POLYMER FOAMS AND COMPOSITES RECYCLING: Rheological and Macromolecular Investigations
Résumé

Cette thèse présente une étude de deux matériaux qui ont connu au cours des dernières décennies une importance croissante dans l'industrie: les polymères moussés et les composites à base de fibres naturelles. L'accent a été mis sur les propriétés rhéologiques et macromoléculaires de ces matériaux lorsque soumis à un procédé de recyclage ou de dégradation. Des tests rhéologiques en cisaillement et en élongation ont révélé l'importance de la rhéologie élongationnelle pour les polymères et les composites. Ces propriétés ont grandement affectées la capacité à mousser du polymère et l'élasticité des composites. Aussi, des tests macromoléculaires ont conduits à la compréhension des processus de dégradation par une compétition entre la rupture et le branchement des chaînes macromoléculaires due à la présence des macro-radicaux. Il a été montré que le processus de recyclage a un effet plus significatif sur le poids moléculaire moyen en nombre que sur le poids moléculaire moyen en masse. Les fibres, ainsi que la présence de bulles dans la matrice polymère ont révélé un effet accru sur les propriétés des matériaux au cours du processus de recyclage par rapport à celles de la matrice polymère soumise aux mêmes conditions.
Abstract

This thesis presents an investigation on materials that displayed a growing industrial importance in the last decades: polymer foams and composites based on natural fibres. A focus was made on rheological and macromolecular properties of both materials under recycling or degradation processes. Shear and elongational rheology tests were performed and revealed the importance of elongational rheology. These properties greatly affected the foamability of the polymer and the elasticity of the composite. Macromolecular tests were also carried out and led to the understanding of the degradation process which is governed by a competition between chain scission and chain branching with the presence of macro-radicals. It was shown that recycling has a more significant effect on the number average molecular mass than on the weight average molecular mass of the polymer. Both fibre and cell presence in the polymeric matrix revealed an increased effect on materials properties during the recycling process in comparison with those of the polymeric matrix processed alone under similar conditions.
Foreword

This Ph.D. thesis consists of four articles, published or submitted which represent each a chapter. To start, a general introduction is also provided. In order to have a better overview, the first two articles are focusing on polymers and foams, while the last ones are mainly on polymer composites based on natural fibres.

The first article investigated the rheological properties, especially in elongation, of polymer foams in the recycling process. A comparison was made between the foam and the polymer matrix alone when subjected to the same conditions. This article was the next step from the Master thesis (Twite-Kabamba E., 2006) where we investigated the mechanical, shear rheological and morphological properties of recycled polymer foams in the extrusion process. This article reveals the importance of elongational rheology, especially in terms of strain hardening which is directly related to the polymer ability to foam. As a major contributor to this article, my role was to prepare samples, to perform the tests, to interpret all the results obtained, as well as to write the first draft of the article. Denis Rodrigue, as the thesis director, contributed to the discussion of the results, to improve the written quality of the article and to supervise the submission with the Journal. The reference is:

In the second article, a comprehensive macromolecular study was performed in order to better understand the thermo-mechanical degradation occurring in an internal batch mixer. Molecular mass distribution, obtained by high-temperature gel permeation chromatography (HT-GPC), revealed a competition between chain scission and chain branching due to the presence of macro-radicals. This phenomenon explained why it is so complex to model the degradation of a polymer. Shear and elongational rheology were also performed and the results indicated the effect of parameters such as input energy and input power on polymer degradation. As a major contributor to this article, my role was to prepare samples, to perform tests, to interpret all the results obtained, as well as to write the first draft of the article. Denis Rodrigue, as the thesis director, contributed to the discussion of the results obtained, improved the written quality of the article and supervised the submission to the Journal. The reference is:


The third article report a complete study of the rheological properties (shear and elongation) of polymer composites based on hemp fibres. The work was a continuation of the Ph.D. thesis of Ahmed Mechraoui (2009) who investigated the properties in the solid state such as morphology and mechanical properties. Since the properties in the melt state have a great influence on the solid properties, this investigation revealed effects of coupling
agent and fibre concentrations, on the loss of elasticity in the composite due to the presence of the fibres. As a major contributor to this article, my role was to perform the rheological tests, to interpret all the results obtained, as well as to write the first draft of the article. Ahmed Mechraoui prepared the compounds (composites). Denis Rodrigue, as the thesis director, contributed to the discussion of the results, improved the written article and supervised the submission to the Journal. The reference is:

Twite-Kabamba E., Mechraoui A. and Rodrigue D., Rheological Properties of Polypropylene/Hemp Fibre Composites, Polymer Composites, 30(10), 1401–1407 (2009).

The last chapter, which is the fourth article, focuses on recycling polymer composites based of wood (birch) fibres. This work was done in collaboration with Zineb Fassi Fehri who was a summer undergraduate student (internship). Previously, mechanical and morphological properties of composites based on birch fibres were studied by Ryan Gosselin in his Master Thesis (Gosselin, 2005). In our work, we investigated the rheological (shear and elongation), morphological and macromolecular properties of the composite submitted to recycling (up to ten regenerations) in the extrusion process. The results led to the following main conclusions: fibre length decreases as a negative exponential law with the number of regeneration and the presence of fibres increases the degradation of the composite in terms of rheological and macromolecular properties when compared with the polymer matrix alone submitted to the same conditions. As a major contributor to this article, my role was to perform the tests, to interpret all the results
obtained, as well as to write the first draft of the article. Zineb Fassi Fehri prepared the samples (extrusion) and measured fibre dimensions by optical microscopy. Denis Rodrigue, as the thesis director, contributed to the discussion of the results obtained, improved the written article and supervised the submission to the Journal. The reference for this work is:

Acknowledgements

Only the Viscotek GPC equipment can explain how tremendous the challenges I had to face were in the last 5 years. In the course of this thesis, I learnt a great deal: to expand my horizons, to be critical and objective, to teach and be taught, to be confident and mostly to be realistic. The assistance of many persons who played a specific and important role in my studies must be mentioned here.

First of all, my director Denis Rodrigue, who had the courage and the patience to supervise my work with great availability. I would like to express my gratitude for his support and all the fruitful discussions we had.

I also would like to express my appreciation to my dissertation committee members for their comments and advices, as well as to all the members of CERMA (previously CERSIM) for their technical support and help in the different phases of this work.

To the members of the chemical engineering Department at Laval University and to my fellow colleague students, I would sincerely like to express my gratitude for their kind cooperation, academic support and friendship over the years.

And last, but certainly not least, to my family. To my mother and my father, I could not have achieved it without your unconditional love and support. I am truly the luckiest child in the world to have parents like you.
« La seule vraie science est la connaissance des faits » Comte Georges-Louis Leclerc de Buffon
# Table of Content

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Résumé</td>
<td>i</td>
</tr>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Foreword</td>
<td>iii</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>vii</td>
</tr>
<tr>
<td>Table of Content</td>
<td>ix</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xiii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xv</td>
</tr>
<tr>
<td>Chapter I. General Introduction</td>
<td>1</td>
</tr>
<tr>
<td>I.1 Recycling Challenges</td>
<td>3</td>
</tr>
<tr>
<td>I.1.1 Polymer foams</td>
<td>3</td>
</tr>
<tr>
<td>I.1.2 Composites based on natural fibres</td>
<td>5</td>
</tr>
<tr>
<td>I.2 Importance of Rheological and Macromolecular Properties</td>
<td>9</td>
</tr>
<tr>
<td>I.2.1 Melt Rheological Properties</td>
<td>9</td>
</tr>
<tr>
<td>I.2.2 Macromolecular Investigations</td>
<td>10</td>
</tr>
<tr>
<td>I.3 Thesis Objectives and Organization</td>
<td>12</td>
</tr>
<tr>
<td>I.4 Thesis Contribution</td>
<td>14</td>
</tr>
<tr>
<td>Chapter II. The Effect of Recycling on LDPE Foamability: Elongational</td>
<td>16</td>
</tr>
<tr>
<td>Rheology</td>
<td></td>
</tr>
<tr>
<td>Résumé</td>
<td>16</td>
</tr>
<tr>
<td>Abstract</td>
<td>17</td>
</tr>
<tr>
<td>II.1 Introduction</td>
<td>18</td>
</tr>
<tr>
<td>II.2 Experimental</td>
<td>22</td>
</tr>
</tbody>
</table>
II.2.1 Material................................................................. 22
II.2.2 Elongational Rheology........................................... 23
II.2.3 Morphology......................................................... 26
II.3 Results and Discussion............................................ 27
   II.3.1 Elongational Results........................................ 27
   II.3.2 Morphology..................................................... 36
II.4 Conclusion........................................................... 42
II.5 Acknowledgements............................................... 43

Chapter III. Rheological and Molecular Investigations of Polyethylene Degradation in a Batch Mixer........................................... 44

Résumé........................................................................... 44

Abstract.......................................................................... 45

III.1 Introduction............................................................ 46

III.2 Material.................................................................... 50

III.3 Methods.................................................................. 50
   III.3.1 Sample Preparation............................................. 50
   III.3.2 Rheological Investigations.................................... 54
      III.3.2.1 Shear Rheology.......................................... 54
      III.3.2.2 Elongational Rheology................................. 54
   III.3.3 Macromolecular Characterizations....................... 55

III.4 Results & Discussion.............................................. 58
   III.4.1 Shear Rheology Results...................................... 58
   III.4.2 Elongational Rheology Results......................... 60
   III.4.3 High Temperature Gel Permeation Chromatography data........................................ 62

III.5 Conclusions............................................................ 69
### Chapter IV. Rheological Properties of Polypropylene/Hemp Fibre Composite

