion conditions. The residence time of the melt in the die is short, while polymer chains move very slowly across the flow stream. The processing conditions offers very insufficient time for significant change of distribution of FE inside the flowing melt. The drive to the mass transfer (migration) therefore must also be independent of time. If the driving force is time-independent, then the migration rate for FE inside the blends should not be a function of time.

For mass transfer occurring at the die wall, however, the situation is more complex. Not only is it affected by factors controlling migration inside the mainstream, but the surface properties of the die also have a strong bearing on the process. The mass transfer therefore will be time-dependent until surface properties attain a steady state. Once the equilibrium is reached, the further transfer is controlled by the rate at which FE is purged from the wall by the flowing mainstream.

In view of the above, the mass transfer rate inside the bulk should be a constant. The transfer rate of FE arriving at the die wall, however, decreases during the induction period, and eventually becomes a constant equal to the purging rate over the total coated area of the die. This means that the transfer at the wall would be largely independent of the migration inside the flowing bulk. This is particularly the case when the residence time of the polymer melt in the die is short, providing insufficient time for the concentration profile of the minor component to be the dominant influence in a migration effect

IV. Conclusions

1) The presence of a small amount of FE in LLDPE/FE blends can significantly reduce flow resistance of the entire material
2) FE may produce both internal and external lubrication in the flow of the blends
3) The external effect of FE on flow is dominant.
4) The external effect increase with time of extrusion to the attainment of an equilibrium
5) The mass transfer rate toward the wall is time-dependent It reduces with the time of extrusion to an equilibrium.
6) The factors favorable to the transfer of FE to the wall include high FE concentration, a strong shear field, incompatibility between polymers, and the low surface energy of FE
7) The process of migration inside the mainstream would be different from that taking

place at the wall.

8) The controlling step for FE to arrive at the wall is phase separation of FE from the mainstream

References

* AUBERT. J.H. and TIRRELL. M., *J. Chem. Phys.*, **72**. 2694 (1980).
* AUBERT. J.H. and TIRRELL. M., J. Liquid Chromat., 6. 219 (1983)
* AUSSERRE. D., et al. Macromolecules, **19**. 85. (1986).
* AGARWAL, U.S., DUTTA, A. and MASHELKAR, R., Chem. Eng. Sci., **49**, 1693 (1994).
* THEY.B.J., THAM. R.C., SOUFFIE. R.D. and CHAPMAN.G.R., SPE. ANTEC. Conf. Proc. **44**. 1149 (1986)
* BLATZ. P.S., US Patent, 3,125,547 (1964).
* BRISCOE, B.J. and KHAN, M., Polym. Eng. Sci., **30**, 173 (1990).
* BRUNN, P.O. and CHI, S., Rheol. Acta, **23**, 163 (1984).
* BRUNN. P.O. and GRISAFI, S., J. Polym. Sci., Polym. Phys., **23**, 73 (1985)
* BUSSE. W.F., J. Polym. Sci., **A2**. 1261 (1967)
* COHEN. Y. and METZNER. A.B., *Rheol. Acta*, **25**. 28 (186).
* DUCHESNE, D., SCHREIBER, H.P. and RUDIN, A., Plastics Compounding, **Jan./Feb.**, 50, 1990.

* GARNER, F.H. and NISSAN, A.H., Nature, **158**, 634 (1946)

* HAN, C.D., Multiphase Flow of Polymers, Ch. **2**, Academic Press, 1990.

* HATZIKIRIAKOS, S.G., and DEALY, J.M., J. Rheol., **35** (4), 497 (1991).

* HATZIKIRIAKOS, S.G., HON G.P., HO, W., and STEWART, C.W., J. Appl. Polym. Science, **55**, 595(1995)

* JOHNSON, B.V., BLONG, T.J. and SCHREIBER, H.P., Fourth Intern. Polym. Proc. Soc. Meeting, Orlando, Fla, May, 1988.

* KANU, R.C. and SHAW, M.T., Polym. Eng. Sci., **22**, 507 (1982).

* KHAN, M., BRISCOE, B. and RICHARDSON, S., Polym.-Plast. Technol. Eng., **33**, 295 (1994)

* LIN, Y.H., J. Rheol., 29, 605(1985).

* LINHTON, D. and ACRIVOS, A., J. Fl. Mech., **181**, 415 (1987).

* METZER, A.B., COHEN, Y., and RANGEL-NAFAILE, C., J. Non-Newt. Fluid Mech., **5**, 449 (1979).

* MURARKA, RAM. Surface Tension measurements of Iron and Iron-oxygen alloys, Thesis of Master Degree, McMaster University (1971)

* PAUL, D.R., Polymer Blends, Chap. 6, Academic Press, New York, 1980.

* RAMAMURTHY, A.V., Antec-**89**, 197 (1989).

* RAMAMURTHY, A.V., J. Rheol., **30** (2), 337 (1986).

* RUDIN, A., WORM, A.T. and BLACKLOK, J.E., J. Plast. Film Sheets, (1), **52**.

1986.

* SCHREIBER. H.P and STOREY. S . J Polym Sci , **B3**. 723 (1965)

* SCHREIBER. H P . STOREY. S . and Bagley. E . Trans Soc Rheol **10**. 275 (1966).

* SHIH, C.K., Polym. Eng. Sci., **16** (11), 742 (1976).

* VALENZA, A. and LA MANITIA, F.P., Intern. Polym. Proc. J. **2**, 220 (1988).

* WU, S., Polymer Interface and Adhesion. Chap **3**. Marcel Dekker Inc . 1990

* XING. K C and SCHREIBER. H P . Antec-95. 167 (1995)

* XING, K.C. and SCHREIBER, H.P., Polym. Eng. Sci., **36**, 387 (1996a).

* XING, K.C. and SCHREIBER, H.P., in preparation (Chap. 5 of this thesis, 1996b).

Figure Captions

Figure 6.1. First Extrusion of control LLDPE and its blends with FE at 143 s^{-1} and 200°C. 1: pure PE, 2: 0.1% FE, 3: 1.0% FE, 4: 3.3% FE.

Figure 6.2. Effect of shear rate on first extrusion of LLDPE/1% FE blend at 160°C. 1: LLDPE, 287 s^{-1}; 2: Blend, 287 s^{-1}; 3: LLDPE, 143 s^{-1}; 4: Blend, 143 s^{-1}

Figure 6.3. External efficiency of FE on flow of various blends at 143 s^{-1} and 200°C. ○: 0.1% FE; ●: 1.0% FE; ▽: 3.3% FE.

Figure 6.4. Influence of shear rate on efficiency of 1% FE additive in the flow of LLDPE at 160°C. ○ 143 s^{-1}; ● 287s^{-1}

Figure 6.5. Influence of FE concentration on its maximum external efficiency and attainment of equilibrium extrusion force at 143 s^{-1} and 200°C. ○ maximum θ; ▼: equilibrium time.

Figure 6.6. Effect of extrusion conditions on the rate of efficiency increase of FE. 1-3: FE was 0.1, 1.0 and 3.3%, respectively, at 200°C and 143 s^{-1}. 4 and 5: extrusion at 143 s^{-1} and 287 s^{-1}, respectively, all samples were LLDPE/1% FE blend at 160°C.

Figure 6.7. Relationship of the increasing rate and efficiency. ○: LLDPE/3.3% FE blend at 200°C and 143 s^{-1}. ●: LLDPE/1% FE blend at 200 C and 143 s^{-1}; ▽: LLDPE/0.1% FE blend at 200°C and 143 s^{-1}. ☐ LLDPE/1% FE blend at

160°C and 143 s^{-1}; ■: LLDPE/1% FE blend at 200°C and 287 s^{-1}

Figure 6.8. Relationship of purging rate and flow modification efficiency of FE on LLDPE at various temperatures and shear rates ○: at 160°C and 143 s^{-1}; ● at 160°C and 287 s^{-1}; ▽: at 200°C and 143 s^{-1}.

Figure 6.9. Estimation of mass transfer rate at various conditions.○: LLDPE/1% FE blend at 160°C and 143 s^{-1};●: LLDPE/1% FE blend at 160°C and 287 s^{-1}; ▽: LLDPE/3.3% FE blend at 200°C and 143 s^{-1}; ▼: LLDPE/1% FE blend at 200°C and 143 s^{-1}; □: LLDPE/0.1% FE blend at 200°C and 143 s^{-1}

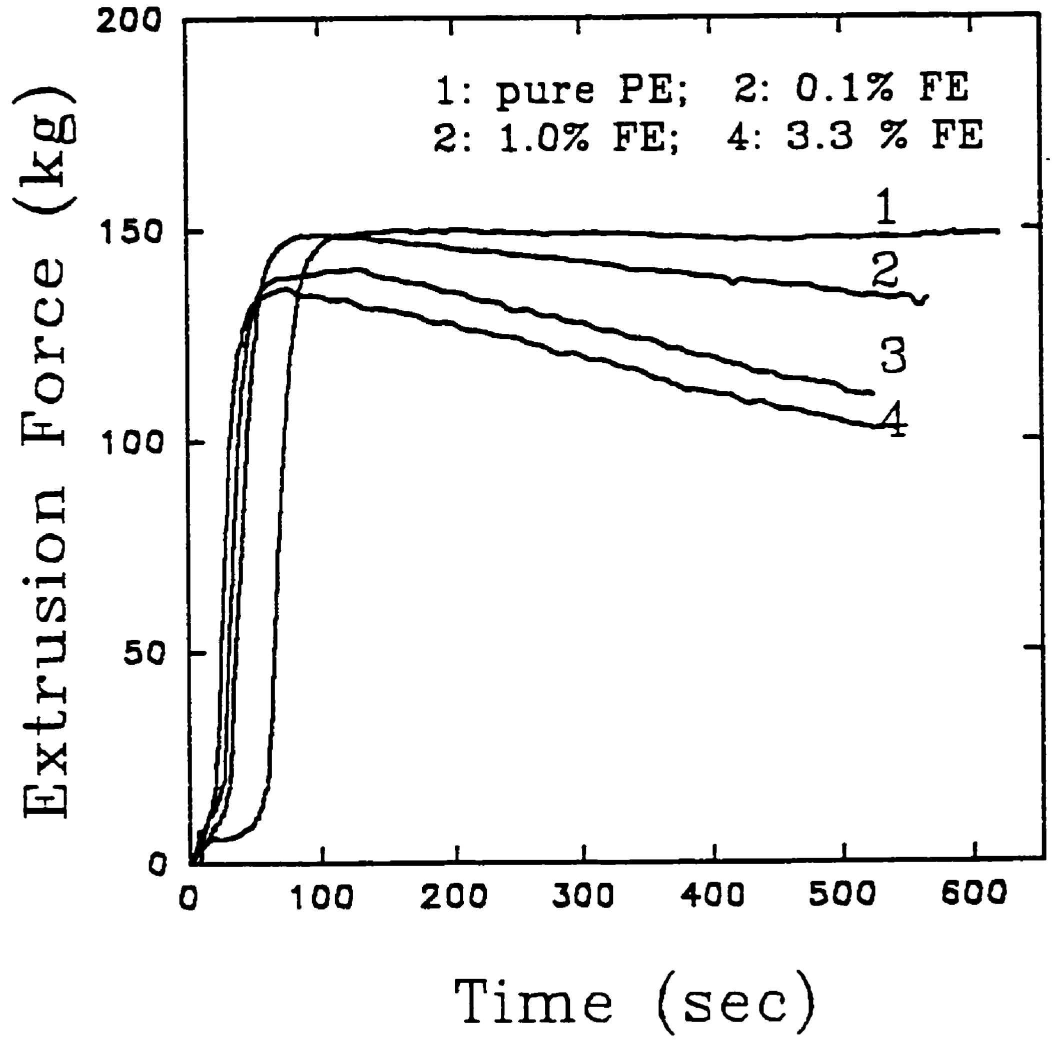


Figure 6.1. First Extrusion of control LLDPE and its blends with FE at 143 s^{-1} and 200°C 1: pure PE. 2: 0.1% FE. 3: 1.0% FE. 4: 3.3% FE

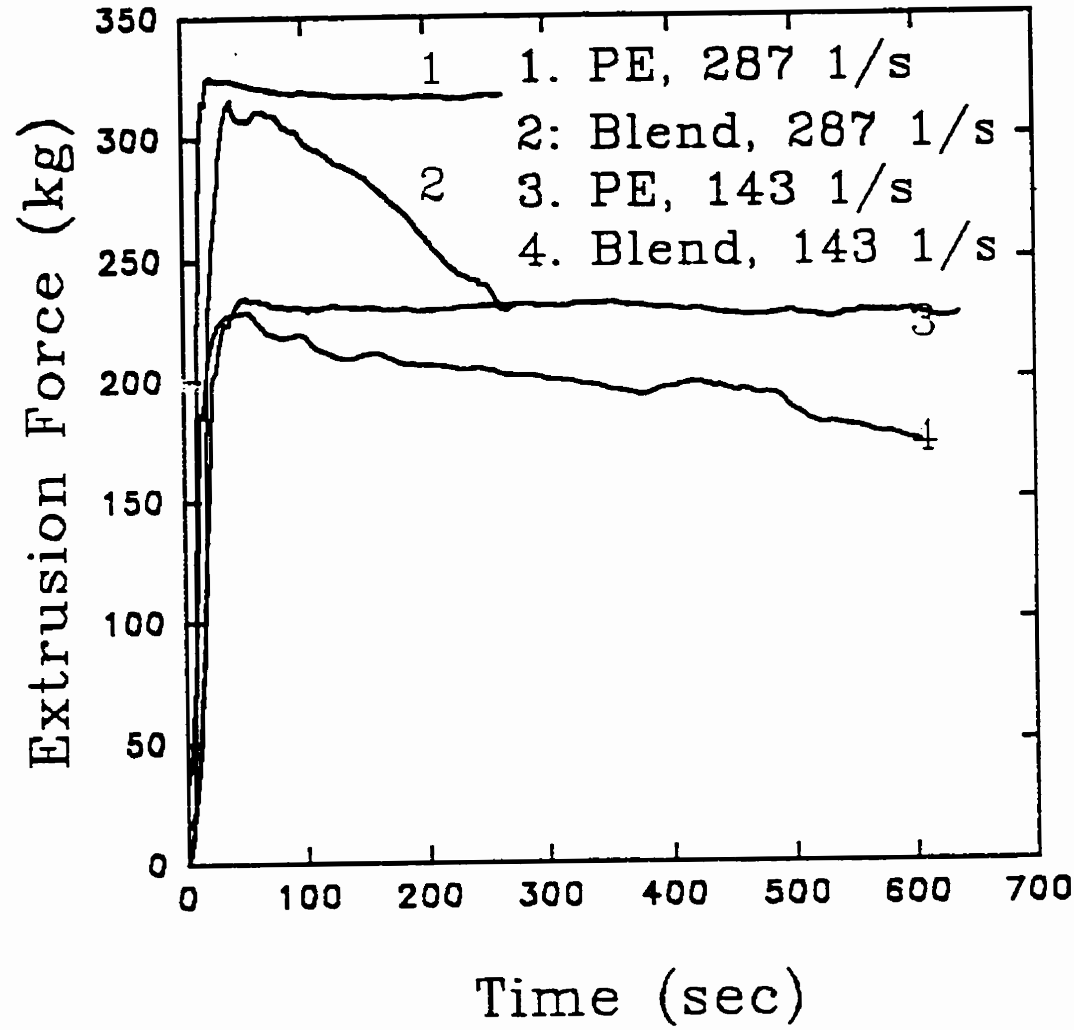


Figure 6.2 Effect of shear rate on first extrusion of LLDPE/1% FE blend at 160°C 1: LLDPE, 287 s^{-1}, 2: Blend, 287 s^{-1}; 3. LLDPE, 143 s^{-1}; 4. Blend, 143 s^{-1}