<table>
<thead>
<tr>
<th>Résumé</th>
<th>71</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>72</td>
</tr>
<tr>
<td>IV.1 Introduction</td>
<td>73</td>
</tr>
<tr>
<td>IV.2 Experimental</td>
<td>77</td>
</tr>
<tr>
<td>IV.2.1 Materials</td>
<td>77</td>
</tr>
<tr>
<td>IV.2.2 Shear Tests</td>
<td>79</td>
</tr>
<tr>
<td>IV.2.3 Elongational Tests</td>
<td>79</td>
</tr>
<tr>
<td>IV.3 Results and Discussion</td>
<td>81</td>
</tr>
<tr>
<td>IV.3.1 Dynamic Shear Results</td>
<td>81</td>
</tr>
<tr>
<td>IV.3.2 Transient Shear Results</td>
<td>87</td>
</tr>
<tr>
<td>IV.3.3 Elongational Results</td>
<td>90</td>
</tr>
<tr>
<td>IV.4 Conclusion</td>
<td>97</td>
</tr>
</tbody>
</table>

### Chapter V. Properties of Recycled LDPE/Birch Fibre Composites

<table>
<thead>
<tr>
<th>Résumé</th>
<th>98</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>99</td>
</tr>
<tr>
<td>V.1 Introduction</td>
<td>100</td>
</tr>
<tr>
<td>V.2 Materials and Experimental</td>
<td>102</td>
</tr>
<tr>
<td>V.2.1 Materials</td>
<td>102</td>
</tr>
<tr>
<td>V.2.2 Composite processing</td>
<td>103</td>
</tr>
<tr>
<td>V.2.3 Thermal analysis</td>
<td>103</td>
</tr>
<tr>
<td>V.3 Rheology</td>
<td>104</td>
</tr>
<tr>
<td>V.3.1 Shear Rheology</td>
<td>104</td>
</tr>
</tbody>
</table>
V.3.2 Elongational Rheology ................................................................. 105
V.3.3 Morphological Investigations ..................................................... 105
V.3.4 Macromolecular Investigations .................................................. 106
V.4 Results and Discussion ............................................................... 107
V.4.1 Thermal Analysis Results ......................................................... 107
V.4.2 Rheological Results ................................................................. 109
  V.4.2.1 Shear Rheology ............................................................... 109
  V.4.2.2 Elongational Rheology ....................................................... 114
V.4.3 Morphological Results ............................................................ 117
V.4.4 Macromolecular Investigations ............................................... 121
V.5 Conclusion ................................................................................. 127

Chapter VI. General Conclusions and Recommendations .................. 130

References ....................................................................................... 134
# List of Tables

Table I.1 Properties of glass and some natural fibres (Brouwer, 2000)............................... 7

Table I.2 Use of natural fibres for automotive composites in Germany (www.nova-institut.de).................................................................................................................. 8

Table II.1 Properties of the LDPE and the chemical blowing agent used........................................... 23

Table II.2 Strain at break ($\varepsilon_{\text{break}}$) as a function of strain rate for foamed (F) and unfoamed (U) LDPE........................................................................................................ 31

Table II.3 Strain at maximum stress ($\varepsilon_{\text{max}}$) as a function of strain rate for foamed (F) and unfoamed (U) LDPE........................................................................................................ 32

Table II.4 Parameters of the power-law model (Equ.8) for foamed (F) and unfoamed (U) LDPE................................................................................................................................. 34

Table II.5 Strain onset ($\varepsilon_{\text{onset}}$), stress onset ($\sigma_{\text{onset}}$), maximum stress ($\sigma_{\text{max}}$), and Strain Hardening Factor (SHF) for foamed (F) and unfoamed (U) LDPE. The data were obtained at a strain rate of 3 s$^{-1}$........................................................................................................... 36

Table III.1 Controlled parameters with their values.............................................................................. 50

Table III.2 Sample identification and input parameters.......................................................................... 53

Table III.3 Crossover frequency ($\omega_c$) and modulus ($G_c$) at 160°C................................................. 60

Table III.4 Elongational rheology data for different samples................................................................... 62

Table III.5 Molecular characteristics of the virgin LDPE (NovaPol LA-0219-A)............................. 63

Table III.6 Molecular characteristic of the samples............................................................................. 66

Table IV.1 Compositions of PP/Hemp/MAPP used with codification.................................................. 78

Table IV.2 PP/Hemp density (kg/m$^3$) at 25 and 180°C........................................................................... 81

Table IV.3 Modified Carreau-Yasuda model parameters for PP/Hemp/MAPP composites (180°C)................................................................................................................................. 84
Table IV.4 Crossover frequency $\omega_c$ (rad/s) and crossover modulus $G_c$ (kPa) for different compositions of PP/Hemp/MAPP composites

Table IV.5 Strain (%) at which the kink occurs for different compositions of PP/Hemp/MAPP composites

Table IV.6 Maximum stress and strain at break for PP/Hemp/MAPP composites at $10 \text{s}^{-1}$

Table IV.7 Elongational power-law parameters ($M$, $N$) for PP/Hemp/MAPP composites ($180^\circ \text{C}$)

Table V.1 Thermal properties of the recycled polymer matrix / recycled composites

Table V.2 Flow activation energy ($E_a$) of selected generations of polymer/composite

Table V.3 Carreau-Yasuda parameters for the polymer matrix / the composites

Table V.4 Maximum stress (MPa) and Strain at break (-) of selected polymer generations under elongational rheology tests

Table V.5 Maximum stress (kPa) and Strain at break of selected composite generations under elongational rheology tests

Table V.6 Fitting parameters for Equ.(V.5) based on the data of Figure IV.5

Table V.7 GPC results of the virgin LDPE (Novapol-LA-0224-A)
# List of Figures

**Figure I.1** End-Use Markets in 2008 for plastic foams (from Industry Canada)............. 2

**Figure I.2** Schematic representation of polyurethane foam applications.......................... 4

**Figure I.3** Natural fibre composite components (more than 30) of Mercedes-Benz E Class from Daimler Chrysler) ................................................................. 6

**Figure I.4** A typical distribution of molecular mass of a random polymer......................... 11

**Figure I.5** Schematic representation of the thesis.......................................................... 14

**Figure II.1** Representation of the Strain Hardening Factor (SHF) for virgin LDPE at 0.1 s\(^{-1}\) and 150\(^{\circ}\)C.................................................................................................................. 25

**Figure II.2** Elongational viscosity as a function of time at 150\(^{\circ}\)C for virgin (□), 5\(^{th}\) (o), and 10\(^{th}\) (△) generation of unfoamed LDPE. The line represents Equ.(6) for the shear viscosity at a rate of 0.003 s\(^{-1}\) for virgin LDPE.................................................................................................................. 28

**Figure II.3** Elongational viscosity as a function of time at 150\(^{\circ}\)C for virgin (□), 5\(^{th}\) (o), and 10\(^{th}\) (△) generation of foamed LDPE. The line represents Equ.(II.6) for the shear viscosity at a rate of 0.003 s\(^{-1}\) for virgin LDPE.................................................................................................................. 29

**Figure II.4** Maximum stress as a function of strain rate for foamed (F) and unfoamed (U) LDPE.................................................................................................................. 33

**Figure II.5** Stress as a function of strain for the virgin, fifth, and tenth generation of foamed (F) and unfoamed (U) LDPE. Data obtained at a strain rate of 3 s\(^{-1}\) .................................................................................................................. 35

**Figure II.6** Cell sizes as a function of the number of time the polymer was recycled.................................................................................................................. 37

**Figure II.7** Cell density (N\(_F\)) as a function of recycling. The line represents Equ.(9).................................................................................................................. 39

**Figure II.8** Transversal micrographs for the 1\(^{st}\) (a) and 10\(^{th}\) (b) generation of foamed LDPE.................................................................................................................. 41
Figure II.9 Longitudinal micrographs for the 1st (a) and 10th (b) generation of foamed LDPE ........................................... 41

Figure III.1 Complex shear viscosity as a function of frequency and temperature for NovaPol LA-0219-A, a low density polyethylene used as the virgin material .................................................................. 52

Figure III.2 Complex viscosity as a function of frequency for different samples at 160°C .................................................................................................................. 59

Figure III.3 Elongational viscosity as a function of time at a strain rate of 10 s⁻¹ for different samples ........................................................................................................ 61

Figure III.4 Chain scission rate as a function of input power (J) and time ................................................................................................................................. 67

Figure III.5 Relative branching factor as a function of specific power (J) and time ............................................................................................................ 68

Figure IV.1 Complex shear viscosity (η*) as a function of frequency at 180°C and 5% strain for different compositions of PP/Hemp/MAPP .................................................................. 82

Figure IV.2 Storage (closed symbols) and loss (open symbols) moduli as a function of frequency at 180°C and 5% strain for different compositions of PP/Hemp/MAPP .................................................................. 86

Figure IV.3A Transient shear viscosity (ηₛ⁺) as a function of frequency at 180°C and 0.03 s⁻¹ for different compositions of PP/Hemp/MAPP .......... 88

Figure IV.3B Illustration of the kink in the transient shear viscosity (ηₛ⁺) vs. frequency curves at 180°C and 0.03 s⁻¹ ................................................................................................................ 89

Figure IV.4 Transient viscosity (ηₜ⁺) as a function of time for neat PP at 180°C and different strain rates. The line represents Trouton’s law obtained from shear transient data .................................................................................................................. 91

Figure IV.5 Elongational viscosity (ηₑ⁺) as a function of time for PP-H30-MAPP at 180°C and different strain rates .................................................................................................................. 92

Figure IV.6 Elongational viscosity (ηₑ⁺) as a function of time at 10 s⁻¹ for different compositions of PP/Hemp/MAPP at 180°C .................................................................................................................. 93

Figure IV.7 Elongational viscosity (ηₑ⁺) as a function of strain rate for different compositions of PP/Hemp/MAPP at 180°C and ε = 0.5 .................................................................................................................. 95
Figure V.1 Complex viscosity of selected polymer generations as a function of frequency at 160°C.......................................................... 110

Figure V.2 Complex viscosity of selected composite generations as a function of frequency at 160°C.......................................................... 111

Figure V.3 Elongational viscosity of selected polymer generations as a function of time for a strain rate of 10 s⁻¹ and a temperature of 150°C............... 115

Figure V.4 Elongational viscosity of selected composite generations as a function of time at a strain rate of 10 s⁻¹ and a temperature of 150°C............... 116

Figure V.5 Fibre length as a function of regeneration. The line represents the fit to Eq.(IV.6) with the parameters of Table IV.6............................... 118

Figure V.6 Fibre diameter as a function of regeneration........................................ 119

Figure V.7 Weight-average molecular mass (Mₗ) as a function of generation number for the polymer and composites............................... 123

Figure V.8 Number-average molecular mass (Mₙ) as a function of generation number for the polymer and composite............................... 124

Figure V.9 Relative branching factor as a function of generation number for the polymer and composite.................................................. 125

Figure V.10 Branching frequency as a function of generation number for the polymer and composite.................................................. 126
Chapter I

General Introduction

For a few decades now, the recycling of plastics has become a major concern in our society who has seen elsewhere, the concept of sustainable development and natural resource management issues become politically and economically sensitive. The plastics industry could not sit idly especially when production capacity, both globally and locally, is staggering to the point where the plastics are pervasive in business sectors ranging from packaging to the automotive industry through (naval and aeronautical), real estate and home appliances (Lokensgard, 2004; Harper and Pétrie, 2003; Chanda and Roy, 2003). In Canada, plastic industries represent a major economic sector as reported by Industry Canada, a government department (www.ic.gc.ca). Canadian export of plastic products has grown spectacularly from 18% of total shipments in 1990 to 44% in 2008, when exports totalled $7.8 billion. Canada’s plastics processing industry represents 4.2% of the manufacturing GDP and 5.3% of total manufacturing employment. Growth in the Canadian plastics industry has been fuelled by a dramatic increase in domestic capacity to produce synthetic resins. Over 2,600 firms process synthetic resins into plastic products generating shipments worth $17.9 billion and employing more than 86,000 people.

More than ever, all these numbers explain why recycling has to be an important issue for next years, especially for foamed products due to their low density. Figure I.1 presents the main application sectors for foamed plastic products in Canada. It is clear that packaging, construction and automotive are the most important sectors.
Figure I.1 End-Use Markets in 2008 for plastic foams (from Industry Canada).

Two kinds of polymeric materials have also shown tremendous growing demand: plastic foams and composites based on natural fibres. The most important materials used are polyurethane and polystyrene for plastic foams, while composites based on sisal, flax and hemp fibres are increasing (Mills, 2007; Müssig, 2010, Baillie, 2005).

Nevertheless, while the development of these new materials is growing, efforts made at industrial levels are not yet enough, especially on their abilities to recycle via different ways the huge amounts of material produced, besides thermal recycling (energy recovery) or simply land filling (discarding) (Goodship, 2007). These issues and challenges are discussed next.
I.1 Recycling Challenges

I.1.1 Polymer foams

Polymer foams are made up of a solid and gas phases mixed together to form a foam. The resulting foam is a polymer matrix with gas bubbles incorporated in it, which has either a closed-cell or open-cell structure. Closed-cell foams are generally more rigid, while open-cell foams are usually more flexible (Eaves, 2004). Polymer foams are extensively used in different applications because of their properties extending beyond the limits of all other classes of engineering materials. A great challenge in engineering foams is to address a wide variety of properties such as light weight, thermal and acoustic insulations, softness, excellent strength/weight ratio, material costs and energy absorption. The main applications for foamed products can be found in thermal insulation, construction, automobile, packaging, sport industries and one of their earliest markets in marine buoyancy (Throne, 1996). It is reported that 23 billion pounds of foamed products were consumed each year around the world in the early 2000’s, and this number is expected to increase considerably in the future as more applications are discovered (Lee et al., 2007). These new applications include today a wide variety of applications like cushioning, carpet underlay, bedding, home furniture, packaging for food containers, disposable dishes, egg cartons and also products for transportation like seat cushions for the airlines, trains, bicycles and cars (Klempner and Sendijarevic, 2004). Foams are also used in a wide range of other car applications such as sound and thermal insulations and vibration dampening. Other applications include clothing, toys and electronics. Polymer foams are widely used in all kinds of different applications because they can be manufactured from many different types of polymers and there are plenty of different blowing agents available to customize the
foam to specific requirements (Lee et al., 2007). Figure 1.2 presents some applications of polyurethane and related foams (Herrington and Hock, 1998).

![Figure 1.2 Schematic representation of polyurethane foam applications.](image)

With respect to the polymer foams importance, the problem of recycling is clearly an emergency, especially when it is still difficult to know the matrix used for each molded part. This thesis modestly aims to contribute to the solution which elsewhere must be global and concerned all kinds of polymeric foams. The thesis focused on polyethylene foams which represents an important market of plastic foams, especially packaging and shipping applications as shock absorbing and cushioning (www.americanfoamgroup.com).
I.1.2 Composites based on natural fibres.

Despite some shortcomings of natural fibres (Müssig, 2010) like their low impact strength, variable quality, moisture absorption, restricted maximum processing temperature, low durability, and poor fire resistance, natural fibres are now emerging as viable alternatives to glass fibres either alone or combined in composite materials for various applications in automotive parts, construction, aerospace, building structures, boat building and rigid packaging materials (Mohanty et al., 2005).

The interest of using natural fibres in composite materials has rapidly grown and encountered a great success especially in automotive industry which is a major leader in research and development of new composites based on natural fibres (Karus and Kaup, 2002; Puglia et al., 2005). The use of natural-fibre composites in automotive industry was motivated by cost and weight reduction. The range of products, as presented in Figure I.3, includes a great deal of interior and non-structural components like door upholstery and panels, seat backs, headliners, package trays, dashboards, trunk/boot liners and rear shelves (Pickering and Pickering, 2008; www.nachwachsende-rohstoffe.info of Nova Institute).
The main advantages of natural fibres are their low cost, low specific weight, renewability resource, friendly processability, good thermal and acoustic insulating properties, competitive specific mechanical properties, sustainability, recyclability and biodegradability. Different types of natural fibres can be found depending on their sources. Three general categories are used: bast fibres like flax, hemp, jute, kenaf and ramie (china grass), leaf fibres like sisal, abaca (banana), pineapple, fique, henequen and palm, and finally seed fibres like cotton, coir and kapok (Müssig, 2010; Mohanty et al., 2005). All of them can be used as reinforcements in polymeric matrices including thermoplastics,
thermosets, elastomers or biopolymers. Table I.1 presents some typical mechanical properties of natural fibres in comparison with those of glass fibres.

**Table I.1: Properties of glass and some natural fibres (Brouwer, 2000).**

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<thead>
<tr>
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<th>Fibres</th>
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<td></td>
<td>E-glass</td>
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<tr>
<td>Density (g/cm³)</td>
<td>2.55</td>
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<tr>
<td>Tensile strength* (N/mm²)</td>
<td>2400</td>
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<tr>
<td>E-modulus (GPa)</td>
<td>73</td>
</tr>
<tr>
<td>Elongation at failure (%)</td>
<td>3</td>
</tr>
<tr>
<td>Moisture absorption (%)</td>
<td>-</td>
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<tr>
<td>Price/kg ($), raw</td>
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*Tensile strength strongly depends on fibre type, being a bundle or a single filament.

New patents are still developed in different countries like India and China, where they are always looking for the new applications for natural fibres from specific regions (Samanta et al., 2007; Peroni, 2009). This state of growing development of new materials constitutes the next generation of materials, products and processes integrating the principles of
sustainability, industrial ecology, eco-efficiency, as well as green chemistry and engineering (Baillie, 2005). Table I.2 presents the use of some natural fibres in the German automotive industry. This shows the importance that composites based on natural fibres will have in the next years, not only in Germany but in Europe and other industrial countries around the world.

Table I.2 Use of natural fibres for automotive composites in Germany (www.nova-institut.de).

<table>
<thead>
<tr>
<th>Fibre type</th>
<th>Year Production (metric ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1996</td>
</tr>
<tr>
<td>Flax</td>
<td>2000</td>
</tr>
<tr>
<td>Exotic (Jute, Kenaf, etc.)</td>
<td>2000</td>
</tr>
<tr>
<td>Hemp</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>4000</td>
</tr>
</tbody>
</table>

*predicted data

The problem of recycling hardly begins to be investigated (Moran et al., 2007). Even though the use of natural fibres in manufacturing composites is considered to be an efficient way to extend their lifetime, the recycling of these new materials was not really investigated yet. Regarding how fast their production increases around the world, there will be big challenges to recycle all this material in sustainable ways.
This thesis offers an overlook on these challenges by providing a first step toward an efficient recycling of natural fibre composites and foams by paying attention to their rheological and macromolecular properties, both being important aspects of their reprocessing.