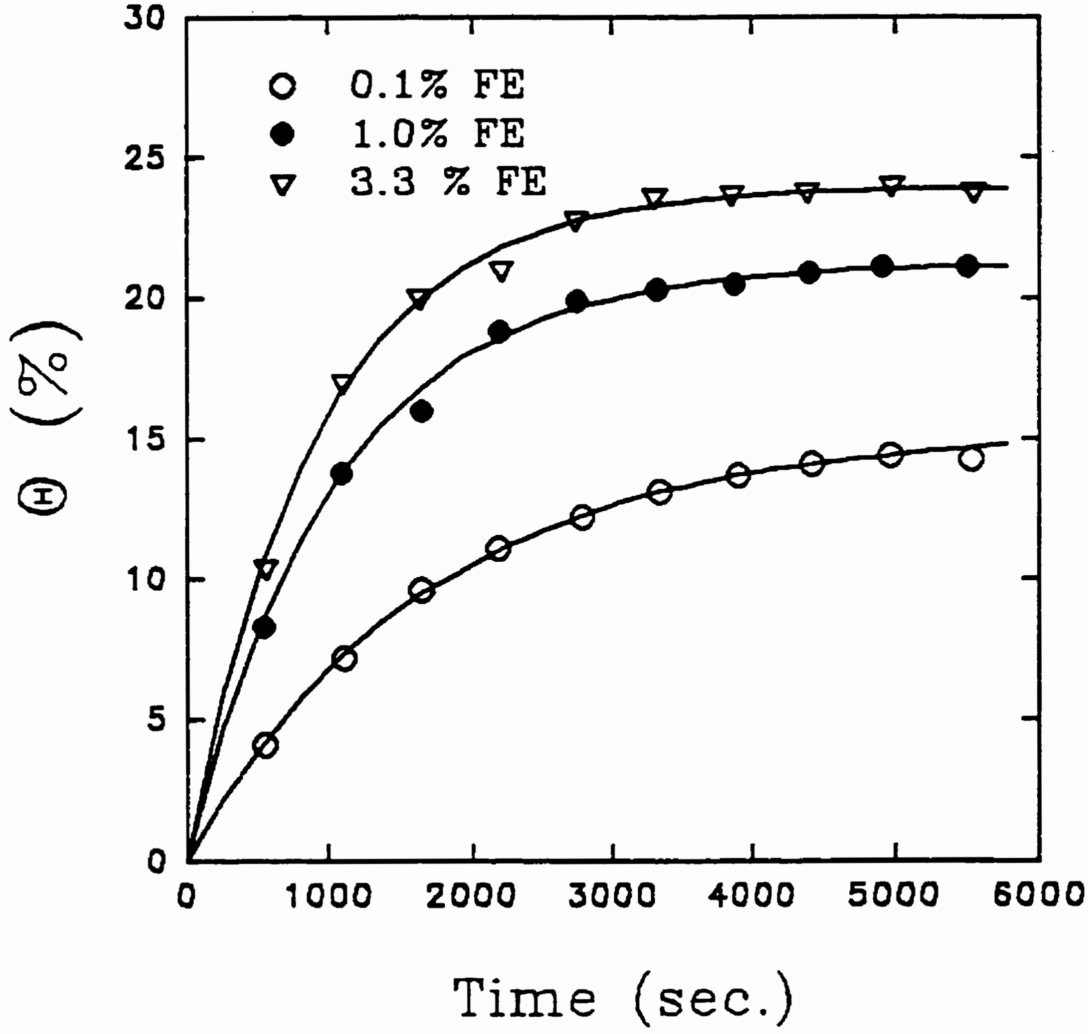


Figure 6.3. External efficiency of FE on flow of various blends at 143 s^{-1} and 200°C. ○ 0.1% FE; ● 1.0% FE, ▽ 3.3% FE

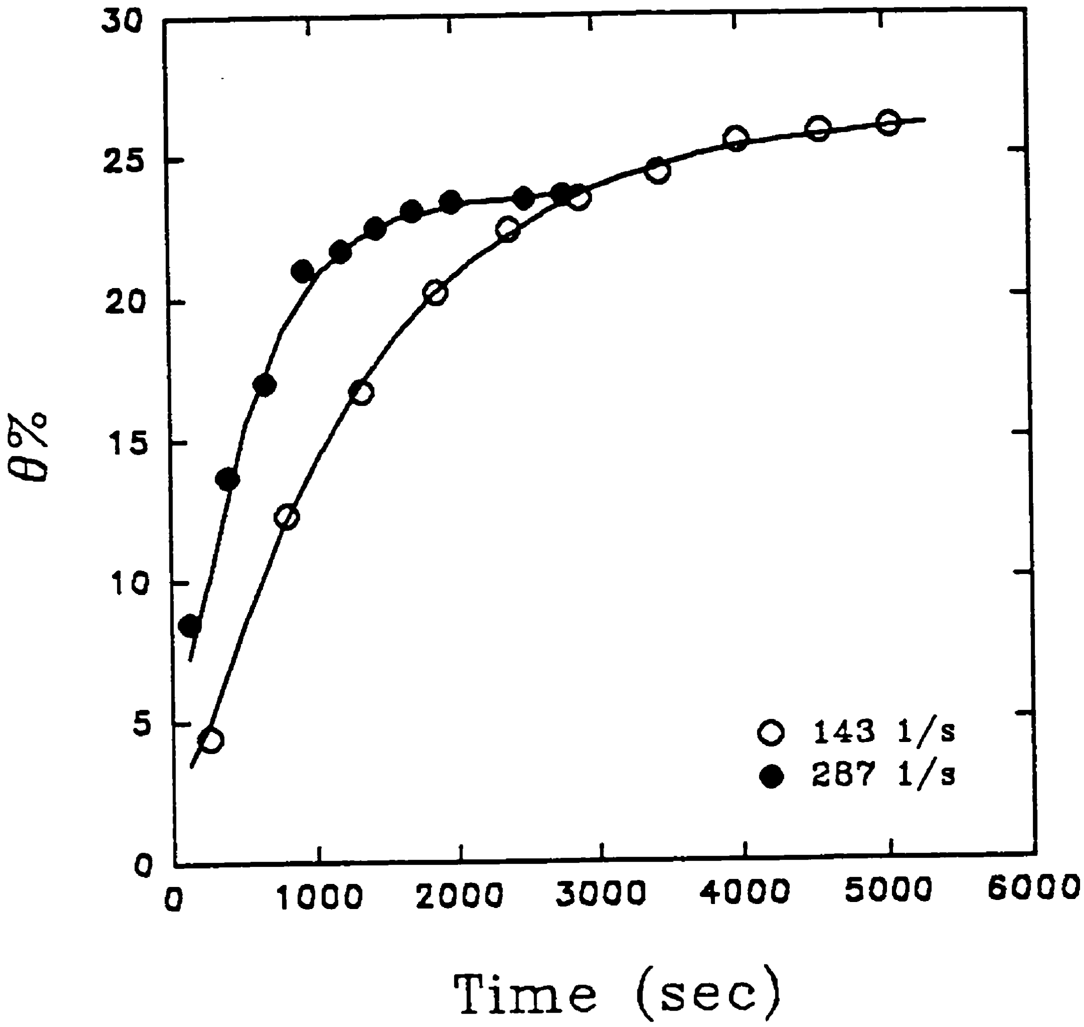


Figure 6.4 Influence of shear rate on efficiency of 1% FE additive in the flow of LLDPE at 160°C. ○ 143 s^{-1}; ● 287s^{-1}.

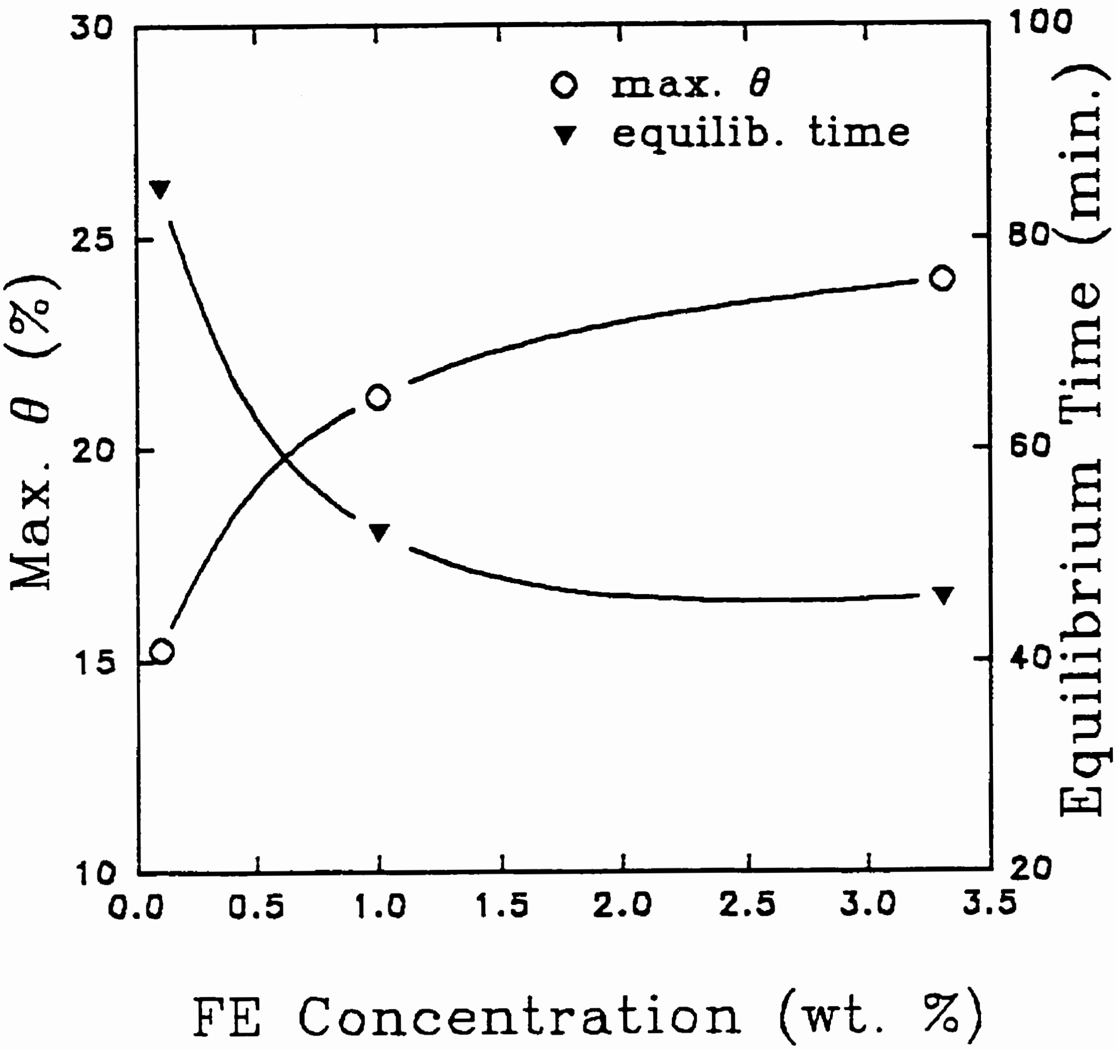


Figure 6.5 Influence of FE concentration on its maximum external efficiency and attainment of equilibrium extrusion force at 143 s^{-1} and 200 C ○ maximum θ. ▼ equilibrium time

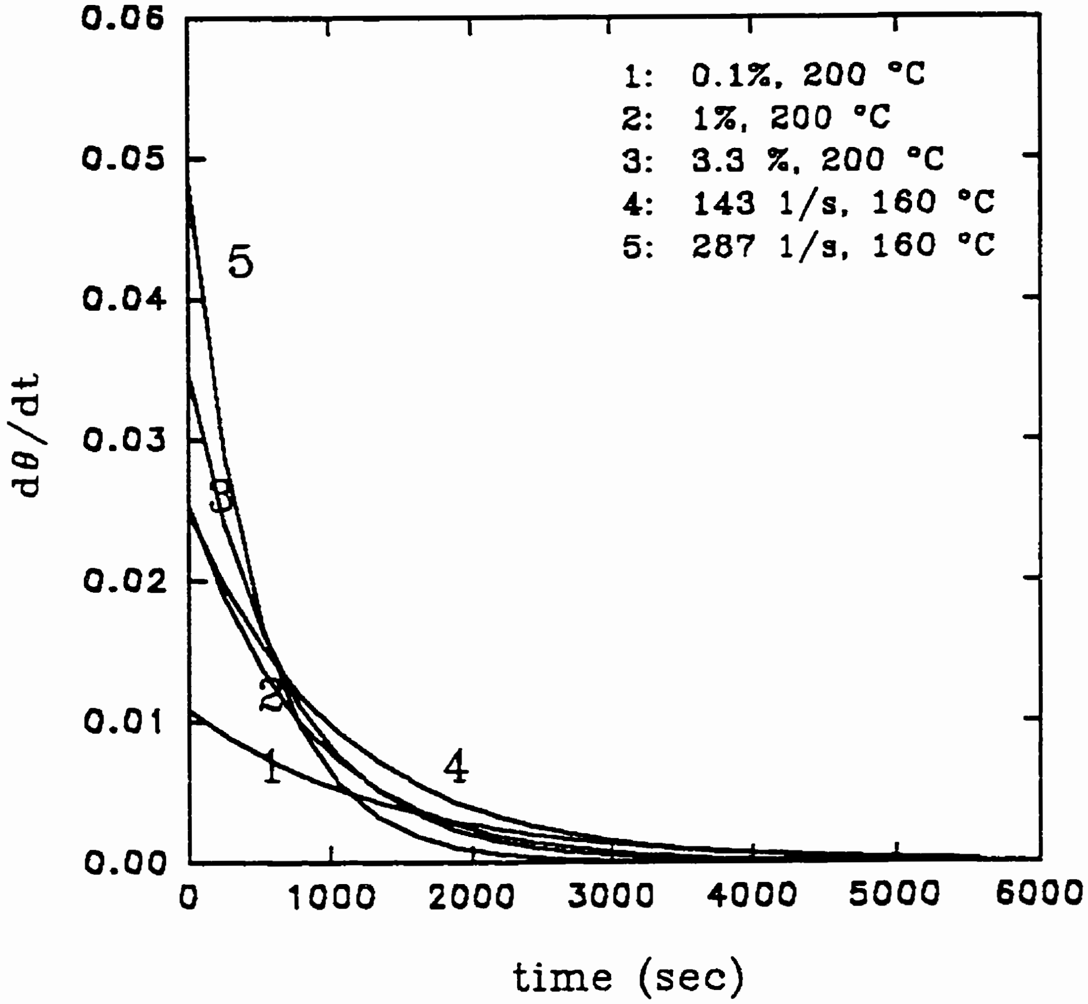


Figure 6.6 Effect of extrusion conditions on the rate of efficiency increase of FE. 1-3: FE was 0.1, 1.0 and 3.3%, respectively, at 200°C and 143 s^{-1}; 4 and 5: extrusion at 143 s^{-1} and 287 s^{-1}, respectively, all samples were LLDPE/1% FE blend at 160°C.