1.2 Importance of Rheological and Macromolecular Properties

1.2.1 Melt Rheological Properties

In all plastic processing, rheological investigations have a critical importance because they describe how the material will behave in its melt state during the process (Agassant et al., 1991). Knowledge of the rheological behaviour of a material is essential to optimize, control and process in ways that allow reaching the required performance of a material. Melt rheological behaviour has a strong effect on solid state properties of plastic products (Dealy and Wissbrun, 1999). In the last years, more studies were devoted to the rheological behaviour of foams, but they were limited to shear rheology and somewhat to transient properties (Chen et al., 2004; Qin et al., 2007). Elongational properties were more difficult to get due to equipment limitations (Stange and Münstedt, 2006). But in the last decade, the Sentmanat device (Sentmanat, 2003) allowed to investigate more easily the elongational rheology of materials in the melt state. It provided more sensitive information and allowed the validation of some assumptions. On the other hand, the rheological behaviour of natural fibre composites is hardly investigated and even less in elongational rheology because the focus was mainly on solid state properties; i.e. mechanical properties (Oksman et al., 2003;
Singleton et al., 2003; Wollerforder and Bader, 1998). For this reason and in view of the huge number of natural fibres available with additives related to the composite formulation like coupling agents, there is still a big challenge to face before reaching a comprehensive rheological behaviour of natural fibre composites. This thesis tries to contribute to better understand the rheological behaviour of foams and natural fibre composites subjected to the recycling processing.

1.2.2 Macromolecular Investigations

Polymers are large molecules made up of smaller molecules called monomers that are joined together by chemical bonding. Polymers can be divided into natural polymers and synthetic polymers. In natural polymer, the selection of molecules and the process of chemical bonding occur naturally. This is the case for materials like wood, leather, cotton, rubber, hair and even finger nails. In synthetic polymers, the selection of molecules and the chemical bonding process is man-made and this gives materials like nylon, polyester and polyethylene commonly named plastics (Painter and Coleman, 1997).

Due to the statistical nature of polymerization, synthetic polymers possess a combination of molecules having a range of different molecular masses creating a wide distribution of molecular chain lengths. The complete extent of the molecular mass distribution mainly depends on the polymerization process which determines the physical characteristics of the polymer (Snyder and Kirkland, 1979). Figure I.4 illustrates a typical distribution of molecular mass, where $M_i$ is the molecular mass of a single chain and $N_i$ is the number of chains with molecular mass of $M_i$.
It is then important to derive an average molecular mass which can be used to characterize each individual polymer. There are two main different averages that are widely used: the number-average molecular mass:

\[ \bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \]  \hspace{1cm} (I.1)

and the weight-average molecular mass:

\[ \bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \]  \hspace{1cm} (I.2)

Both equations are used to define a Polydispersity Index (PDI) as the ratio of the weight-average molecular mass and number-average molecular mass.

**Figure I.4** A typical distribution of molecular mass of a random polymer.
The simplest polymer architecture is a linear chain: a single backbone with no branches. A branched polymer molecule is composed of a main chain with one or more substituent side chains or branches. Branching of polymer affects the ability of the chains to slide past one another by altering intermolecular forces, in turn affecting bulk physical polymer properties. Long chain branches may increase polymer strength, toughness and the glass transition temperature due to an increase in the number of entanglements per chain (Rubinstein and Colby, 2006). From this fact, the structure of a polymer has a strong influence on other properties and justifies the importance of macromolecular investigations to completely understand its behavior.

Because of the recycling process and/or the addition of natural fibres, the polymer structure will change and modify the final properties of the material. Changes in molecular mass distribution points out the importance of macromolecular investigations which can be elsewhere related to the rheological behavior (Stadler et al., 2006).

1.3 Thesis Objectives and Organization

This thesis aims at getting some information on changes in the behaviour of polymer foams and composites based on natural fibres during a recycling or degradation process. As described previously, most of the earlier studies were dedicated to the solid state properties, especially for composites and foams, for which major efforts are still focusing on the development of the new industrial applications. Here, we tackled the recycling abilities of these materials in terms of the melt state properties and macromolecular changes. The rheological properties are well known to govern the processability of polymeric materials
and have a great impact on solid state properties like mechanical properties (Dealy and Wissbrun, 1999). To explore the possibilities of these materials to be reused or recycled, it is the main objective of this research investigation to focus on how much the polymeric material is degraded and how can we predict its degradation degree or severity.

This thesis follows the organization illustrated in Figure I.5. Since this is a paper-based thesis, the research is divided in two parts. The first part covers the investigation of the elongational rheology properties of recycled polymer foam (chapter II) and the polymer degradation in terms of macromolecular and rheological properties (chapter III). The second part is dedicated to the composites. The rheological properties are first studied (chapter IV) and composite recycling is examined in terms of macromolecular and rheological properties (chapter V). The thesis is concluded by an overall summary and research propositions and opportunities for further developments (chapter VI).
I.4 Thesis Contribution

Performing up to 10 extrusion regenerations was done to quantify how severe a recycling process can be for both composites and foams. As a result, a negative exponential law was established for both the bubble density in foams and the fibre size in composites. These changes will have a direct effect on the material's solid state properties.

The importance of elongational rheology techniques as an efficient way to investigate any changes occurring in the melt state in combination with those of the shear rheology is
presented. For foams, while shear rheology tests did not exhibit significant changes with recycling, a Strain Hardening Factor (SHF) was defined which is a measure of the maximum elastic energy storable by the polymeric material. This parameter was obtained via elongational rheology to better represent loss in polymer foamability. On the other hand, it was found that an optimum in coupling agent concentration can be determined for a given polymer matrix-natural fibre blend. This thesis also provide very interesting results on loss of elasticity of a composite due to fibre rigidity which is responsible for the strain softening effect, clearly pointed out in this work.

Finally, an empirical approach was used to study macromolecular changes in a polymer process. This led to a better understanding of the competition between chain scission and chain branching occurring when thermo-mechanical strains are applied to a polymer system in the melt state. For composites, these macromolecular investigations allowed to quantify degradation in a recycling process.
Chapter II

The Effect of Recycling on LDPE Foamability:
Elongational Rheology*

RÉSUMÉ

Le but de ce travail était d'étudier au cours d'un processus de recyclage les modifications engendrées dans un polyéthylène de basse densité (LDPE) au niveau de ses propriétés rhéologiques. Le LDPE, sous forme moussé et non moussé, a été recyclé jusqu'à 10 générations dans un circuit fermé sous des conditions constantes d'extrusion et de moussage avec comme agent gonflant chimique l'azodicarbonamide. Dans les deux cas, une réduction des performances rhéologiques a été observée par la diminution du caractère 'rhéo-épaississant' indiquant ainsi une perte progressive de la 'moussabilité' avec le nombre de recyclage. Il a également été constaté une diminution plus rapide des performances rhéologiques en élongation du polymère moussé. Ce fait pourrait être attribué à des contraintes mécaniques plus importantes dans la mousse et qui seraient induites par des taux de déformations plus élevées (bi-axiales) associés à la formation des bulles et à l'accumulation de résidus d'agent gonflant limitant la mobilité des chaînes macromoléculaires et leur taux d'enchevêtrement.
ABSTRACT

The purpose of this work was to investigate changes in the elongational rheology of low density polyethylene (LDPE) when recycled. Both foamed and unfoamed LDPE were submitted up to 10 generations in a closed loop using constant extrusion conditions and azodicarbonamide as a chemical blowing agent. For both foamed and unfoamed polymers, decreasing elongational properties in terms of strain hardening was observed, indicating progressive loss of foamability with the number of time the polymer is recycled. It was also found that the elongational properties of the foamed polymer decreased more rapidly than its unfoamed counterpart. It is believed that higher mechanical degradation of polymer may be the result of higher deformation rates (biaxial) associated with foaming and the accumulation of blowing agent residues limiting polymer chain mobility and entanglement.

II.1 INTRODUCTION

It is now known that the foaming process is highly dependent on the molecular structure of the matrix polymer. Good foaming performance is usually associated with a high degree of long-chain branching (Throne, 1996; Nam et al., 2005). Low density polyethylene (LDPE) is generally better than linear low density polyethylene (LLDPE) in a foaming process because of higher molecular entanglement density and higher molecular chain interactions leading to increased melt strength (Ajji et al., 2003; Ramesh et al., 2003). In the blowing stage of the process, gas expansion within the polymer matrix and thermo-mechanical stresses are the origin of shear and elongational strains, which magnitudes are important to control foam quality (Wagner et al., 2000; Ruinaard, 2005).

In relation with the concept of sustainable development, material recycling in nowadays an active field of research because of multiple reasons bound to the management of resources as well as economic incentives. The producers are expected to investigate means to improve recycling processes of different plastic products (Boffat, 1996). Due to high production levels which are still increasing at important rates, recycling polymer foams will require a great deal of effort. The main objective is to understand the loss of polymer performance, in terms of foaming quality (foamability), undergone in processing under known specific conditions (time, temperature, pressure, composition, etc.).

One way to quantify polymer foamability is through rheological measurements of the base polymer in the melt state. Recently, the development of different types of rheometers and
testing geometries enabled the scientific community to enlarge its characterization possibilities. One important achievement is elongational rheology. Using deformations which are more representative of the foaming process (uniaxial, biaxial, etc.) than simple shear tests, more information can be used to discriminate between different polymer resins.

In the last 2-3 years, some elongational investigations of polymers used in foaming applications have been published and provided very useful information to quantify foamability (Laun and Schuch, 1989; Sentmanat, 2005; Spitael and Macosko, 2004; Micic and Bhattacharya, 2000). These studies mainly emphasized the importance of strain hardening which is related to the inability of macromolecular chains to disentangle quickly enough to follow the applied strain at a given strain rate. This phenomenon is important in the polymer foaming process leading to the stabilization of growing cells by preventing cell coalescence. Since elongational measurements are more sensitive to the polymer molecular structure than simple shear tests, elongational characterization can be viewed as a tool to determine polymer foamability (Sentmanat, 2003; Sentmanat, 2004).

The general field of polymer recycling has been the subject of several investigations for over 30 years, but only a few works are related to recycling polymer foams into foams. These are reviewed next by presenting the main approach used to study foam recycling. It was found that they mainly focus on morphological investigations with limited data on mechanical or rheological properties.
Naguib and coworkers (Naguib et al., 2003) investigated the properties of recycled polypropylene (PP) foams produced by extrusion using talc and butane as nucleating and blowing agents, respectively. Only two recycling generations were produced and the authors reported negligible loss of PP foamability. Measuring the polymer’s shear rheological properties revealed some differences between each generation although their respective foaming behaviour did not present significant difference for various blowing agent contents and working temperatures. In spite of some differences observed in the molecular structure of the various generations, it was difficult to conclude that polymer degradation was taking place within experimental uncertainty.

In another study, Japon and coworkers (Japon et al., 2000) investigated the possibility of recycling polyethylene terephthalate (PET) into PET foams. In their case, the control or improvement of recycled polymer properties for foaming was made in a batch process, by using a supercritical CO$_2$ and the chemical cross-linking with a tetra-functional epoxy: tetraglycidyl-diamino-diphenyl-methane (TGDDM). Partial cross-linking increased the average molecular mass (MW) and polydispersity index (PI), modifying the molecular mass distribution (MWD). Their results clearly showed increased elongational viscosity with TGDDDM addition for both virgin and recycled PET foams, leading to better foamability.

Similarly, improved foamability of industrial PET was reported by Di Maio and coworkers (Di Maio et al., 2005) using pyromellitic dianhydride (PMDA) as a tetrafuctional chain
extender. The foams were blown using a chemical blowing agent (Hydrocerol CT 534) and the results showed that PMDA increased both PET molecular mass and branching, allowing the production of closed cell foams. Their results also indicated a net improvement of the recycled PET foamability at low concentrations of PMDA and CBA contents. PMDA addition was found to increase PET melt strength leading to decreased cell size and increased cell density.

In view of the limited amount of data on the use of elongation rheology to predict polymer foamability, it is the objective of this work to determine if small changes in the polymer molecular structure can be detected by this tool and to relate this information to foam quality. As a first step, LDPE was foamed and subjected up to ten generations in a closed loop scheme (Twite-Kabamba and Rodrigue, 2006). To detect any effect of the foaming process itself, the same treatment was also applied to the unfoamed LDPE. A detailed characterization of the resulting materials is presented in terms of elongational rheology.

This paper presents a new approach to investigate performance losses of polymer foams in a recycling process by producing up to ten generations of the unfoamed and foamed polymer. The high number of generation at the laboratory scale may correspond to the polymer degradation after two or three generations at the industrial scale, and allows a better study of the evolution of the foam’s degradation. The focus is put on elongational rheology related to polymer foamability and morphology. These tools are used to quantify degradation.
II.2 EXPERIMENTAL

II.2.1 Material

Table II.1 presents the characteristics of the low density polyethylene (LDPE) (www.novachem.com) and activated azodicarbonamide (ACA) (www.harwickstandard.com) used as the polymer matrix and the chemical blowing agent, respectively. No nucleation agent was directly added to the process. Nevertheless, residues from ACA decomposition (Eq.II.1) are produced and ACA content was maintained constant at 0.3%wt for each foam generation. For our ACA, the amount of residues produced is 35% by weight as reported elsewhere (Zweifel, 2001; Rodrigue et al., 2006):

\[ H_2N-CO-N=N-CO-NH_2 \rightarrow N_2 + CO + CO_2 + \text{Residues (35%)} \]  

The samples were produced on a laboratory scale extrusion line. A co-rotating twin-screw extruder (Haake Rheomex TW-100) was coupled with a cylindrical die (D = 1.5 mm, L/D = 1), a cooling water bath (room temperature) and take-off rolls to collect the extruded strand (draw speed of 4 cm/sec). The temperature profile used in the extruder was: 102°C in the feeding zone, 142°C in the compression zone, 172°C in the metering zone, and 152°C at the die. Other extrusion conditions were: flow rate of 0.5 kg/hr and screw speed of 40 RPM.
Table II.1 Properties of the LDPE and the chemical blowing agent used.

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Grade</th>
<th>Density (g/cm³)</th>
<th>Melt Temperature (°C)</th>
<th>Melt Index (g/10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>Nova Chemicals</td>
<td>NOVAPOL LA-0219-A</td>
<td>0.919</td>
<td>110</td>
<td>2.3</td>
</tr>
<tr>
<td>Azodicarbonamide</td>
<td>UNIROYAL</td>
<td>Chemicals 754-A</td>
<td>1.68</td>
<td>(165)</td>
<td>-</td>
</tr>
</tbody>
</table>

II.2.2 Elongational Rheology

An SER Universal testing Platform (Sentmanat, 2003; Sentmanat, 2004) from Xpansion Instruments was used to obtain elongation data. The SER unit is a dual windup extensional fixture that can be mounted on most commercially available rotational rheometer host platform (ARES rheometer from Rheometric Scientific). The SER model used in this study was SER-HV-A01. Elongational data were obtained by measurement of the transient elongational viscosity after application of a constant strain rate. The tests were performed at a temperature of 150°C (die temperature) on rectangular samples with dimensions of 17 x 10 x 1.3 mm in length, width, and thickness, respectively. Due to transducer sensibility limits, rheological measurements were performed in the range of available deformation rates for this particular LDPE which was between 0.01 and 3 s⁻¹.
In order to quantify the effect of the number of times the polymer is recycled and based on elongational viscosity data reported earlier, polymer degradation can be characterized in terms of mechanical properties using four parameters:

1- The maximum stress ($\sigma_{\text{max}}$) which is the product of the maximum elongational viscosity $(\eta^*\varepsilon)_{\text{max}}$ with the strain rate ($\dot{\varepsilon}$):

$$\sigma_{\text{max}} = (\eta^*\varepsilon)_{\text{max}} \dot{\varepsilon}$$  \hspace{1cm} (II.2)

2- The strain at maximum stress ($\varepsilon_{\text{max}}$) is the product of the time corresponding to the maximum elongational viscosity ($t_{\text{max}}$) with the strain rate ($\dot{\varepsilon}$):

$$\varepsilon_{\text{max}} = t_{\text{max}} \dot{\varepsilon}$$ \hspace{1cm} (II.3)

3- The strain at break ($\varepsilon_{\text{break}}$) is the product of the time corresponding to sample rupture ($t_{\text{break}}$) with the strain rate ($\dot{\varepsilon}$):

$$\varepsilon_{\text{break}} = t_{\text{break}} \dot{\varepsilon}$$ \hspace{1cm} (II.4)

4- The Strain Hardening Factor (SHF) is the ratio of the maximum stress and the stress at the strain hardening onset (see Figure II.1):

$$\text{SHF} = \sigma_{\text{max}} / \sigma_{\text{onset}}$$ \hspace{1cm} (II.5)
The onset of strain-hardening indicates a deviation from the linear viscoelastic growth curve according to Trouton’s law (Wagner et al., 2000):

\[ \eta_E^+ = 3 \eta_S^+ \]  \hspace{1cm} (II.6)

It has been reported that the transition from the linear viscoelastic domain defined by Trouton's law to the nonlinear viscoelastic domain may occur at a constant strain value (independent of elongational strain rate) which may vary from one polymer to another (Gendron, 2005). This strain, called critical strain (Micic and Bhattacharya, 2000), represents the strain onset and serves as a parameter indicating strain hardening effects.

**Figure II.1** Representation of the Strain Hardening Factor (SHF) for virgin LDPE at 0.1 s\(^{-1}\) and 150°C.
Another way to quantify the strain hardening is by using the so-called Strain Hardening Ratio or SHR (Ruinaard, 2005). This parameter is calculated as the ratio between the maximum of the $\eta^+_E$ curve and three times the value of $\eta^+_S$ obtained from the shear curve at the same strain:

$$\text{SHR} = \frac{\eta^+_E \text{ max}}{3 \eta^+_S \text{ at } t \text{ max}}$$ (II.7)

The main disadvantage of this parameter is the need to perform frequency sweep tests in shear at the same strain as the maximum viscosity in elongation ($\eta^+_E \text{ max}$) and for each elongational curve performed at different strain rates. This maximum strain at which the frequency sweep has to be made is not independent from other properties to be measured ($G'$, $G''$ or $\eta^*$) in the frequency sweep test (which is certainly out of the linear viscoelastic domain) and can make difficult comparison between two polymers of different structures. In addition, it is necessary to make the measurement for each elongational curve under different strain rates.

II.2.3 Morphology

According to morphological analyses developed in our group (Rodrigue and Gosselin, 2002) and using an Olympus SZ stereomicroscope coupled with the Image Pro-Plus software, cell density ($N_F$) was determined for the foamed samples. For each extrusion condition, at least five foam samples were used. From the micrographs, cell dimensions
were also determined in three dimensions where at least 100 cells in each direction (transverse and longitudinal) were used to calculate the average and standard deviations.

II.3 RESULTS and DISCUSSION

As previously mentioned, the production of the ten generations was performed under constant processing conditions. When foamed, ACA concentration was maintained constant at 0.3 phr. As a first step, each foam generation was extruded without ACA and no foaming was observed. This was important to assure that no blowing agent (undecomposed ACA) or gas accumulation (cell gas trapped) was happening in the recycling loop. Only solid residues from ACA decomposition were accumulated as described later. In order to simplify notation, samples are referred to by a letter for foamed (F) and unfoamed (U) samples followed by a number indicating the number of time the material was recycled. For example, sample F-10 indicates that the LDPE has been foamed ten times.

II.3.1 Elongational Results

Figures II.2-3 present the results of elongational measurements obtained for the virgin polymer, the 5th and 10th generations of unfoamed LDPE (U), and the 5th and 10th generations of foamed LDPE (F), respectively. As expected, differences between each generation of LDPE can be observed, especially as strain rate increases. Larger differences at higher strain rates indicate that molecular chains do not have sufficient time to reorganize
and adjust to a new equilibrium state in relation with deformations applied. This inability can be related to the presence of long chain branching in LDPE.