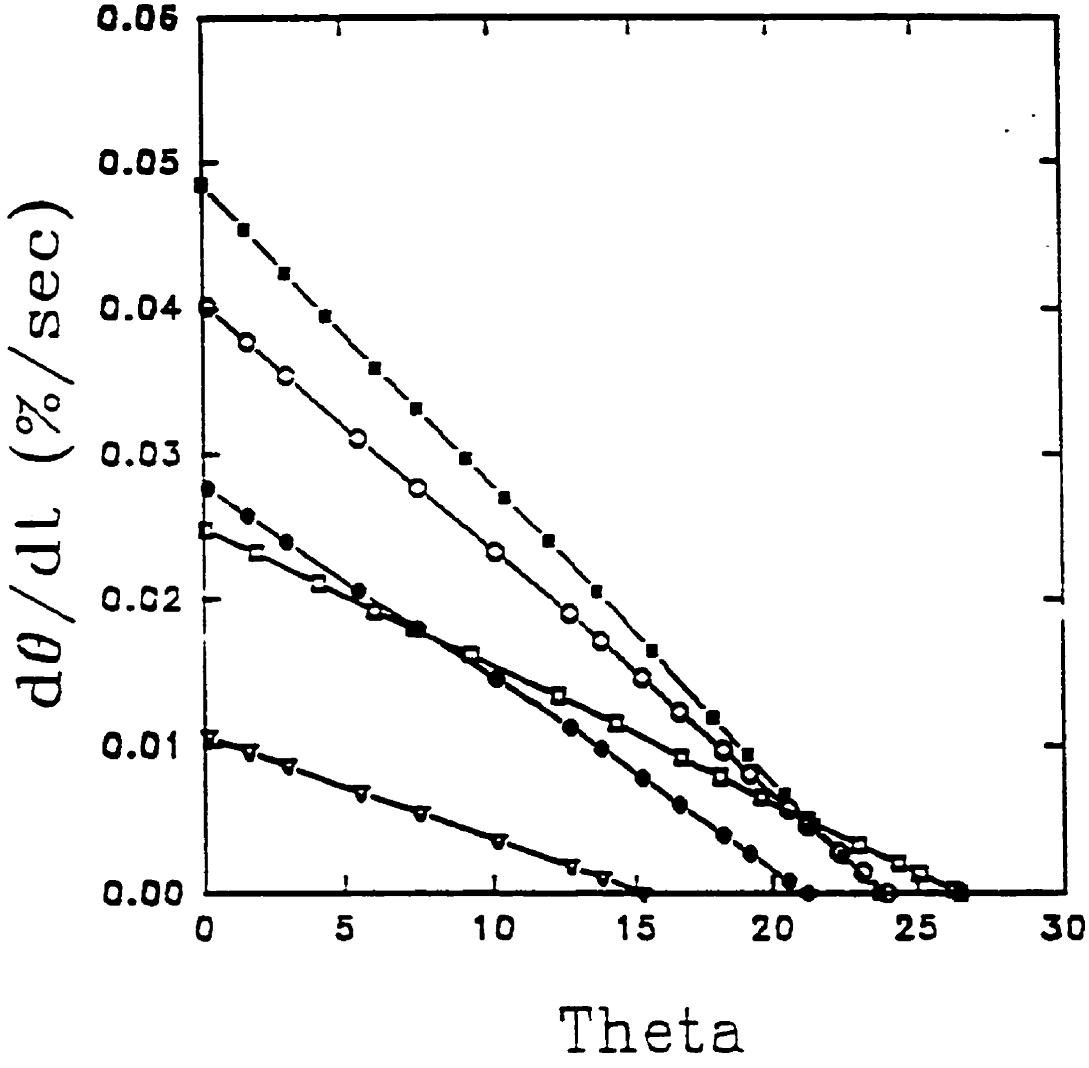


Figure 6.7 Relationship of the increasing rate and efficiency ○: LLDPE/3.3% FE blend at 200°C and 143 s^{-1}. ● LLDPE/1% FE blend at 200°C and 143 s^{-1}. ▽ LLDPE/0.1% FE blend at 200°C and 143 s^{-1}. ☐ LLDPE/1% FE blend at 160°C and 143 s^{-1}. ■ LLDPE/1% FE blend at 200°C and 287 s^{-1}

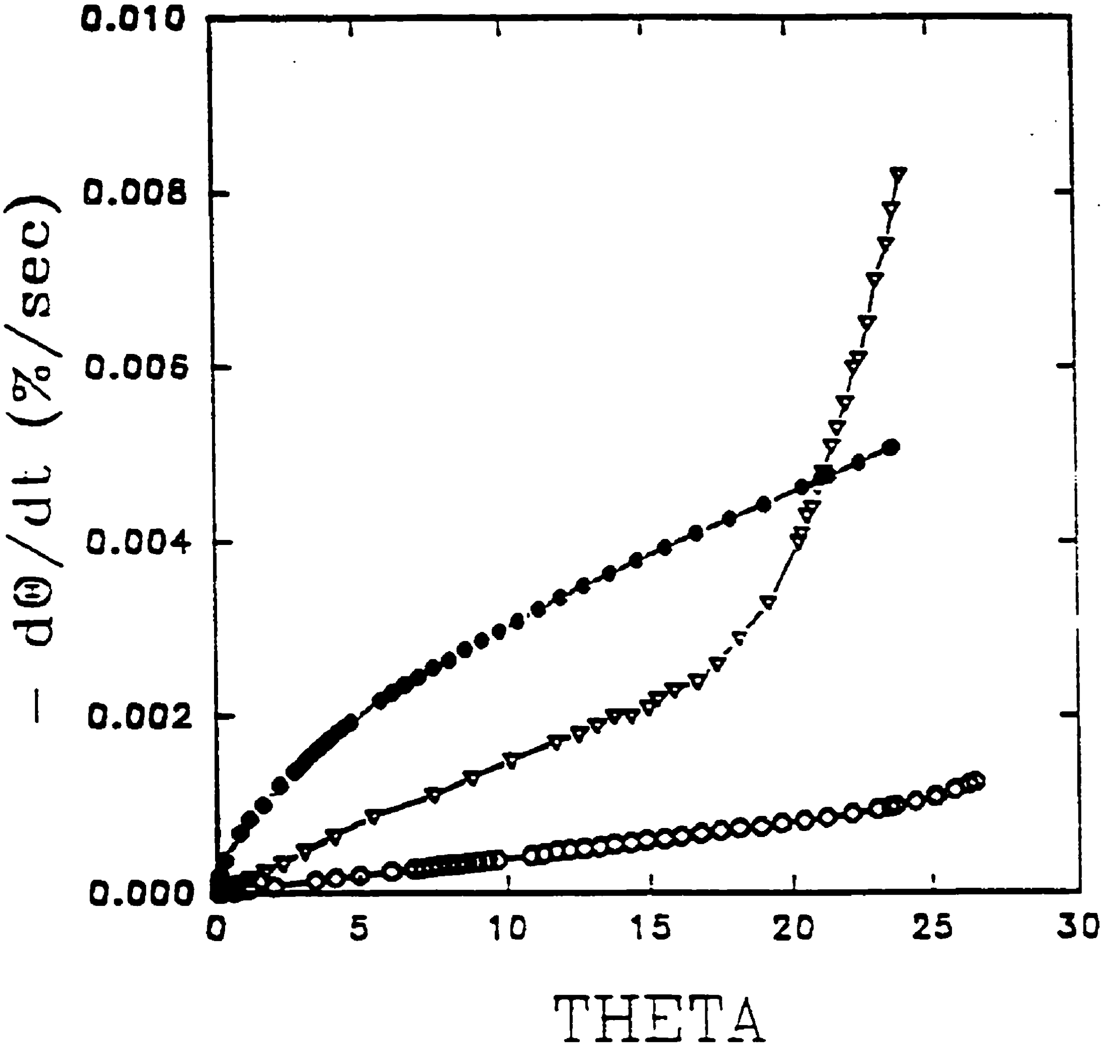


Figure 6.8 Relationship of purging rate and flow modification efficiency of FE on LLDPE at various temperatures and shear rates. ○: at 160°C and 143 s^{-1}; ●: at 160°C and 287 s^{-1}; ▽: at 200°C and 143 s^{-1}

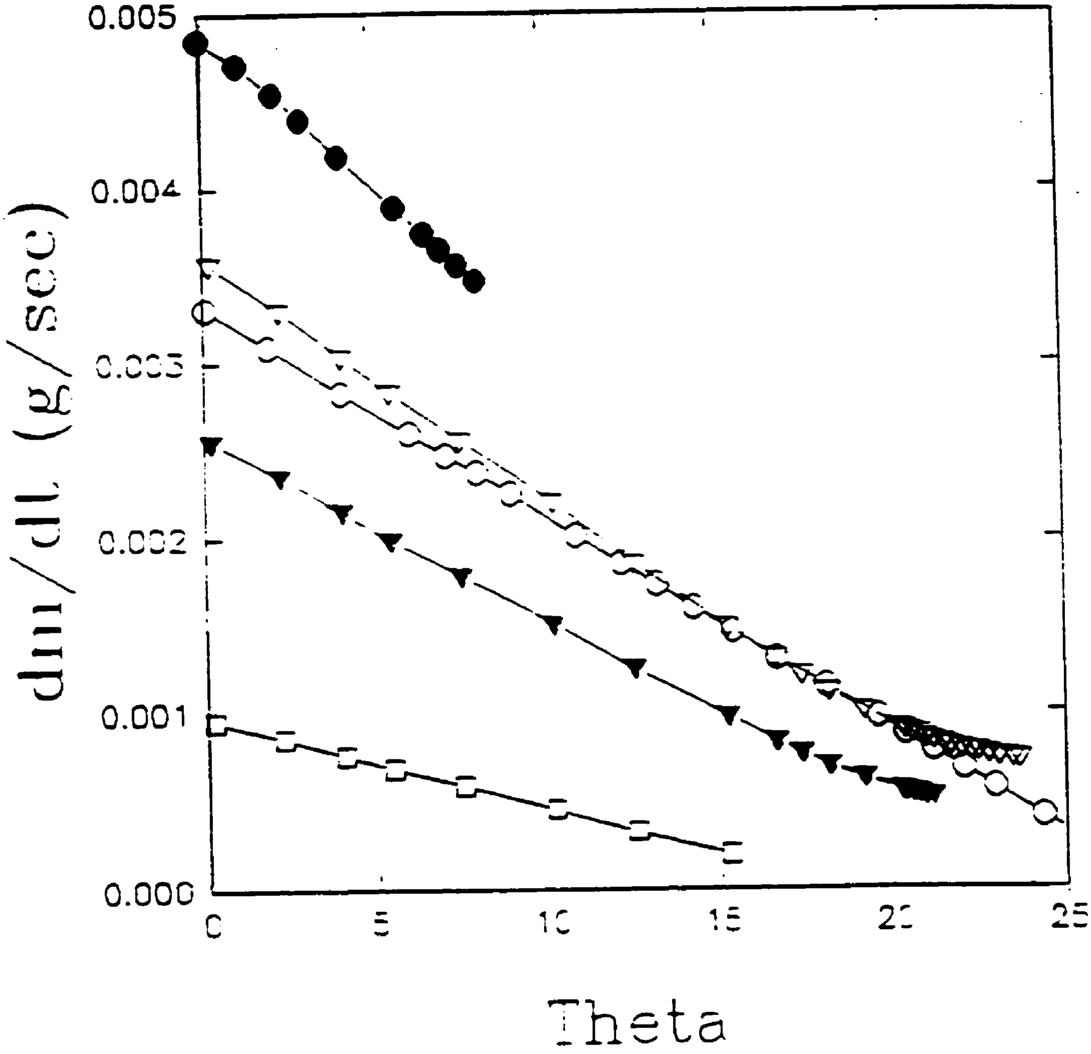


Figure 6.9 Estimation of mass transfer rate at various conditions ○: LLDPE/1% FE blend at 160°C and 143 s^{-1}. ● LLDPE/1% FE blend at 160°C and 287 s^{-1}. ∇ LLDPE/3.3% FE blend at 200°C and 143 s^{-1}. ▼ LLDPE/1% FE blend at 200°C and 143 s^{-1}. □ LLDPE/0.1% FE blend at 200°C and 143 s^{-1}

7. Use of A Fluoroelastomer Processing Aid With Non-Polyolefinic Polymers

K.C. Xing, W. Wang and H.P. Schreiber

Department of Chemical Engineering, Ecole Polytechnique
PO Box 6079, Stn. Centre-Ville
Montreal, QC. H3C 3A7, Canada

A die coated with fluoroelastomeric polymer (FE) has been used in the extrusion of thermoplastics other than conventional polyolefins, and including chlorinated polyethylene, polystyrene, polycarbonate and an ionomer. Inverse gas chromatography was the source of acid/base interactions between FE and each of these matrix polymers. FE was found to be effective in reducing the apparent melt viscosity when the host polymer was acidic, or non-interactive. With strongly interactive, the effectiveness of FE flow modifier on basic polymers was annulled. These polymers may be considered as effective purging agents for extrusion equipment containing FE residues.

Accepted by ***Polym. Eng. Sci.*** April, 1996

1. Introduction

Fluoroelastomers (FE) are among the fluoropolymers which have become widely used in processing polyolefins, notably linear, low-density polyethylene (LLDPE). Their presence leads to the suppression of instabilities known as shark-skin and slip-stick fracture, which limit the range of output rates in which the polymer may be processed. Several empirical and theoretical accounts of the function of FE and of related additives conclude that the additive acts as a die lubricant, modifying the properties of the interface between flowing polymer and die wall[1-7]. As a result, the onset of instabilities is shifted to much higher output rates and the force of extrusion is reduced, signalling a lowered apparent melt viscosity. Two previous publications from this source[8,9] have contributed to the current state of knowledge. In one[8], it was shown that the effectiveness of FE action, expressed as a dimensionless coefficient (θ) could be related to the diffusion of FE through the host polymer matrix and to the mechanical strength of the interface between FE and the die wall. In a subsequent paper [9], we examined the problem of purging FE from a coated die by the extrusion of LLDPE.