Figure II.2 Elongational viscosity as a function of time at 150°C for virgin (□), 5th (○), and 10th (△) generation of unfoamed LDPE. The line represents Equ.(II.6) for the shear viscosity at a rate of 0.003 s⁻¹ for virgin LDPE.
Figure II.3 Elongational viscosity as a function of time at 150°C for virgin (■), 5th (○), and 10th (△) generation of foamed LDPE. The line represents Equ.(6) for the shear viscosity at a rate of 0.003 s⁻¹ for virgin LDPE.

For both foamed and unfoamed LDPE, the major difference can be seen from the maximum of each curve and can be associated to lower strain hardening. Lower strain hardening is the result of thermo-mechanical strains and stresses which are known to decrease the average molecular mass and broaden its molecular mass distribution (Zahavich and al., 1997). One interesting results is the fact that foamed samples presented higher degradation (lower
strain hardening levels) than their unfoamed counterparts. Two effects can explain this behaviour. First, it is believed that larger strains (biaxial stretching) induced by gas cells expansion induced higher strains within the polymer melt in the foaming stage. These additional strains would produce higher levels of mechanical degradation. Second, there could be a reduced polymer chain mobility related to the accumulation of solid particles, nucleating agent from ACA decomposition (from 0.105 wt% for the first generation to 1.05 wt% for the 10th generation), and limiting macromolecular chain mobility.

Tables II.2-3 presents the results for the strain at break and the strain at maximum stress, respectively. Taking into account the experimental uncertainty, the values reported cannot be differentiated. It can be concluded that under the range of conditions tested, these parameters are almost constant with respect to strain rate and the number of time the polymer is recycled, weather the polymer was foamed or not; i.e. they are not good choices to quantify changes in polymer foamability.
Table II.2 Strain at break ($\varepsilon_{\text{break}}$) as a function of strain rate for foamed (F) and unfoamed (U) LDPE.

<table>
<thead>
<tr>
<th>Strain rate (s$^{-1}$)</th>
<th>0.01</th>
<th>0.03</th>
<th>0.1</th>
<th>0.3</th>
<th>1</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>4.8</td>
<td>6.2</td>
<td>5.4</td>
<td>5.3</td>
<td>5.7</td>
<td>5.1</td>
</tr>
<tr>
<td>U-05</td>
<td>4.7</td>
<td>5.7</td>
<td>5.7</td>
<td>5.5</td>
<td>5.5</td>
<td>5.4</td>
</tr>
<tr>
<td>F-05</td>
<td>5.6</td>
<td>5.4</td>
<td>5.6</td>
<td>5.9</td>
<td>5.5</td>
<td>4.9</td>
</tr>
<tr>
<td>U-10</td>
<td>5.5</td>
<td>5.1</td>
<td>5.8</td>
<td>5.9</td>
<td>5.8</td>
<td>5.7</td>
</tr>
<tr>
<td>F-10</td>
<td>4.9</td>
<td>6.2</td>
<td>6.0</td>
<td>4.7</td>
<td>4.8</td>
<td>4.8</td>
</tr>
</tbody>
</table>
Table II.3 Strain at maximum stress ($\varepsilon_{\text{max}}$) as a function of strain rate for foamed (F) and unfoamed (U) LDPE.

<table>
<thead>
<tr>
<th>Strain rate (s$^{-1}$)</th>
<th>0.01</th>
<th>0.03</th>
<th>0.1</th>
<th>0.3</th>
<th>1</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>4.7</td>
<td>5.5</td>
<td>4.9</td>
<td>5.1</td>
<td>5.0</td>
<td>4.7</td>
</tr>
<tr>
<td>U-05</td>
<td>4.5</td>
<td>5.1</td>
<td>5.1</td>
<td>5.0</td>
<td>5.2</td>
<td>5.2</td>
</tr>
<tr>
<td>F-05</td>
<td>4.5</td>
<td>4.8</td>
<td>4.6</td>
<td>5.4</td>
<td>4.2</td>
<td>4.4</td>
</tr>
<tr>
<td>U-10</td>
<td>5.3</td>
<td>4.8</td>
<td>5.4</td>
<td>5.4</td>
<td>5.5</td>
<td>5.3</td>
</tr>
<tr>
<td>F-10</td>
<td>4.8</td>
<td>5.5</td>
<td>4.8</td>
<td>4.2</td>
<td>4.1</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Figure II.4 presents the maximum stress for different generations of unfoamed and foamed LDPE. From Figure II.4, a clear relation exists between the maximum stress and the strain rate and a power-law model is proposed to fit the data as:

$$\sigma_{\text{max}} = M \dot{\varepsilon}^N$$  \hspace{1cm} (II.8)

The parameter $M$ reflects the strength of polymer chains while the exponent $N$ indicates how melt strength changes with the applied strain rate. Both parameters are function of the polymer molecular structure; i.e. chain length and degree of long chain branching. These values are believed to decrease each time the polymer is recycled. Table II.4 presents results obtained by fitting Equation (II.8) to the data obtained for unfoamed and foamed
LDPE. The table also reports the goodness of fit by the correlation coefficient ($R^2$). As expected, both $M$ and $N$ values are decreasing with the number of time the polymer is recycled. Foamed samples always have lower values than their unfoamed counterparts reflecting higher polymer degradation (or foamability loss) through the total thermo-mechanical history applied while processing LDPE.

![Graph of Maximum Stress vs. Strain Rate](image)

**Figure II.4** Maximum stress as a function of strain rate for foamed (F) and unfoamed (U) LDPE.
Another way to represent the data is to switch from a rheological point of view (plotting viscosity as a function of strain rate) to a mechanical point of view (plotting stress as a function of strain). Typical plots for unfoamed and foamed LDPE are presented in Figure II.5 for data obtained at a strain rate of 3 s$^{-1}$. From Figure II.5, a similar trend is obtained for each polymer generation, the only differences being at high strain values; i.e. between the strain at maximum stress ($e_{\text{max}}$) and the break strain ($e_{\text{break}}$). This indicates that these two parameters might not be good choices to discriminate between each generation. In relation with the strain at maximum stress, it is also possible to use the Strain Hardening Factor (SHF), as defined by Equ.(II.5) to quantify polymer degradation and loss of foamability related to recycling. SHF values are better to use since they are evaluated at high strains where the difference are maximized between each sample.
Table II.5 presents the values for $\varepsilon_{\text{onset}}$, $\sigma_{\text{onset}}$, $\sigma_{\max}$, and SHF for the unfoamed and foamed LDPE. As expected, SHF values decrease with the number of times the polymer is recycled. Once again lower values are reported for foamed samples. Knowing the changes in the rheological response of the polymer, the effect on foam morphology is presented next.

Figure II.5 Stress as a function of strain for the virgin, fifth, and tenth generation of foamed (F) and unfoamed (U) LDPE. Data obtained at a strain rate of $3\ \text{s}^{-1}$. 
**Table II.5** Strain onset ($\varepsilon_{\text{onset}}$), stress onset ($\sigma_{\text{onset}}$), maximum stress ($\sigma_{\text{max}}$), and Strain Hardening Factor (SHF) for foamed (F) and unfoamed (U) LDPE. The data were obtained at a strain rate of 3 s$^{-1}$.

<table>
<thead>
<tr>
<th>LDPE</th>
<th>$\varepsilon_{\text{onset}}$ (-)</th>
<th>$\sigma_{\text{onset}}$ (kPa)</th>
<th>$\sigma_{\text{max}}$ (MPa)</th>
<th>SHF (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>1.09</td>
<td>77.4</td>
<td>6.92</td>
<td>89.4</td>
</tr>
<tr>
<td>U-05</td>
<td>1.00</td>
<td>71.4</td>
<td>6.15</td>
<td>86.1</td>
</tr>
<tr>
<td>F-05</td>
<td>0.99</td>
<td>69.0</td>
<td>5.28</td>
<td>76.5</td>
</tr>
<tr>
<td>U-10</td>
<td>1.03</td>
<td>70.2</td>
<td>4.08</td>
<td>58.1</td>
</tr>
<tr>
<td>F-10</td>
<td>1.08</td>
<td>70.6</td>
<td>0.77</td>
<td>10.9</td>
</tr>
</tbody>
</table>

**II.3.2 Morphology**

From the morphological analysis performed on the produced LDPE foams, their respective cell structure was characterized in terms of cell size and cell density. For cell sizes, each cell was approximated as an ellipsoid characterized by three semi-axes: L (longitudinal direction), B and W (transversal section). A complete 3D cell analysis was used since cell deformation was occurring because of the small stretching force applied on the foamed extruded strand as it came out of the die (Gosselin and Rodrigue, 2005). As presented in Figure II.6, L values (flow direction) increased up to the second generation, and then
became almost constant with further recycling. For both B and W dimensions, the behaviour was similar. Since foam density (mass per volume) was almost constant due to the constant blowing agent concentration, larger cells may be the result of lower nucleation rates (less cells produced), lower resistance to cell growth (lower viscosity of the polymer melt) or cell coalescence.