If FE functions as a die lubricant, then it seems logical to ask whether its usefulness is restricted to LLDPE and other polyolefins, and whether it may not also be useful with other thermoplastics. So far this topic appears not to have been addressed. It forms the focus for the present study, where FE was used as a potential flow modifier for the extrusion of polystyrene (PS), a chlorinated polyethylene (CPE), polycarbonate (PC) and Surlyn ionomer (SN). An attempt is made to relate the performance of FE in these cases to the thermodynamic interaction between the polymers, as evaluated by methods of inverse gas chromatography (IGC).

II. Experimental

I) *Materials*: The polymers involved in this research are specified in Table 7.1. They were selected on the basis of their ability to act as Lewis acids and bases and were used as received from the supplier. The CPE of course qualifies as a polyolefin, but the presence of specifically interactive halide linkages differentiates it from previously studied LLDPE resins.

ii) *IGC*: IGC measurements were used to specify the surface interaction characteristics of the polymers noted in Table 7.1. Thus, the polymers were coated from solution onto Chromosorb G (AW-DMCS treated, 60/80 mesh). Ashing procedures showed the weight of supported polymer to be in the 7% range. The coated support was dried and packed in previously washed and degreased stainless steel columns, 6 mm in diameter and about 40 cm. in length. Packed columns were placed in a Varian 3400 gas chromatograph equipped with both thermal conductivity and flame ionization detectors. The columns were conditioned for at least 4 hours at 120°C in a flow of He, which also served as carrier gas in IGC experiments. These involved probing the polymer surfaces with the following vapors, injected at extreme dilution: n-alkanes from hexane (*n*-C6) to nonane (*n*-C9), diethyl ether (Ether), tetrahydrofuran (THF), ethyl acetate (EtAc), acetone and chloroform ($CHCl_3$). All probes were analytical grade, used without further purification. Measurement temperatures for PC were 80 - 120 °C, and 40 - 70 °C for PS, well below the T_g values of these polymers. Absorption of probes into the bulk of PC and PS could therefore be neglected, and retention characteristics were dominated by surface adsorption. For CPE, SN and FE the measurements were made between 30 - 90 °C, above the T_g values for the polymers. Since under these circumstances retention volumes are the sum of contributions from surface adsorption and bulk absorption [10,11], a separation is required if surface characteristics are to be secured. We followed previously reported procedures [10] based on increasing carrier gas flow rates. In these cases He gas flow rates varied from 20-70 mL/min.

iii) *Flow measurements*: The experimental protocols for evaluating the flow-modifying effectiveness of FE, described previously [8], were followed in this work. They made use of an Instron Rheometer connected to an on-line recording computer. A flat-entry die, 1.75 mm in diameter and with L/D = 20, was used throughout. To quantify the effectiveness of FE as a flow modifier, flow resistance measurements were made in two types of extrusion:

Type I: In every run of this type, host polymer was extruded through a freshly-cleaned die.

Type II: Host polymer was extruded through the die which had been precoated with FE

As before [8], the FE effectiveness coefficient (θ) was calculated from:

$$\theta=(1-\frac{F_{II}}{F_{I}})x100\% \qquad (1)$$

where F is the force on the rheometer piston. FE benefits the extrusion process by lowering the force on the rheometer piston, $\theta > 0$ under these circumstances. In contrast a reported negative θ indicates that the extrusion force has actually risen, hindering the extrusion process. At constant extrusion rates, force readings were averaged over the period of stable force readings[8]. Maximum readings of F were used in comparisons between type I and II procedures when extruding at varying output rates. Details of processing conditions for each of the polymers will be stated in pertinent sections of the Results and Discussion section.

III. Results and Discussion

1) *Polymer surface properties*: The route followed was based on the well established relationship [12,13] between the net retention volume V_n of a probe and its characteristic dispersive surface energy (γ^D_L):

$$RT\ln V_N = 2N(\gamma^D{}_S)^{1/2} a(\gamma^D{}_L)^{1/2} + c \qquad (2)$$

where $\gamma^D{}_S$ is the dispersion surface energy of the polymer phase, N is Avogadro's number, c is an integration constant relating to a given column. R and T have their usual meaning and a is the molecular area of the adsorbed probe molecule. In this work the "a" values used were those reported by Schultz and coworkers [13], as given in Table 7.2. Also given in the table are acceptor and donor numbers AN*, DN, describing the probes' (Lewis) acid and base properties (in kCal/mole), respectively. These numbers are drawn from Gutmann's theory of acids and bases [14], as modified by Riddle and Fowkes [15]

Equation 2 calls for a straight line to be generated when RTlnVn is plotted *vs.* $a(\gamma^D{}_L)$ for the alkane probes. From the slope of that line $\gamma^D{}_S$ is readily obtained. An example of this is shown in Figure 7.1 for PS at 40°C. Specific interactions between polar probes and polymer surfaces are estimated by using the straight line as a reference for the position of the polar probes, also illustrated in Figure 7.1. Formally, the normal distance from the placement of each point to the corresponding one on the reference line evaluates ΔG_{sp}, the contribution of specific, or acid-base, interactions to the free energy of desorption:

$$\Delta G_{SP} = RT\ln \frac{V_N}{V^{REF}{}_N} \qquad (3)$$

The ΔG_{sp} datum is then used to obtain the acid and base interaction constants, K_a and K_b, for the polymer. A requirement is the evaluation of ΔG_{sp} over a suitable temperature range, leading to the computation of the acid/base enthalpy parameter ΔH_{sp}. This is then used, as suggested by Papirer [12], in the expression:

$$\Delta H_{sp} = K_a \cdot DN + K_b \cdot AN^* \tag{4}$$

so that a plot of $\Delta H_{sp}/AN^*$ *vs* DN/AN^* should yield the desired acid-base parameters. Figure 7.2 illustrates the expected excellent linearity for PS in the upper portion, and for FE in the lower portion. A summary of dispersion surface energies, of typical ΔG_{sp} values and of the K_a, K_b parameters for the polymers of this work is given in Table 7.3

The surface energy values are in good agreement with previously published data [16], but the datum for PC seems surprisingly low. In part the cause may be the more elevated temperature for this reading. Each of the polymers is able to act as both electron donor and acceptor in the temperature ranges pertaining to these determinations. Basicity is dominant in all but the CPE which is a net acid. The degree of acid-base interaction between polymer pairs can be quantified by empirical formulae, as discussed in earlier papers [16,17]. The simplest of these, applied in this work, is:

$$I_{sp} = K_{a(X)} \cdot K_{b(F)} + K_{b(X)} \cdot K_{a(F)} \tag{5}$$

where I_{sp} is the acid-base pair interaction parameter. X represents any one of the host polymers and F the FE flow modifier. Values of I_{sp} are listed in Table 7.4. Also shown, for reasons to be clarified later in this section, are values of the parameter normalized to the I_{sp} for CPE-FE.

In a preceding publication [9], it was argued that the effectiveness of FE in reducing extrusion force, and its capability to function over significant flow times depended on the rate of diffusion of FE into the flowing host polymer, and on the tendency of the host polymer to strip the FE from the die wall by mechanical, or frictional forces Both of these factors should increase in importance with a rise in the degree of molecular contact established between matrix and FE, and thus on the I_{sp} value. In other words, we would expect increasing values of I_{sp} to designate interfacial states which are less suited for the performance of FE as a beneficial flow modifier. The pair interaction parameters classify acid/base interactions between FE and the present polymers in the following descending order: SN > PC > PS > CPE (We note here parenthetically, that for polyolefins such as LLDPE, K_a=K_b=0, so that I_{sp} for FE/LLDPE also = 0). In terms of the above supposition, we would then expect initial values of θ to decrease in the order LLDPE > CPE > PS > PC > SN, and variations of θ with extrusion time to change in the reverse order. The expectations will be examined in following portions of the paper

ii) *FE as modifier of flow behavior*: Quantitative analyses of the effects on extrusion exerted by the FE followed the steps outlined earlier in this paper and given in detail in reference[8]. The effectiveness coefficient θ was evaluated according to equation 1, by comparing the flow resistance generated under identical settings of melt temperature and output rate in runs of Type I and Type II. Furthermore, by reloading the rheometer barrel after an initial run without cleaning the die, Type II (and occasionally Type I) runs were repeated several times, allowing the θ parameter to be followed over a number of extrusion cycles. This procedure lead to the evaluation of an average decay rate in θ, thus providing a measure of the rate at which FE was purged from the extrusion die. An example of the results obtained by these steps is shown in Figure 7.3 for the extrusion of CPE at 160 °C and a shear rate = 71.4 s^{-1}. Clearly, the substantial drop in extrusion force in Type II runs confirms the beneficial effects exerted by the FE coating. The purging rate is low, since only minor differences exist between the initial and subsequent runs of Type II.

A more detailed summary of the extrusion results for all of the host polymers is presented in Table 7.5. Necessarily, the temperatures and output rates varied somewhat from polymer to polymer, as indicated in the table. Returning to the CPE matrix, the average reduction in θ of 0.5% per run is indeed low, albeit greater than the 0.09 % per run reported earlier [8,9] for LLDPE under similar extrusion conditions. By inference the CPE melt slips over the FE layer without massive diffusion across the boundary, nor does this melt cause major losses of FE due to mechanical stripping from the extrusion die. As noted above, the degree of specific interaction for this pair of polymers is low. Thus, acid-base coupling appears to provide little driving force for contact at molecular levels.

The system PC/FE is more strongly interactive, and the flow data appear to reflect this. The initial θ value here is not greatly different from the preceding case, but the decay rate of 3.3 % per run far exceeds corresponding values for CPE and LLDPE. The strongly interactive PC therefore may classify as a good purging agent for FE, but little lasting benefit from reduction in extrusion force should be expected. Of course, the effect may not be due entirely to acid-base interaction effects, since, at the elevated temperature of this case, the adhesion of FE to the die wall may be seriously affected and the diffusion kinetics into the flowing matrix polymer accelerated.

Extrusion of PS and Surlyn ionomer was under identical settings of shear rate and temperature. The initial effect of FE on the extrusion of PS is slight and the decay rate is rapid. The PS exerts a strong purging effect on the FE deposit. The data for SN are perhaps the most interesting in the set. Here the presence of FE actually raises the flow resistance, indicative of a viscosity increase. The loss rate from the die is very rapid, and the viscosity characteristic of Type I runs is soon established. The SN/FE system is the most strongly interactive in the present selection of materials, raising the possibility that these polymers may form bonds through interspecies entanglements, or via chemical interaction. It is to be noted, however, that no evidence was found for chemical bonding from DSC and infrared spectroscopic data.

iii) *Acid-base interaction and FE effectiveness*: The inferences, above, of possible correlations between acid-base pair interactions and the effectiveness of FE as a flow modifier warrant further examination. This is done by means of Figures 7.4 and 7.5, the former showing the variation of the initial θ value with the normalized I_{sp} parameter, the latter the average rate of change in θ per run with that parameter. Earlier reported data for LLDPE are included in the comparison. The existence of significant correlations in both cases is indicated. Figure 7.4 documents the decrease in the initial θ with rising acid-base interaction and suggests that FE ceases to be a flow modifier when the normalized I_{sp} value exceeds about 2 (corresponding to an absolute I_{sp} of about 0.65). Whether a crossing of the θ =0 boundary displayed by the ionomer is a general occurrence at high levels of acid-base interaction remains a point to be resolved by additional experimentation. The relationship in Figure 7.5 is unambiguous, showing the accentuated loss in FE effectiveness with increasing acid-base coupling. As stated earlier in this article, the findings are consistent with mechanisms postulated to account for the flow modifying action of the FE [8,9]. At higher levels of acid-base interaction, the diffusion of FE into the polymer matrix would be enhanced. Under these conditions we may assume the rapid creation of an interphase between matrix polymer and FE, and this would also enhance the random mechanical stripping of FE from the die.

The inferred correlations are to be viewed with caution, however, since other factors, not taken into consideration, may also influence the effectiveness of FE flow additives No account has been taken of the contribution made by dispersion forces to events at the FE/polymer interface. An exact calculation of interfacial surface energies under appropriate conditions of temperature and shear, currently unavailable, would be needed for this purpose. The viscoelastic properties of the polymers under the defined extrusion conditions would also affect diffusion and mechanical stripping. Each of the polymers in this study has a characteristic dependence of melt viscosity and elasticity on extrusion variables; a full rationalization of the variation in FE effectiveness over the range of extrusion variables pertaining to this study would call for a consideration of these dependencies. Finally, attention is drawn to the temperature differences between IGC measurements from which the interaction parameters are drawn, and the extrusion measurements These differences, imposed by experimental limitations, are significant in all cases, but particularly so for PC Earlier studies by Panzer and Schreiber [16] and ongoing work [18] show that the acid-base functionalities of PC and of other polymers are temperature dependent, with a tendency to decrease with rising temperature. Consequently, the relationships in Figs.4 and 5 are indicative of trends but do not necessarily define quantitative correlations

IV Conclusions

- The extrusion behavior of thermoplastics other than LLDPE was shown to be affected by FE coatings applied to the extrusion die. The flow modifier was effective in reducing the apparent melt viscosity of CPE, but less so in processing PC, PS and Surlyn ionomer.
- IGC techniques have been applied to determine the acid-base functionalities of FE and the matrix polymers of this study, showing that acid-base pair interactions varied in decreasing order: Surlyn/FE > PS/FE ≥ PC/FE > CPE/FE
- As a consequence of the above statement, FE is considered to be an effective flow modifier when the matrix polymer is acidic, but strongly interactive, basic polymers will purge the FE rapidly from the die surface.
- While acid-base interaction is an evident factor in the performance of FE and related flow modifiers, the presented relationships only approximate true correlations, because of significant differences in the temperatures at which extrusion and IGC determinations could be carried out.

V. Acknowledgment

We thank the Natural Sciences and Engineering Research Council, Canada for financial support of this research through Operating and Cooperative Research and

Development grants. The assistance of Drs. D. Duchesne and A. Sengupta, and of other members of 3M Canada research staff, through the supply of flow modifiers and valuable discussions, is acknowledged with gratitude.

VI. References

[1] BLATZ, P.S., US Patent, 3,125,547 (1964).

[2] SHIH, C.K., Polym. Eng. Sci., **16** (11), 742 (1976).

[3] RAMAMURTHY, A.V., J. Rheol., **30** (2), 337 (1986).

[4] RAMAMURTHY, A.V. Adv Polym Technol. **6**, 489 (1986)

[5] KALIKA, D.S. and DENN, M.M., *J. Rheology* **31**, 815 (1987)

[6] HATZIKIRIAKOS, S.G., and DEALY, J.M., J. Rheol., **35** (4), 497 (1991).

[7] HATZIKIRIAKOS, S.G., and DEALY, J.M., J. Rheol., **36**, 703 (1992)

[8] XING, K.C. and SCHREIBER, H.P., Polym. Eng. Sci., **36**, 387 (1996a)

[9] XING, K.C. and SCHREIBER, H.P., Int. J. Polym. Proc., In Press

[10] P. MUKHOPADHYAY and SCHREIBER, H.P., Macromolecules **26**, 6391 (1993)

[11] P. MUKHOPADHYAY and SCHREIBER, H.P., Colloids and Surfaces A: Physicochem. Eng. Aspects, **100**, 47 (1995)

[12] SAINT FLOUR, C. and PAPIRER, E., Colloid Interface Sci. **91**, 63 (1983)

[13] SCHULTZ, J. and LAVIELLE, L., ACS Symposium Series **391**, LLOYD, D.R.,

Amer.Chem.Soc., Washington, D.C., 1989.

[14] GUTMANN, V., The Donor-Acceptor Approach to Molecular Interactions, Plenum Press, New York, 1978

[15] RIDDLE F.L. Jr and Fowkes, F.M., J. Amer. Chem.Soc. **112**, 3259 (1990)

[16] PANZER, U., and SCHREIBER, H.P., Macromolecules, **25**, 3633 (1992)

[17] KLOUBEK, J. and SCHREIBER, H.P. J. Adhesion, **42**, 87 (1993)

[18] TOVAR, G., CARREAU, P.J. and SCHREIBER, H.P. To be published.

Figure Captions:

Figure 7.1. Application of equation 1, with retention volume plotted vs. the product of probe dimension and dispersion surface free energy. Substrate is PS at 40 °C.

Figure 7.2. Illustrating graphical representation used to determine K_a and K_b parameters, in accordance with equation 4. Upper portion is for PS, lower portion for FE

Figure 7.3 Extrusion force vs extrusion time for CPE polymer

———— Type I, run 1

——-—— Type II, run 1, —·—·—·— Type II, run 2

—··—··— Type II, run 3, ············ Type II, run 4

Figure 7.4. Initial effectiveness of FE, defined by coefficient θ, as function of normalized acid-base pair interaction parameter

Figure 7.5 Rate of change in FE effectiveness as function of normalized acid-base pair interaction parameter.

Table 7.1. Polymeric Materials Used in This Work

Sample	Type	Specification	Supplier
PS	PS 204-00	Mn=9.1x10^4, Mw =1.9x10^5	Polysar Ltd.
PC	Lexan 130-111	Bisphenol-A	General Electric Inc.
Surlyn	Surlyn 9950	MI = 5.5, Cation type = Na	DuPont Inc.
CPE	Tyrin 4213	Cl=42%	Dow Chemicals
FE	Dynamar L-11216	Mooney Viscosity = 48	3M Inc

Table 7.2. Characteristics of Molecule Probes Used in IGC

Molecule	Probe	a Å^2	γ^D_L mJ/m^2	DN kcal/mol	AN* kcal/mol
n-Hexane	*n*-C6	51.5	18.4	-	-
n-Heptane	*n*-C7	57.0	20.3	-	-
n-Octane	*n*-C8	62.8	21.3	-	-
n-Nonane	*n*-C9	68.9	22.7	-	-
Tetrahydrofuran	THF	45.0	22.5	20.0	0.5
Ethyl ether	Ether	47.0	15.0	19.2	1.4
Chloroform	$CHCl_3$	44.0	25.0	0	5.4
Acetone	Acetone	42.5	16.5	17.0	2.5
Ethyl acetate	EtAc	48.0	19.6	17.1	1.5

Table 7.3. Surface Characteristics for Each Polymer at 70 °C

	γ^D_S, mJ/m^2	ΔG_{sp}^{THF}, kJ/mol	$\Delta G_{sp}^{CHCl_3}$, kJ/mol
PS	24	11.0	8.6
CPE	29	5.8	3.4
PC*	8	9.0	8.1
Surlyn	38	3.6	1.0
FE	19	17.9	83

PC*: measurement temperature 110 °C

Table 7.4. Specific Components ΔH_{sp} (kJ/mol) of the Enthalpy of Adsorption of Solutes

Probe	PS	CPE	PC	Surlyn	FE
THF	33.2	52.7	46.4	64.0	64.0
Ether	34.3	48.5	49.2	71.9	67.4
$CHCl_3$	22.2	10.0	40.0	39.3	28.2
Acetone	40.6	49.8	50.6	82.8	79.5
EtAc	41.0	41.4	51.0	72.3	65.7

Table 7.5. Summary of FE Effectiveness in Extrusion of Various Polymers.

1) CPE: Extrusion at 160°C, and shear rate = 71.4 s^{-1}

Run type	I	II	II	II	II
Run number	1	1	2	3	4
Average extrusion Force (kg)	358.0	296.1	296.1	297.3	303.6
θ %		17.3	17.3	17.0	15.2
d(θ)/d(Run)	0.52				

2) PC: Extrusion at 250°C, and shear rate = 143 s^{-1}

Run type	I	II	II	II
Run number	1	1	2	3
Average extrusion force (kg)	247.6	215.2	231.9	239.3
θ %		13.1	6.3	3.3
d(θ)/d(Run)	3.3			

3) PS: Extrusion at 180°C, and shear rate = 143 s^{-1}

Run type	I	II	II	II
Run number	1	1	2	3
Average Extrusion Force (kg)	143.5	151.8	147.3	144.6
θ %		-5.7	-2.7	-0.8
d(θ)/d(Run)	1.8			

4) Ionomer: Extrusion at 180°C, and shear rate = 143 s^{-1}

Run type	I	II	II	II	II
Run number	1	1	2	3	4
Average extrusion Force (kg)	48.8	56.0	49.8	48.1	48.4
θ %		-14.6	-2.0	0	0
d(θ)/d(Run)	3.7				

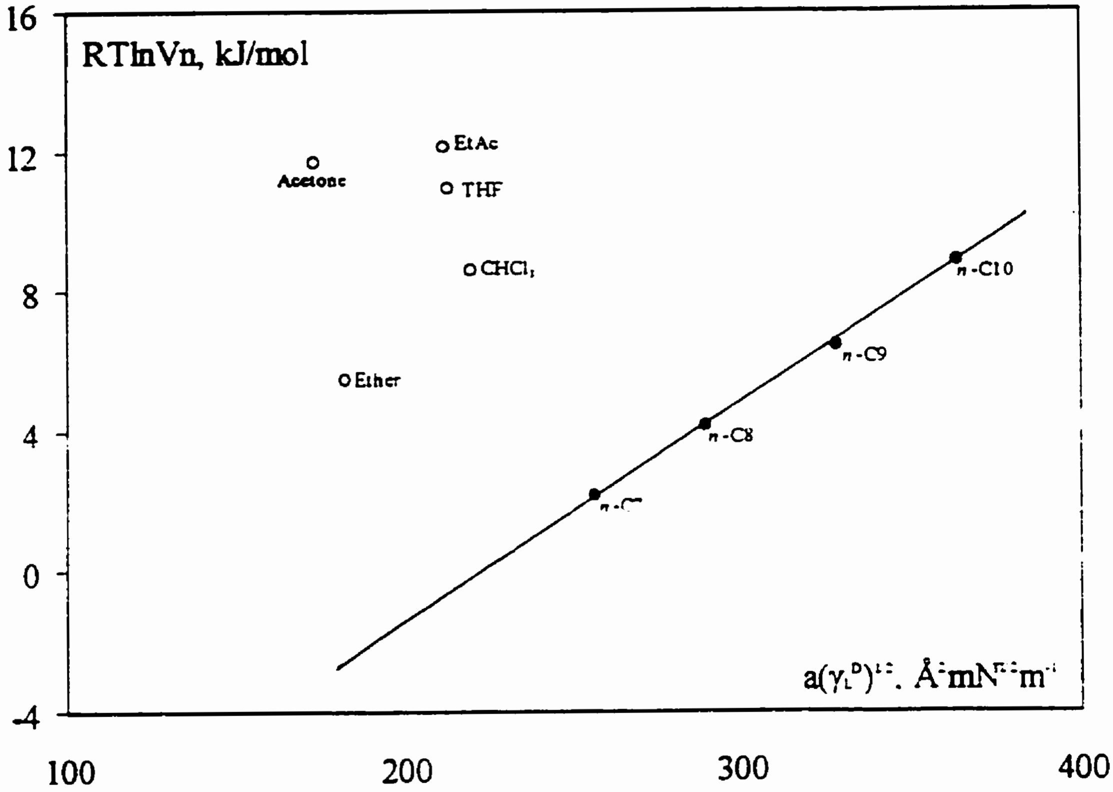


Figure 7.1 Application of equation 1, with retention volume plotted vs the product of probe dimension and dispersion surface free energy. Substrate is PS at 40 °C

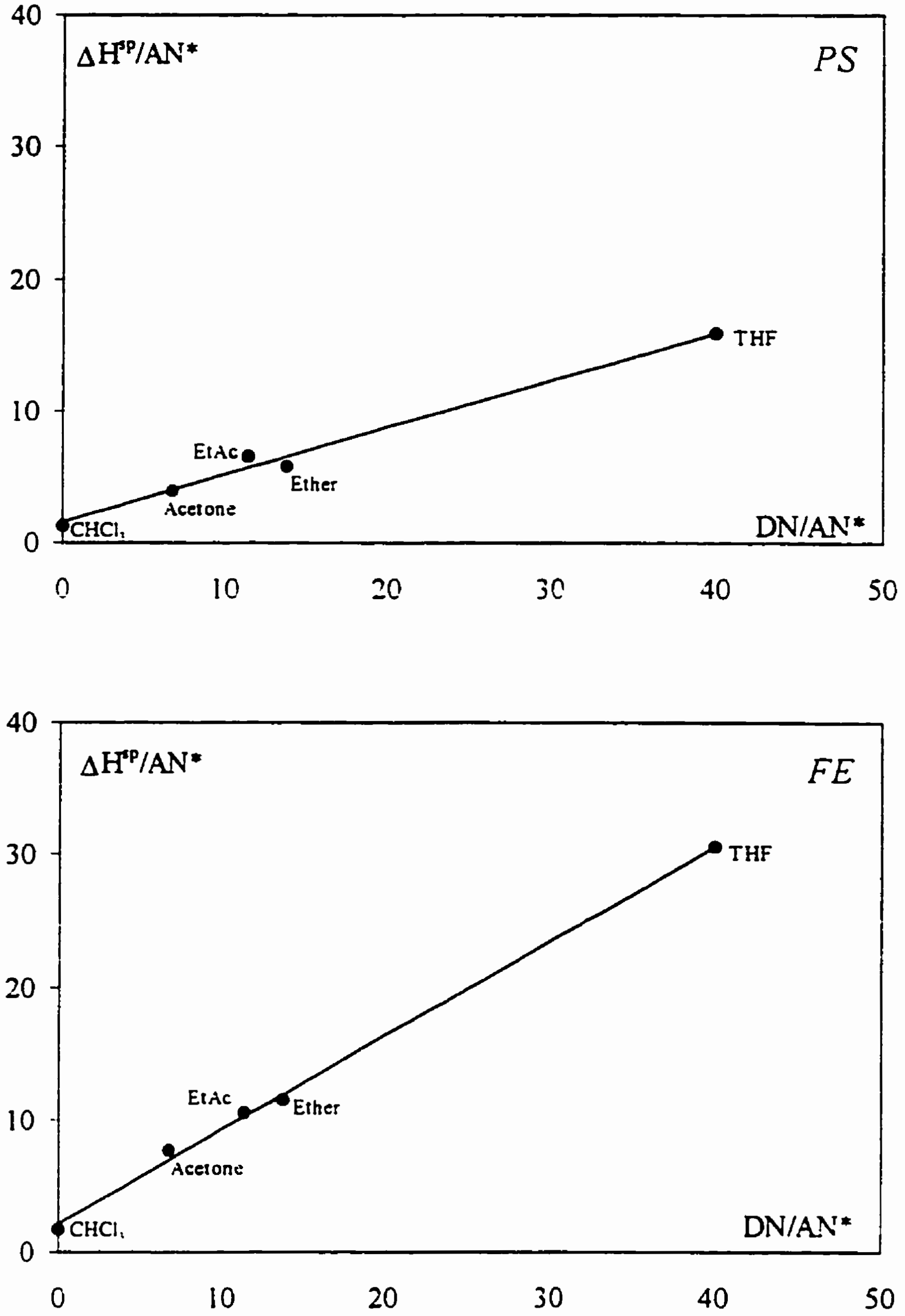


Figure 7.2 Illustrating graphical representation used to determine K_A and K_D parameters, in accordance with equation 4. Upper portion is for PS, lower portion for FE.