Figure II.6 Cell sizes as a function of the number of time the polymer was recycled.
Cell density results are presented in Figure II.7 where it can be seen that $N_F$ decreases substantially with recycling indicating polymer degradation. The reduction is about 75% from the first to the tenth generation and confirms possible coalescence with the loss of melt strength. The loss in cell density could be approximated by an exponential law as:

\[
\frac{N_F - N_F^\circ}{N_F^\infty - N_F^\circ} = 1 - e^{-\alpha(z-1)}
\]

where $N_F^\circ$ is the initial cell density (first generation, $z = 1$), $N_F^\infty$ is the cell density after an infinite number of generations ($z = \infty$), $\alpha$ is the foamability lost coefficient, and $z$ is the generation number. The parameters in Equ.(II.9) are not universal but are directly related to the processing conditions and the polymer/blowing agent system used. In this case, the results of Figure II.7 give: $N_F^\circ = 8.5 \times 10^4$, $N_F^\infty = 1.5 \times 10^4$, and $\alpha = 0.32$ ($R^2 = 0.99$). One interesting prediction of Equ.(II.9) is the fact that the polymer does not loose completely its capacity to foam in the long run ($N_F^\infty \neq 0$).
The exponential relation proposed for the cell density behaviour can be justified by the fact that the rate of density nucleation ($J$) obeys to an exponential law (Eq. II.10) where the critical work of formation for a new bubble ($W^*$) is directly related to the pressure drop in the system (Eq.II.11) (Colton and Suh, 1987). Classical nucleation theories state that:

$$J = K \exp \left[ -\frac{W^*}{kT} \right]$$  \hspace{1cm} \text{(II.10)}
with \( k \) the Boltzmann's constant, \( T \) the absolute temperature, and \( W^* \) is inversely proportional to the square of the pressure drop (Colton and Suh, 1987):

\[
W^* \propto \frac{1}{(\Delta P)^2}
\]  

(II.11)

Since the pressure drop in the extruder (through the die) is related to the rheology of the polymer (viscosity and elasticity), reduced rheological properties as presented in Figures II.2-3 are producing lower nucleation rates (Colton and Suh, 1987). Nevertheless, lower cell densities can also be the result of cell coalescence. A careful look at the micrographs revealed possible cell coalescence resulting from decreased melt strength with recycling and Figures II.8-9 present typical examples. From Figures II.8-9, it is clear that the recycled polymer (F-10) has a lower number of larger cells in both longitudinal and transversal directions. The recycled foam also has larger "dead areas" where no cells are present. Nevertheless, further work needs to be done in order to get more insight on foaming dynamics to completely explain the effect of recycling.
Figure II.8 Transversal micrographs for the 1\textsuperscript{st} (a) and 10\textsuperscript{th} (b) generation of foamed LDPE.

Figure II.9 Longitudinal micrographs for the 1\textsuperscript{st} (a) and 10\textsuperscript{th} (b) generations of foamed LDPE.
II.4 CONCLUSION

Rheological investigations in elongation were found to be sufficiently sensitive to detect any changes in a polymer loss of foamability. The maximum stress is probably the best parameter to represent the decreasing strain hardening of the polymer. It is also possible to use the Strain Hardening Factor (SHF) defined by Equ.(II.5).

The morphological investigations clearly showed that a polymer loses foam performance due to thermo-mechanical degradation related to its recycling. Cell sizes increased and cell density decreased with the number of time the polymer was recycled. It was also shown that the foaming process may increase polymer degradation with respect to recycling the polymer matrix under the same processing conditions. This observation may be related to additional elongational strains imposed on the polymer melt during gas expansion (cell growth phase). In our case, nucleating agent (ACA residues) content may also have an effect. It has been possible to define an empirical equation for the loss of polymer foamability with a new parameter $\alpha$ called the foamability lost coefficient. This parameter is a function of processing conditions and the type of polymer.

Finally, there is a direct relation between LDPE loss of foamability and decreasing strain hardening with respect to recycling. To apply sustainable development concepts and in view of increasing production rates, more work needs to be done to understand how polymer foams can be recycled. In our case, a focus was made on a single polymer and temperature profile. Further investigations are under way to study the influence of
processing conditions and the nature of the polymer on the analysis and results presented here.

II.5 ACKNOWLEDGEMENTS

The authors would like to thank NOVA Chemicals (J. Bayley) for providing the polymer, Uniroyals Canada for the blowing agent and the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support.
Chapter III

Rheological and Molecular Investigations of Polyethylene Degradation in a Batch Mixer*

RÉSUMÉ

Dans cette étude, on a investigué l'effet de l'histoire thermo-mécanique induite par des contraintes au sein d'un mélangeur interne sur la dégradation d'un polymère. L'accent a été mis sur les propriétés rhéologiques et moléculaires du polymère (un polyéthylène de basse densité, LDPE) soumis à différentes conditions de traitement engendrées par des paramètres d'opérations tels que la température, la vitesse du rotor et le temps du procédé. Les résultats indiquent que, bien que les propriétés rhéologiques en cisaillement aient légèrement été modifiées, celles en élongation ont été sensiblement modifiées, en particulier la contrainte maximale et l'allongement à la rupture. En raison de la formation de macro-radicaux lors du traitement, les changements macromoléculaires ont été caractérisés en termes de distribution de poids moléculaires. Les résultats ont révélé une compétition entre les taux de scission et de branchement des chaînes macromoléculaires. Il a été constaté que le principal paramètre pour caractériser le comportement de dégradation a été la puissance appliquée au système.
ABSTRACT

In this study, polyethylene degradation is related to its thermo-mechanical history from processing in a batch mixer. A focus is made on the rheological and molecular properties of the polyethylene subjected to different processing conditions by changing the temperature, the rotor speed and the time of process. The results indicate that while shear rheological properties changed slightly, the elongational properties were substantially modified, especially the maximum stress and the elongation at break. Due to the formation of macroradicals while processing, macromolecular changes were characterized in terms of molecular mass distribution and the results represent a balance between rates of chain scission and chain branching. It was found that the main parameter to characterize the degradation behaviour was the input power.

III.1 INTRODUCTION

Degradation of polymers while processing is always difficult to determine since several parameters are involved. Nevertheless, the phenomena associated with reprocessing were studied in the last years. Most of the studies aimed at understanding how the polymer loses its performance in terms of mechanical properties (Kausch, 2005), shear rheological properties (Berzin et al., 2001), thermal properties (Cameron and Davie, 1971) or even in terms of molecular properties (Viebke et al., 1994). But the final behaviour of the polymer after processing is directly related to the operating conditions: type of process used (injection, extrusion, etc.), the thermo-mechanical history (strain, time and temperature), the type of polymer (linear, branched, etc.) and specifics of the environment (presence of oxygen, radiation, etc.). Due to the complex nature of polymer processing and the interaction between all the processing parameters, it is very difficult to predict how a polymeric material loses its performance each time it is processed. Nevertheless, this information is highly important today in view of polymer recycling and sustainable development.

To mimic the degradation of polymeric materials, several experimental set-ups were proposed. The literature describes works using organic peroxides (Oliveira et al., 2006) to accelerate or control the thermo-oxidative degradation in a batch mixer or in extrusion. For the moment, these contributions proposed mechanisms for the degradation process and dynamics (Tobita, 2003a; Hamielec et al., 1991). One trend is the possible formation of microradicals leading to branching or even crosslinking (Tobita, 2003b).
Scaffaro et al. (2009) investigated the rheological and structural properties of two different grades of high-density polyethylene (HDPE) in a batch mixer. The effect of different processing parameters like temperature (180°C to 260°C), rotor speed (20 to 200 rpm) and antioxidant concentration (250 to 5000 ppm) coupled with the presence of different stabilizers (Irgafos 168, Irganox 1010 and Irganox 1076) were studied. Based on their results, it was concluded that a competition between branching, crosslinking and chain scission occurs with one phenomenon being promoted for specific conditions. Their results also indicated that low mobility of molecular chains at lower temperature, lower mixing speed and higher initial molecular mass led to the predominance of branching, while high chain mobility led mainly to chain scission at higher temperature, higher mixing speed and lower initial molecular mass. However they showed that crosslinking did not occurred because of the presence of stabilizers (depending on their concentration and type) and specific operating conditions interfered with both branching and scission mechanisms to provide a decisive role of each parameter on the final molecular structure.

On the other hand, Parmar et al. (2009) studied the effect of organic peroxide on the rheological and molecular properties of recycled and virgin high density polyethylene. The main role of the organic peroxides used (dicumyl peroxide and 1,3,1,4 Bis (tert-butylperoxyisopropyl) Benzene) was to induce long chain branching during a reactive extrusion process for various compositions (0 to 0.15% wt) of different peroxides in a twin-screw extruder. When up to 0.15%wt of peroxide is added, the materials exhibited increased viscoelastic properties and complex viscosity compared to the base material with 1,3,1,4 Bis (tert-butylperoxyisopropyl) Benzene being more effective. They also observed
that the weight average molecular mass ($M_w$) decreased and their molecular mass distribution (MWD) widened with peroxide addition, as well as increased in branching index confirming that the formation of branching is predominant at the molecular level. They concluded that the use of organic peroxide, even at low concentrations, can produce major changes in the molecular structures in both virgin and recycled material. Baum (1959) also proposed a mechanism of polyethylene oxidation induced by an organic peroxide leading to branching and crosslinking. Scorah and coworkers (Scorah et al., 2009) used organic peroxides (a new tetra-functional peroxide, polyether tetrais(t-butylperoxy carbonate) in ethylbenzene and a 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane) to control the degradation of polyethylene in a batch mixer. These works led to the conclusion that the presence of oxygen in the system, causing the thermo-oxidation of the polymeric material, can also produce branching or crosslinking. Since different phenomena can occur while processing, the notion of degradation is a complex concept because processing does not always lead to lower properties of polymeric materials.