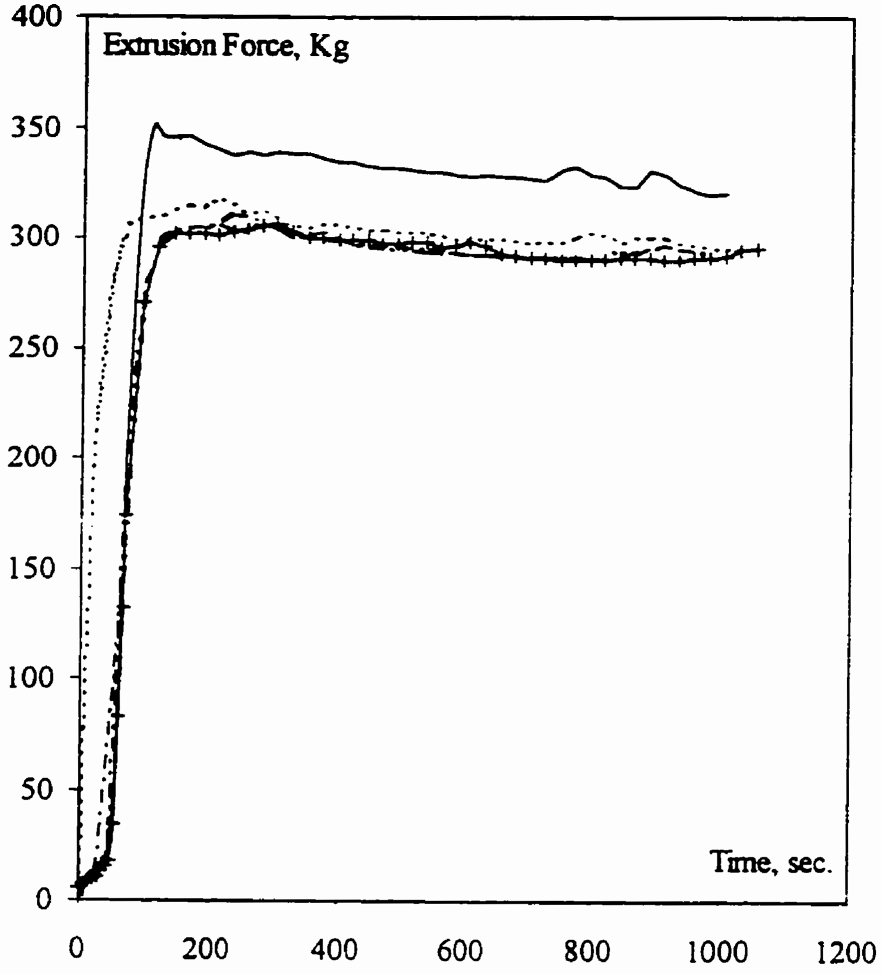


Figure 7.3 Extrusion force vs extrusion time for CPE polymer

——————— Type I, run 1

———–——— Type II, run 1, –·–·–·–·– Type II, run 2

–··–··–··– Type II, run 3, ··········· Type II, run 4

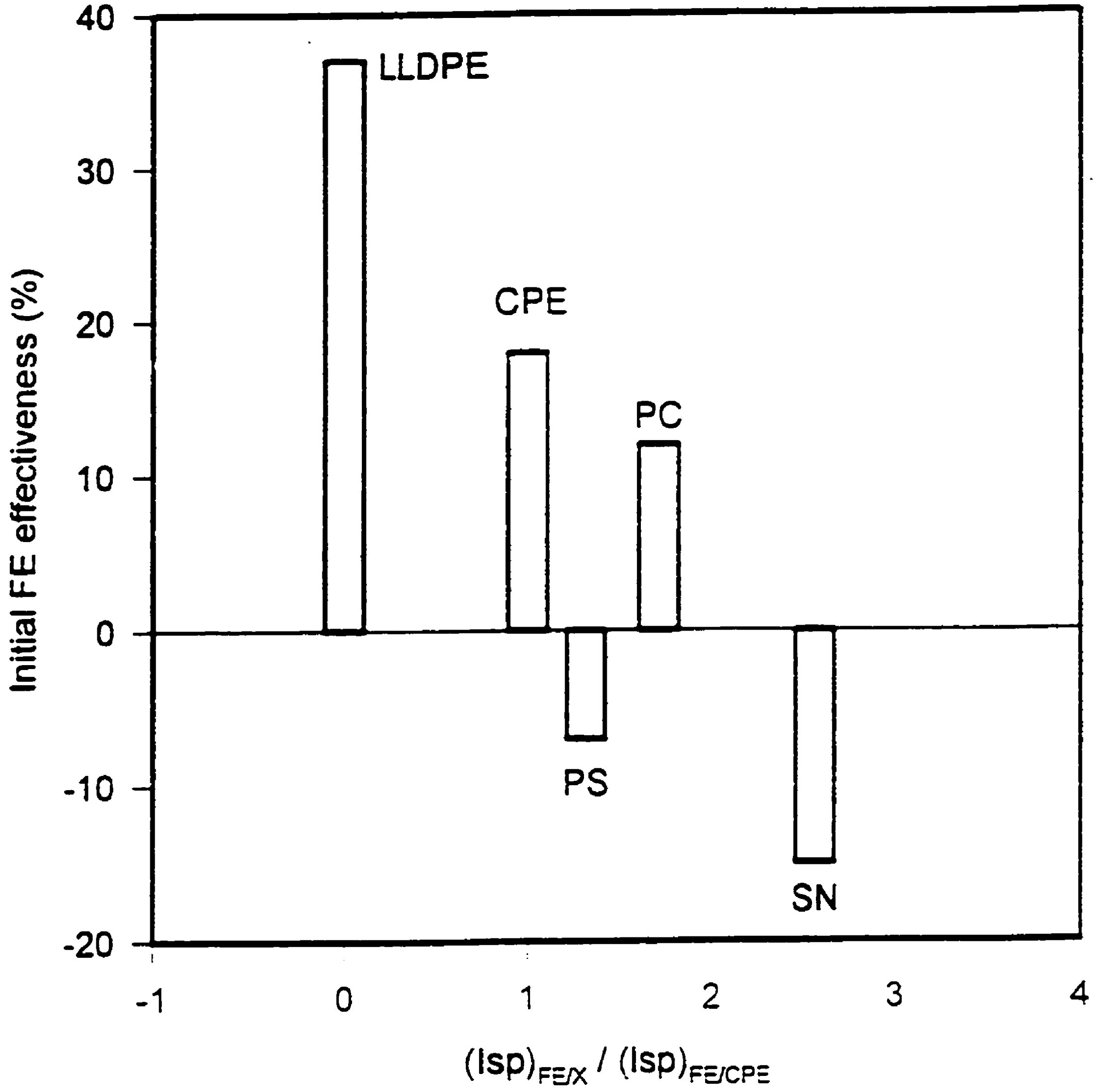


Figure 7.4 Initial effectiveness of FE, defined by coefficient θ, as function of normalized acid-base pair interaction parameter

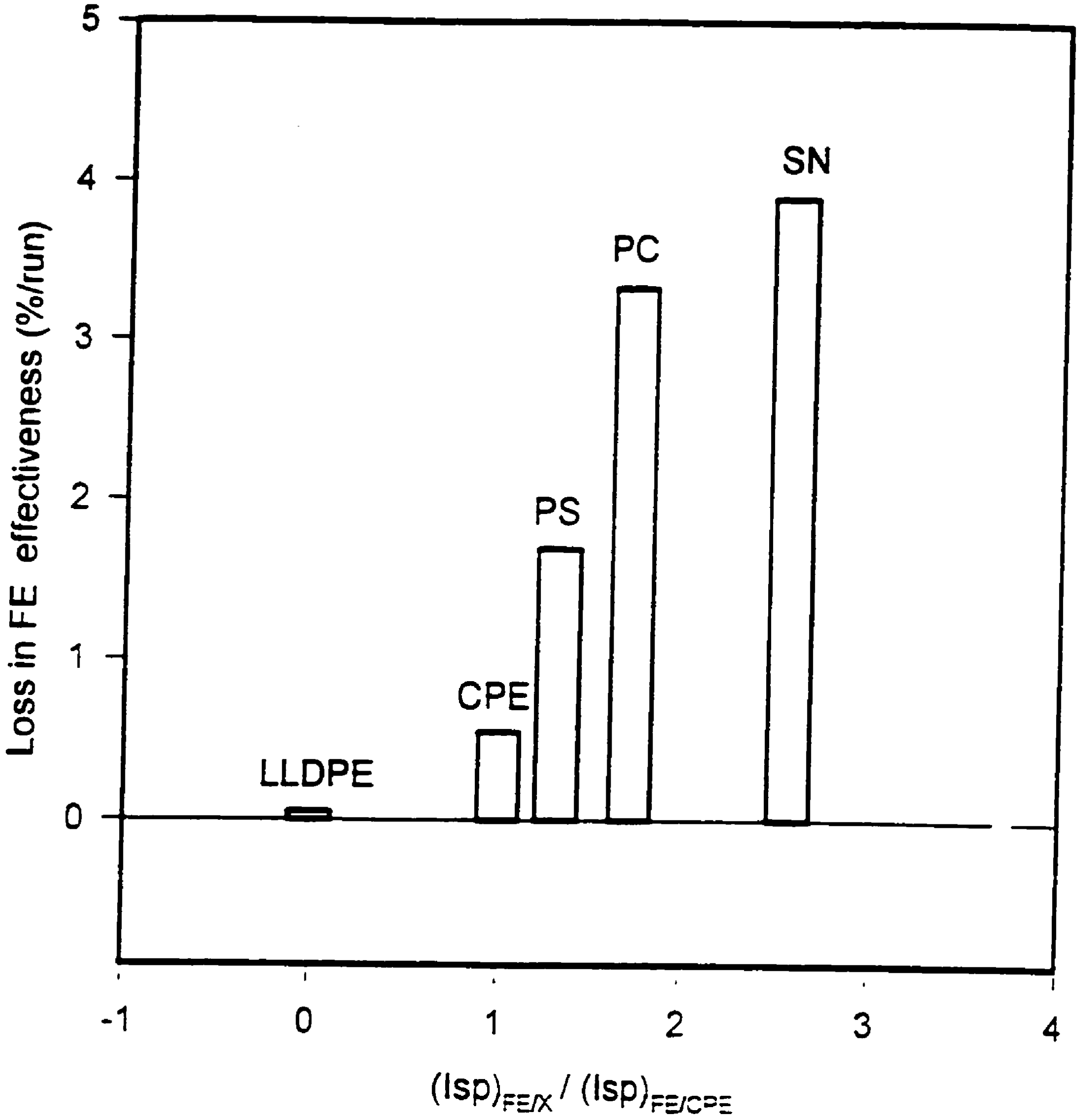


Figure 7.5 Rate of change in FE effectiveness as function of normalized acid-base pair interaction parameter.

8. CONCLUSIONS AND RECOMMENDATIONS

1) Conclusions:

* FE coatings applied on extrusion dies have promoted the slip of LLDPE polymer at the die boundary, with a resulting reduction in the flow resistance.

* The effectiveness of FE coatings to reduce process viscosity is a function of the shear rate. In this work, optimum effectiveness was associated with a shear rate range of 100-200 s^{-1}.

* Slippage of LLDPE occurs at the FE/LLDPE interface along the die wall; FE effectiveness as a flow modifier therefore also rises with increasing die length.

* In slip-stick flow of LLDPE, the fractional time during which the melt slips increases with shear rate to a characteristic maximum, but cannot attain the limit of 100%.

* Theories of molecular dynamics and of adhesive failure, alternatively proposed as the origins of sporadic flow in LLDPE, have been linked by equations based on

concepts drawn from both approaches.

- For the removal of FE deposited on a die land by the extrusion of LLDPE, both diffusion mechanism and mechanical stripping of the FE by the flowing matrix polymer may be responsible for the purging process.

- Both experiment indicate that purging rates are higher at initial stages of the process. Higher temperatures and lower extrusion rates promote the purging process with same amount of host polymer.

- Blending a small amount of FE in LLDPE/FE blends can significantly reduces flow resistance of the entire material.

- FE causes both internal and external lubrication to the flow of the blends, but external effect of FE on the flow is more remarkable than the internal one. The external effect increase with time of extrusion till an equilibrium is reached.

- The migration rate of FE from the blends toward the wall is also time-dependent. It reduces along the time of extrusion till the equilibrium. The factors favorable to the migration to the wall include strong shear field, incompatibility between polymers, and low surface energy of FE. The process of migration inside the mainstream is different with that arriving at the wall. The controlling step for FE to accumulating at the wall is phase separation of FE from the mainstream.

* Being applied to non-olefinic polymers, FE can improve their processability when weak interaction between FE and host polymer occurs; otherwise, strong interaction between FE coating and host polymer make processing difficult.

2) Recommendations for Further Study

* A relationship needs to be established between the chemical structure, molecular weight, etc. of FE and their effects on modifying the flow behavior of polymers. This will make it possible for tailoring FE additives to maximize the effectiveness of flow modifications.

* Additional non-olefinic polymers should be used as hosts, to clarify the relationships between FE effectiveness and interaction concepts.

* Alternative process steps should be studies to define the most beneficial procedure for the use of FE. Among these, attempts should be made to produce permanent

coating of FE on the surface of die walls, avoiding the need for out-of-line blending of the additive into host polymers. Further, the efficiency should be studied of extruding polymers with very low level of FE content over FE-coated die.

* Exploratory work should be done to establish what other polymer properties are affected by the surface localization of FE. Candidates for study include dielectric and barrier properties, and the printing adhesion to these surface.

9. REFERENCES

- * AJJI, A., VARENNES,S.and SCHREIBER, H. P., *Polym. Eng.Sci.*, **33**, 1524 (1993)
- * AUBERT, J.H. and TIRRELL, M., *J. Chem. Phys.*, **72**, 2694 (1980).
- * AUBERT, J.H. and TIRRELL, M., *J. Liquid Chromat.*, **6**, 219 (1983).
- * AUSSERRE, D., et al, *Macromolecules*, **19**, 85, (1986).
- * AUSSERRE, D., *Europhys. Lett.*, **14**, 33 (1991).
- * AGARWAL, U.S., DUTTA, A. and MASHELKAR, R.,*Chem. Eng. Sci.*, **49**, 1693 (1994).
- * ATHEY, B.J., THAMM, R.C., SOUFFIE, R.D. and CHAPMAN, G.R., *SPE Antec 44 Conf. Proc.*, 1149 (1986).
- * BAGLEY, E.B., *J. Appl. Phys.*, **28**, 624 (1957).
- * BAGLEY, E.B.., CABBOT, I.M., and WEST, D.C., *J.Appl. Phys.*, **29** 109 (1958).
- * BIRD, R.B., STEWARD, W.E., and LIGHTFOOT, E.N., *Transport Phenomena*, Chap. **3** and **10**, Academic Press, New York (1960).
- * BLATZ, P.S., *U.S. Patent*, 3,125,547 (1964).
- * BRUNN P.O. and CHI, S., *Rheol. Acta*, **23**, 163 (1984).
- * BRUNN, P.O. and GRISAFI, S., *J. Polym. Sci., Polym. Phys.*, **23**, 73 (1985).
- * BRUNN, P.O., *J. Rheol.* **29**, 859 (1985).
- * BUSSE, W.F., *J. Polym. Sci.*, **A2**, 1261 (1967).
- * CARREAU, P.J.,Transport Processes in Bubbles, Drops,and Particles, Chap. **8**, Hemisphere Publishing Corporation, New York (1992).

* CARREAU, P.J., and WANG, X., etc., *Polym. Eng. & Sci.* (1993).
* COHEN, Y. and METZNER, A.B., *Rheol. Acta*, **25**, 28 (186).
* DUERING, E. and Y. RABIN, *J. Rheol.*, **35**, 213 (1991)
* DIPAOLA-BARANYI,G.,*Inverse Gas Chromatography*,Chap. 9, American Chemical Society, Washington,DC (1989).
* DOI, M. and ONUKI, A., Dynamic Coupling between Stress and Composition in Polymer Solutions and Blends, *J. Phys. (Paris)*, **2**, 1631(1992).
* DUCHESNE, D., SCHREIBER, H.P., and RUDIN, A., *Plastics Compounding*, **Jan./Feb.**, 50 (1990).
* FOWKES, F.M., *J. Adhesion Sci. Tech.*, **1**, 7 (1987)
* FUJIYAMA, M., and KAWASKI, Y., *J. Appl. Polym. Sci.*, **42**, 467 (1991).
* GANNER, F.H. and NISSAN, A.H., *Nature*, **158**, 634 (1946).
* GLASS, A.S. and LARSEN, J.W., *Macromolecules*, **26**, 6354 (1993)
* GLASSOS, S., *Polymer Melt Rheology*, Chap 2, Cambridge Press, London, 1982.
* HAN, C.D., *Multiphase Flow of Polymers*, Chap. 2, Academic Press, 1990.
* HAN, C.D., *Rheology in Polymer Processing*, Chap. 3, Academic Press, 1976.
* HATZIKIRIAKOS, S.G. and DEALY, J.M., *J. Rheol.*, **35**, 497 (1991);
* HATZIKIRIAKOS, S.G. and DEALY, J.M., *J. Rheol.*, **36**, 845 (1992).
* HATZIKIRIAKOS, S.G. and DEALY, J.M., *J.Rheol.*, **36**,703,(1992)
* HATZIKIRIAKOS, S.G., HONG, P., HO, W., and STEWARD, C.W.,*J. Appl. Polym. Science*, **55**, 595(1995).
* HILL, D.A., HASEGAWA, T. and DENN, M.M., *J. Rheol.* **34**,891 (1990).

* IANNIRUBERTO, G., GRECO, F. and MARRUCCI, G., "The Two-fluid Theory of Polymer Migration in Slit Flow", *Ind. Eng. Chem. Res.*, **33**, 2404 (1994).

* JOHNSON, B.V., BLONG, T.J. and SCHREIBER, H.P., *Fourth Intern. Polym. Proc. Soc. Meeting*, Orlando, Fla, May, 1988.

* KALIKA, D.S., and DENN, M.M., J. Rheol., **31**, 815 (1987).

* KANU, R.C. and SHAW, M.T., *Polym. Eng. Sci.*, **22** (8), 507(1982).

* KHAN, M., BRISCOE, B. and RICHARDSON S., *Polym.-Plast. Technol. Eng.* **33**, 295 (1994).

* N. El KISSI and J. PIAU, *J. Non-Newtonian Fluid Mech.*, **37**, 55 (1990).

* KLEIN, D.F., *RETEC polyolefins V, 5th Intern. Conf. on polyolefins*, 285 (1987).

* LAUN, H.M., Rheol. Acta, **22**, 171 (1983).

* LEBLANC, J.L., VIEMAIRE, J.P. and VERGNES, B., *Plast. and Rubber Proces. & Appl.*, **11**(1), 53 (1989).

* LEE, L., *J. Phys.*, **30**, 143 (1973).

* LIM, F.J., and SCHOWALTER, W.R., *J.Rheol.*, **33**, 1357 (1989).

* LIN, Y.H., *J. Rheol.*, **29**, 605 (1985).

* MCLEISH, T.C.B., and BALL, R.C., J. Polym. Sci., Part B, **24**, 1735 (1986).

* METZER, A.B., COHEN, Y., and RANGEL-NAFAILE, C.,*J. Non-Newt. Fluid Mech.*, **5**, 449 (1979).

* METZNER, A.B., WHITE, J.L., and DENN, M.M., Chem. Eng. Prog., **62**, 81 (1966).

* MOONEY, M., *J. Rheol.*, **2**, 210 (1931).

* MUKHOPADHY, P. and SCHREIBER, H.P., *Macromolecules*, **26**, 6391 (1993).

* NIELSEN, L.E., Polymer Rheology, Chap. 6, Marcel Dekker, New York (1977).

* OSMONT, E. and SCHREIBER, in "*Inverse Gas Chromatography*", ed. by LLOYD,D.R., WARD,T.C., SCHREIBER, H.P., Chap. **17**. American Chemical Society. Washington,DC (1989).

* OTTINGER, H.C., *J. Chem. Phys.*, 87, 6185(1987).

* PAUL, D.R., "Polymer Blends", Chap. 6, Academic Press, New York, 1980.

* PANZER, U. and SCHREIBER, H.P., Macromolecules, **25**, 3633 (1992).

* PETRIE, C.J.S., and DENN, M.M., AIChE, **22**, 209 (1976).

* PIGGOT, M.R., Abstracts-Eighth Annual Meeting, The Adhesion Society, Savannah, USA (Dec., 1985).

* RAVI PRAKASH, J. and MASHELKAR, R.A., *J. Rheol.*, 36, 789 (1992).

* RIDDLE, J. F. L. and FOWKES, F. M., J. Am. Chem. Soc., **112**, 3259 (1990).

* RUDIN, A., WORM, A.T. and BLACKLOCK, J.E., SPE Antec **43** Conf. Proc., 987 (1985);

* RUDIN, A., WORM, A.T. and BLACKLOCK, J.E., Plast. Eng., **March**, 63 (1986).

* RUDIN, A., A.T. WORM and BLACKLOCK, J.E.,*J. Plast. Film Sheets*, (1), **52**, 1986.

* RUDIN, A., SCHREIBER, H.P. and DUCHESNE,D., *Polym. Plast. Technol. Eng.* 29,199 (1990).

* RUMAMURTHY, A.V., J. Rheol., **30**, 337 (1986a);

* RUMAMURTHY, A.V., Adv. in Polym. Tech., **6**, 489 (1986b);

* RUMAMURTHY, A.V., SPE Antec **47** Conf. Proc., 1197 (1989).

* SAINT-FLOUR, C. and PAPIREr, E. , Ind. Eng. Chem. Prod. Res. Dev., **21**, 666 (1982)

* SCHREIBER, H.P., STOREY, S.H., and BAGLEY, E.B., *Trans. Soc. Rheol.*, 10, 275

(1966).

- * SCHREIBER, H.P. and STOREY, S.H., *J. Polym. Sci.*, B3, 723 (1965).
- * SCHULTZ, J. and LAVIELLE, L., in *Inverse Gas Chromatography*, ACS Syposium Series 391, D.R. LLORD, T. C. WARD and H. P. SCHREIBER Eds ACS Washington D.C. 1989
- * SCHULTZ,J., LAVIELLE, L., and MARTIN, C., *J. Adhes.*, **23**, 45 (1987)
- * SHIH, C.K., Polym. Eng. & Sci., **16**, 742 (1976).
- * SILBERZAN P. and LEGER, L., Macromolecules, **25**, 1267 (1992).
- * SHIDARA, H. and DENN, M.M., *J. Non-Newt. Fluid Mech.*, **48**,101 (1993).
- * THEY, B.J., THAM, R.C., SOUFFIE, R.D. and CHAPMAN, G.R, *SPE. ANTEC-86*, 1149 (1986)
- * TORDELLA, J.P., Rheology, Chap. **2**, Vol. 5, Academic Press, New York (1969).
- * TOVAR, G. and SCHREIBER, H. P., work to be published.
- * UTRACKI, L.A., Polymer Alloys and Blends, Chap. **3**, Hanser Publishers, New York (1992).
- * VALENZA, A. and LA MANITA, F.P., *Intern. Polym. Proc.* **3**, 189 (1987).
- * VALENZA, A. and LA MANITA, F.P., Intern. Polym. Proc., **II**(3/4), 220 (1988).
- * VARENNES, S. and H.P. SCHREIBER, *J. Adhesion*, **46**, 3 (1994)
- * WU, S.H., in *Polymer Blends*, Vol. **1**, Ed.by Paul, D.R., Academic Press, New York (1979);
- * WU, S.H., *Polymer Interfaces and Adhesion*, Chap., **2**, Marcel Dekker, New York (1982).
- * XIA, Y. and CALLAGHAN, P.T., *Macromolecules*, 24, 4777(1994).
- * XING, K. and SCHREIBER, H.P., *Antec-95*, 167 (1995)

* XING, K. and SCHREIBER, H.P., *Polym. Eng. Sci.*, **32,** 367 (1996).

10. Appendix

This section is to demonstrate calculation of rheological data and generation of figures such as figure 7 in chapter 4

1. Rheological Data Processing

1) Extrusion Pressure(ΔP):

$$\Delta P = \frac{9.8F}{\pi R_b^{\,2}} \tag{1}$$

where ΔP is in Pa, F is extrusion force in kg, and R_b is the radius of the barrel of Instron Rheometer in m.

2) Flow Rate (Q)

$$Q = \pi R_b^{\,2} V \tag{2}$$

where Q is in m^3/s, and V is the speed (m/s) of the piston of the Rheometer.

3) Apparent Shear Stress (τ_a) at Die Surface

$$\tau_a = \frac{\Delta P R}{2L} \tag{3}$$

where τ_a is in Pa, and R and L are radius and length of the die in m.

4) Apparent Shear Rate ($\dot{\gamma}_a$) at the Die Surface:

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \tag{4}$$

where $\dot{\gamma}_a$ is in s^{-1}.

5) Shear Stress (τ) after Bagley Correction

$$\tau = \frac{(\Delta P - P_e)R}{2L} \tag{5}$$

where P_e is determined at L/2R=0 in a plot of ΔP vs. L/2R.

2. Generation of Rheological Figures from Experimental Data:

1) data from extrusion at 200°C

Table 1. Record of Type I Extrusion, L/D=5

Piston	Extrusion Force (kg)			
Rate (cm/m.)	Test-1	Test-2	Test-3	Average
0.05	3.4	2.9	3.3	3.2
0.125	5.5	5.9	5.8	5.7
0.25	8.9	8.5	8.8	8.7
0.5	14.1	13.7	14.0	13.9
1.25	24.0	23.5	23.7	23.7
2.5	32.4	32.8	32.1	32.4
5	42.6	42.9	43.2	42.9
10	52.9	54.6	53.7	53.7

Table 2. Apparent Shear Rate and Shear Stress of Type I Extrusion, L/D=5

Shear Rate (s^{-1})	Shear Stress (kPa)			
	Test-1	Test-2	Test-3	Average
2.856	23	20	23	22
7.141	38	41	40	39
14.28	61	58	61	60
28.56	97	94	96	96
71.41	165	162	163	163
142.8	223	226	221	223
285.6	293	295	297	295
571.3	364	375	369	370

Table 3. Record of Type II Extrusion. L/D=5

Piston Rate(cm/m)	Extrusion Force (kg)			
	Test-1	Test-2	Test-3	Average
0.05	3.2	3.4	3.1	3.2
0.125	4.9	5.2	5.1	5.1
0.25	6.5	7.0	7.0	6.8
0.5	8.4	8.6	8.0	8.3
1.25	11.6	12.0	11.7	11.8
2.5	19.0	18.4	18.6	18.7
5	27.8	28.4	28.1	28.1
10	39.1	40.1	38.8	39.3

Table 4. Apparent Shear Rate and Shear Stress of Type II Extrusion. L/D=5

Shear Rate (s^{-1})	Shear Stress (kPa)			
	Test-1	Test-2	Test-3	Average
2.856	22	23	21	22
7.141	34	36	35	35
14.28	45	48	48	47
28.56	58	59	55	57
71.41	80	83	80	81
142.8	131	127	128	128
285.6	191	195	193	193
571.3	269	276	267	270

Table 5. Record of Type I extrusion, L/D=20

Piston Rate (cm/m.)	Extrusion Force (kg)			
	Test-1	Test-2	Test-3	Average
0.05	11.5	12.2	12.0	11.9
0.125	21.8	20.8	21.1	21.2
0.25	31.4	33.0	33.0	32.5
0.5	52.0	50.9	50.5	51.1
1.25	86.0	85.3	87.1	86.1
2.5	118.0	116.5	116.0	116.8
5	154.0	156.9	159.0	156.6
10	197.4	200.3	195.8	197.8

Table 6. Apparent Shear Rate and Shear Stress of Type I extrusion. L/D=20

Shear Rate (s^{-1})	Shear Stress (kPa)			
	Test-1	Test-2	Test-3	Average
2.856	79	84	83	82
7.141	150	143	145	146
14.28	216	227	227	223
28.56	358	350	347	352
71.41	591	587	599	592
142.8	811	801	798	803
285.6	1059	1079	1093	1077
571.3	1357	1377	1346	1360

Table 7. Record of Type II Extrusion at 200°C and L/D=20

Piston Rate (cm/m.)	Extrusion Force (kg)			
	Test-1	Test-2	Test-3	Average
0.05	11.8	11.5	11.9	11.7
0.125	19.4	18.2	18.0	18.5
0.25	23.9	24.7	24.9	24.5
0.5	29.7	31.0	30.3	30.3
1.25	43.5	42.3	43.0	42.9
2.5	68.0	66.9	66.2	67.0
5	104.2	106.1	106.4	105.6
10	152.5	157.1	156.5	155.4

Table 8. Apparent Shear Rate and Shear Stress of Type II Extrusion, L/D=20

Shear Rate (s^{-1})	Shear Stress (kPa)			
	Test-1	Test-2	Test-3	Average
2.856	81	79	82	81
7.141	133	125	124	127
14.28	164	170	171	168
28.56	204	213	208	209
71.41	299	291	296	295
142.8	468	460	455	461
285.6	717	730	732	726
571.3	1049	1080	1076	1068

With data in table 2,4,6 and 8, figure A-1 is generated.

2) data from extrusion at 180°C

Table 9. Record of Type I Extrusion, L/D=5

Piston Rate (cm/m)	Extrusion Force (kg) Test-1	 Test-2	 Test-3	 Average
0.05	4.1	3.8	4.3	4.1
0.125	7.9	8.4	8.3	8.2
0.25	13.5	13.3	13.5	13.4
0.5	20.4	20.4	20.2	20.3
1.25	33.3	34.0	33.8	33.7
2.5	48.2	47.4	48.2	47.9
5	66.2	66.4	67.0	66.5
10	94.8	93.2	95.3	94.4

Table 10. Apparent Shear Rate and Shear Stress of Type I extrusion, L/D=5

Shear Rate (s^{-1})	Shear Stress (kPa) Test-1	 Test-2	 Test-3	 Average
2.856	28	26	30	28
7.141	54	58	57	56
14.28	93	91	93	92
28.56	140	140	139	140
71.41	229	234	232	232
142.8	331	326	331	330
285.6	455	457	461	458
571.3	652	641	655	649

Table 11. Record of Type II Extrusion at 180°C and L/D=5

Piston Rate(cm/m)	Extrusion Force (kg)			
	Test-1	Test-2	Test-3	Average
0.05	4.3	3.8	4.1	4.1
0.125	7.7	8.0	8.2	8.0
0.25	12.4	12.3	12.7	12.5
0.5	18.6	18.9	18.2	18.6
1.25	28.4	27.9	28.6	28.3
2.5	39.8	40.7	40.0	40.2
5	58.8	60.4	60.1	59.8
10	84.3	86.4	85.9	85.5

Table 12. Apparent Shear Rate and Shear Stress of Type II Extrusion, L/D=5

Shear Rate (s^{-1})	Shear Stress (kPa)			
	Test-1	Test-2	Test-3	Average
2.856	30	26	28	28
7.141	53	55	56	55
14.28	85	85	87	86
28.56	128	130	125	128
71.41	195	192	197	195
142.8	274	280	275	276
285.6	404	415	413	411
571.3	580	594	591	588

Table 13. Record of Type I extrusion, L/D=20

Piston	Extrusion Force (kg)			
Rate (cm/m)	Test-1	Test-2	Test-3	Average
0.05	13.6	13.8	12.9	13.4
0.125	26.0	26.6	26.1	26.2
0.25	41.2	42.1	41.9	41.7
0.5	67.0	66.9	67.5	67.1
1.25	111.9	112.7	112.4	112.3
2.5	155.0	153.9	155.7	154.9
5	207.0	208.0	206.0	207.0
10	252.0	261.0	262.3	258.4

Table 14. Apparent Shear Rate and Shear Stress of Type I extrusion, L/D=20

Shear Rate (s^{-1})	Shear Stress (kPa)			
	Test-1	Test-2	Test-3	Average
2.856	94	95	89	92
7.141	179	183	179	180
14.28	283	290	288	287
28.56	461	460	464	462
71.41	769	775	773	772
142.8	1066	1058	1071	1065
285.6	1423	1430	1417	1423
571.3	1733	1795	1804	1777

Table 15. Record of Type II Extrusion at 180°C and L/D=20

Piston Rate (cm/m.)	Extrusion Force (kg)			
	Test-1	Test-2	Test-3	Average
0.05	13.4	12.9	13.8	13.4
0.125	24.4	24.9	25.2	24.8
0.25	37.0	35.6	36.5	36.4
0.5	49.7	49.3	49.5	49.5
1.25	67.7	68.0	67.9	67.9
2.5	93.6	95.0	98.3	95.6
5	143.0	141.0	141.3	141.8
10	206.7	204.0	205.7	205.5

Table 16. Apparent Shear Rate and Shear Stress of Type II Extrusion, L/D=20

Shear Rate (s^{-1})	Shear Stress (kPa)			
	Test-1	Test-2	Test-3	Average
2.856	92	89	95	92
7.141	168	171	173	171
14.28	254	245	251	250
28.56	342	339	340	340
71.41	466	468	467	467
142.8	644	653	676	658
285.6	983	970	972	975
571.3	1421	1403	1415	1413

With data in tables 10, 12, 14 and 16, figure A-2 can be generated. Combination of these data with those in table I of chapter 4 presents details of generating figure 7 in that chapter.

Figure Captions

Figure A-1. Effect of FE on Apparent Flow Curves of LLDPE Extrusion at 200°C. ○ Type I, L/D=5; ● Type I, L/D=20; □ Type II, L/D=5; ■ Type II, L/D=20

Figure A-2. Effect of FE on Apparent Flow Curves of LLDPE Extrusion at 200°C. ○ Type I, L/D=5; ● Type I, L/D=20; □ Type II, L/D=5; ■ Type II, L/D=20

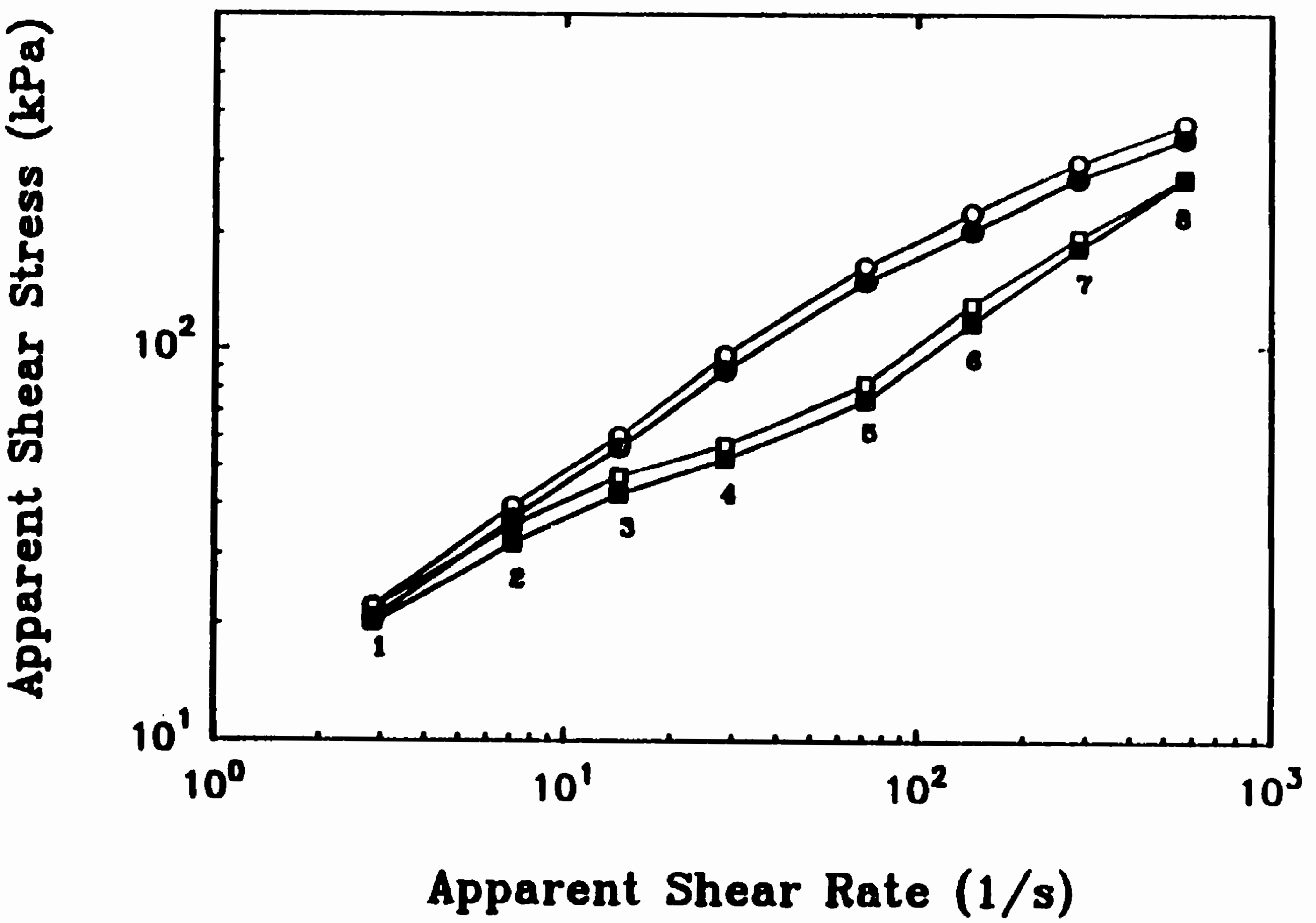


Figure A-2. Effect of FE on Apparent Flow Curves of LLDPE Extrusion at 200°C. ○ Type I, L/D=5; ● Type I, L/D=20, □ Type II, L/D=5; ■ Type II, L/D=20.

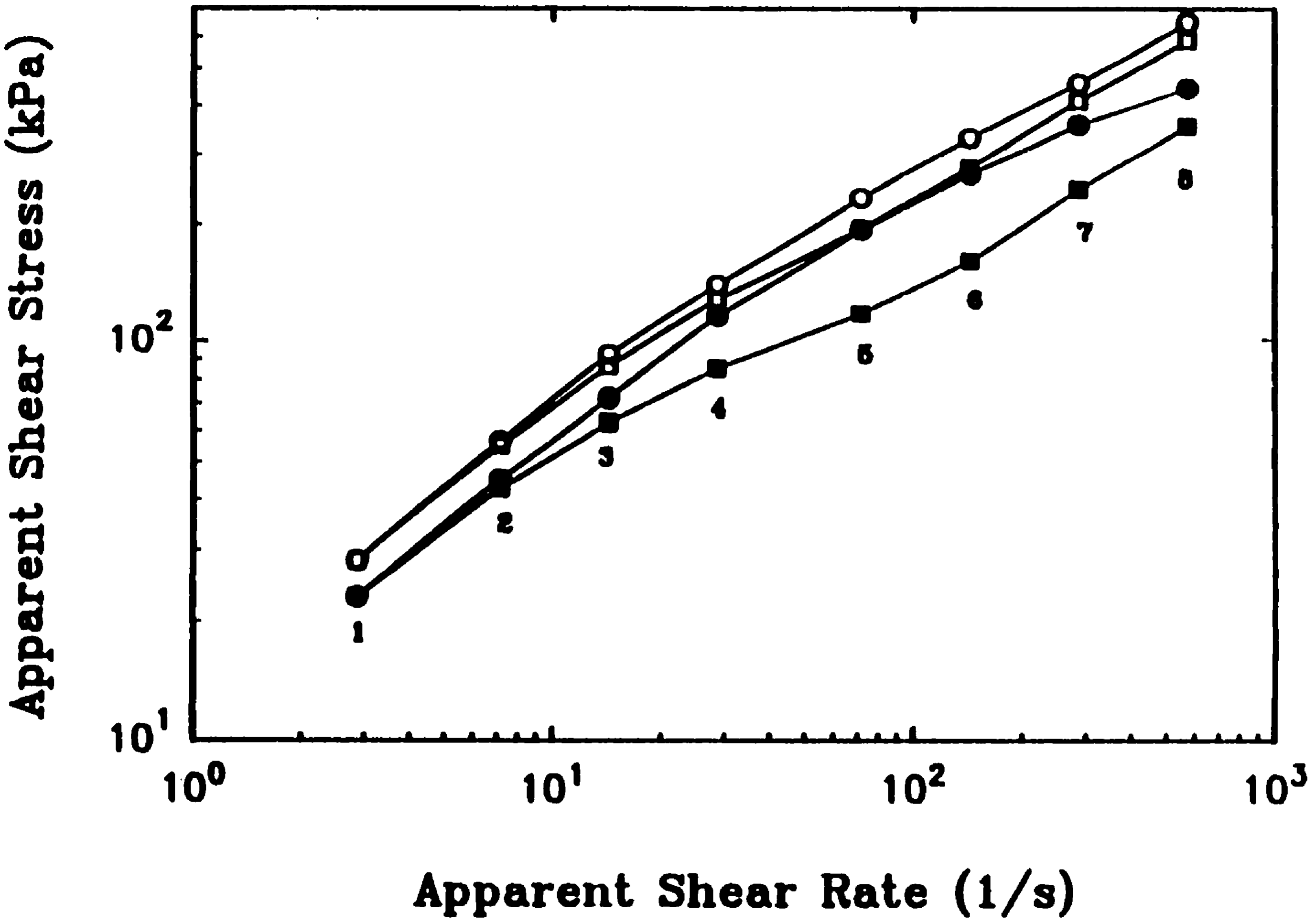
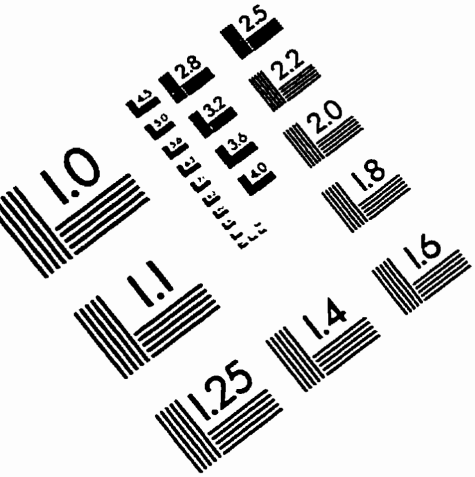
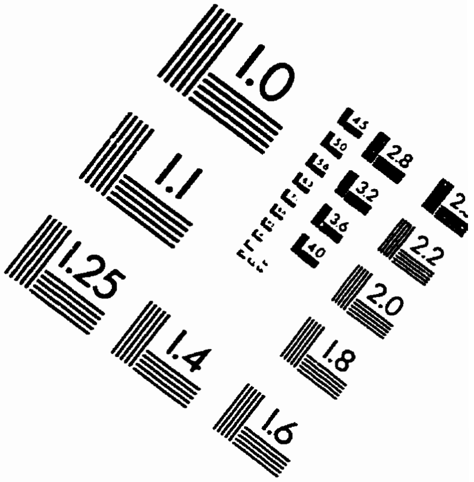
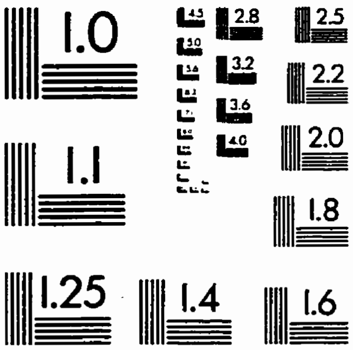


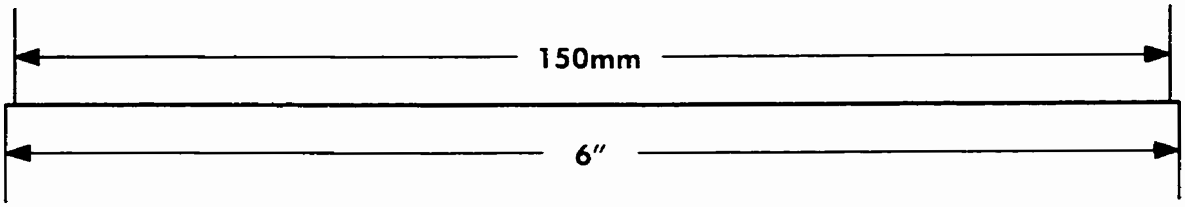
Figure A-1 Effect of FE on Apparent Flow Curves of LLDPE Extrusion at 200°C, ○ Type I, L/D=5, ● Type I, L/D=20, □ Type II, L/D=5, ■ Type II, L/D=20

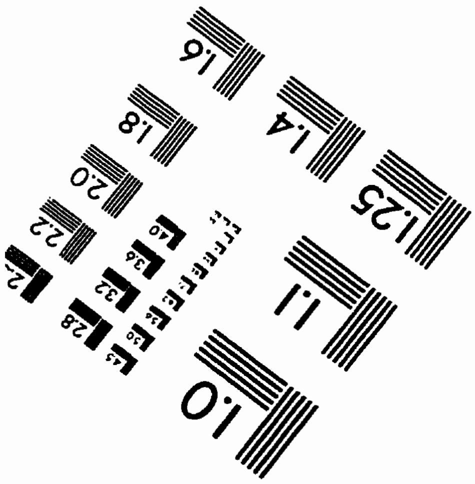
IMAGE EVALUATION
TEST TARGET (QA-3)

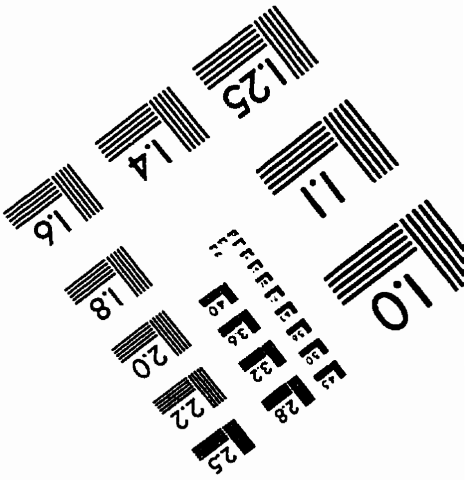












APPLIED IMAGE . Inc
1653 East Main Street
Rochester, NY 14609 USA
Phone: 716/482-0300
Fax: 716/288-5989