Other works are available on the simulation of polymeric materials degradation. Viebke et al. (1996) studied the degradation of medium density polyethylene (MDPE) pipes of 2.1 mm in diameter subjected to a long-term hydrostatic pressure induced by stagnant deionized water as an internal medium and a moderately circulating air as an external medium at different temperatures between 70°C and 105°C. Their work simulates the changes in molar mass distribution allowing to obtain the best fits between a simulated molar mass distribution and a molar mass distribution determined by size exclusion chromatography (SEC) using some assumptions like the probability of a chain to react in scission or in crosslinking being proportional to its mass fraction and that crystallinity should be related
to the molar mass because in the solid state, the thermal oxidation of a polymer occurs only in the amorphous component. They found good fits with experimental data obtained after various exposure times at different temperatures and for different positions in the pipe wall. They also showed that the ratio of the number of chain scission to crosslinking events was generally decreasing with increasing exposure time and decreasing accessibility to oxygen in the pipe wall. They showed that long-chain branching effects led to significant changes in the optimum chain scission and crosslinking values obtained.

Chain scission is not only considered as a passive phenomenon caused by thermo-mechanical strains, but also as the initiator of polymer structure changes having a major impact on the properties of the polymeric material, especially by the formation of macro-radicals. To determine which parameters have more influence on degradation for a specific polymeric material, operating conditions and environments, become a new challenge in the race for sustainable management of resources.

This paper presents another point of view for a better understanding of polymer degradation when the material is subjected to different operating conditions. To start, a simple batch mixer process is used to simulate the processing conditions. This configuration enables to easily control the processing conditions in terms of temperature, time and rotor speed. As a first step, no peroxides or stabilizers are added to the system.
III.2 MATERIAL

The polymer used in this study was low density polyethylene (LDPE), NovaPol LA-0219-A, from Nova Chemicals (Calgary, Canada). This polymer has a density of 919 kg/m$^3$ and a melt flow index of 2.3 g/10 min. The polymer pellets were used as received.

III.3 METHODS

III.3.1 Sample Preparation

The batch mixer used was a Haake Büchner model 40 (Rheomix) with an internal volume of 40 cm$^3$. The chamber was filled with 30 g of polymer for each experiment. It is the same mixer used in the work of Bousmina et al. (1999). The experimental design was chosen as to change three parameters at three levels and the values are presented in Table III.1.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rotors Speed</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>(°C)</td>
<td>(rpm)</td>
<td>(min)</td>
</tr>
<tr>
<td>150</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>160</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>170</td>
<td>90</td>
<td>30</td>
</tr>
</tbody>
</table>

Of the 27 possibilities, only nine of them, which represent a truncated experimental design of three factors with three levels, have been carried out to do a complete characterization.
The retained samples are described in Table III.2. The samples were described by letters A, B and C for the lowest, middle and highest values of the different variables (time, temperature and rotation speed), respectively.

In order to determine the thermo-mechanical energy applied to the system, the work of Bousmina et al. (1999) is used here. They established an expression to determine the shear rate ($\dot{\gamma}$) in the mixer using the principle of equivalent Couette rheometer to get:

$$\dot{\gamma} = \frac{2\pi}{60} \frac{\omega}{\ln \left( \frac{Re}{R_i} \right)}$$  \hspace{1cm} (III.1)

where $\omega$ is the rotors speed and $R_i$ and $R_e$ are the equivalent internal and external radius of the batch mixer, respectively. In our case, the ratio $(R/R_e)$ was 0.88.

Based on the definition of shear rate, two parameters are introduced: the input power ($J$) which is the product of viscosity and the square of shear rate (Tadmor and Gogos, 2006):

$$J = \frac{1}{2} \eta_\dot{\gamma} \dot{\gamma}^2$$  \hspace{1cm} (III.2)

and the input energy ($E$) which is the product of the specific power and time:

$$E = \frac{1}{2} \eta_\dot{\gamma} \dot{\gamma}^2 t = J t$$  \hspace{1cm} (III.3)

In all cases, the value of viscosity $\eta_\dot{\gamma}$ was taken at the shear rate calculated by Eq.(III.1).
From the data presented in Figure III.1, the parameters $J$ and $E$ were calculated for each sample and their values are reported in Table III.2.

**Figure III.1** Complex shear viscosity as a function of frequency and temperature for NovaPol LA-0219-A, a low density polyethylene used as the virgin material.
Table III.2 Sample identification and input parameters.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Conditions</th>
<th>J</th>
<th>Time</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C-min-rpm)</td>
<td>(kW/m³)</td>
<td>(s)</td>
<td>(MJ/m³)</td>
</tr>
<tr>
<td>C-A-A</td>
<td>170-10-30</td>
<td>114</td>
<td>600</td>
<td>68.4</td>
</tr>
<tr>
<td>A-A-A</td>
<td>150-10-30</td>
<td>145</td>
<td>600</td>
<td>87.0</td>
</tr>
<tr>
<td>A-B-A</td>
<td>150-20-30</td>
<td>145</td>
<td>1200</td>
<td>174</td>
</tr>
<tr>
<td>B-C-A</td>
<td>160-30-30</td>
<td>132</td>
<td>1800</td>
<td>238</td>
</tr>
<tr>
<td>B-A-C</td>
<td>160-10-90</td>
<td>593</td>
<td>600</td>
<td>356</td>
</tr>
<tr>
<td>A-B-B</td>
<td>150-20-60</td>
<td>376</td>
<td>1200</td>
<td>451</td>
</tr>
<tr>
<td>B-C-B</td>
<td>160-30-60</td>
<td>343</td>
<td>1800</td>
<td>617</td>
</tr>
<tr>
<td>C-C-C</td>
<td>170-30-90</td>
<td>518</td>
<td>1800</td>
<td>932</td>
</tr>
<tr>
<td>A-C-C</td>
<td>150-30-90</td>
<td>655</td>
<td>1800</td>
<td>1180</td>
</tr>
</tbody>
</table>
III.3.2 Rheological Investigations

III.3.2.1 Shear Rheology

A parallel plate geometry of 25 mm in diameter was used on an ARES rheometer for shear characterization. The same preparation was done as in our previous works (Twite-Kabamba and Rodrigue, 2008a). All the tests were made in the linear viscoelastic zone at a strain of 5% and at three temperatures: 150°C, 160°C and 170°C. The viscosity data was used to build a master curve at 160°C for each sample using the time-temperature principle. The data was also used to get the crossover frequency (\(\omega_c\)), as well as the crossover modulus (\(G_c\)).

III.3.2.2 Elongational Rheology

A SER Universal testing Platform (Sentmanat, 2004) from Xpansion Instruments was used on the ARES rheometer to obtain elongational viscosity data. Description of this instrument was also done in our previous work (Twite-Kabamba and Rodrigue, 2008b). All tests were done at 150°C for a strain rate of 10 s\(^{-1}\).

Moreover, according to the work of Wagner (2006), a parameter \(\beta\) is introduced to quantify the entanglement degree of the polymer. This parameter is defined as the ratio of the number average molecular mass of the branched polymer (\(M_n\)) to the number average molecular mass of the backbone (\(M_{n_{bb}}\)) to give:

\[
\beta = \frac{M_n}{M_{n_{bb}}}
\]  

(III.4)
The value was experimentally obtained as the slope of the linear region of the elongational viscosity curve between the inception of strain-hardening and the maximum value of elongation viscosity. For linear polymers, \( \beta \) is close to unity.

### III.3.3 Macromolecular Characterizations

The molecular mass distribution (MWD) and the weight/number average molecular mass (\( M_w/M_n \)) of the samples were determined by high temperature gel permeation chromatography (HT-GPC). The model 350 High Temperature Triple Detector Array (HT-TDA) from Viscotek (Malvern Company), featuring a Differential Refractive Index (RI) detector, a four-capillary Differential Viscometer detector and a Low Angle Light Scattering (LALS) detector was used. The solvent was 1,2,4-trichlorobenzene stabilised by 2,6-Di-tert-butyl-4-methylphenol at a flow rate of 1.00 ml/min and 140°C. PL gel columns are composed of styrene divinyl benzene copolymer particles with a diameter of 10 μm and a length/internal diameter of 300/75 mm were used. The sample concentration range was between 2 and 4 mg/ml and calibration was made with three standards: PS99K, PS280K and PE1475 samples in the same range of concentration. The sensitivity range of the HT-GPC was comprised between \( 10^4 \) and \( 10^7 \) Da in Mw.

By using the OmniSec GPC software, determination of the branching frequency (BF) was based on the Zimm-Stockmayer equation for a random, tri-functional monodisperse polymer (Wagner, 2006; Drott, 1977):
\[ g_M = \left[ \left( 1 + \frac{B_M}{7} \right)^{1/2} + \frac{4B_M}{9\pi} \right]^{-1/2} \]  

(III.5)

where \( g_M \) is the ratio of intrinsic viscosity of a linear polymer over the branched polymer and \( B_M \) is the number of branches. The polyethylene standard (PE1475) was used as the linear reference. A structure factor of 0.75 and a repeat factor of 14 000 were also used.

It is also known that Zimm and Stockmayer (1949) stated that the radius of gyration of a long chain branched macromolecule (\( R_b \)) is smaller than that of a linear macromolecule (\( R_l \)) containing the same number of repeating units. The ratio of the radii (\( g \)) gives:

\[ g = \frac{R_b}{R_l} \]  

(III.6)

which is called the branching factor. The authors also developed formulae to calculate the value of \( g \) for various branched and cyclic polymer molecules. The ratio of the intrinsic viscosity of a long-chain branched polymer \([\eta]_{br}\) to that of a linear polymer \([\eta]_l\) of the same molecular mass can be calculated as:

\[ \frac{[\eta]_{br}}{[\eta]_l} = g^\varepsilon \]  

(III.7)

where \( \varepsilon \) is a constant determined experimentally by Foster et al. (1980) to be 0.75 for long chain branched polyethylene with tri-functional branching points.
In this study, we defined the Relative Branching Factor \( g_{rel} \) as the ratio of the branching factor of the processed polymer to that of the virgin polymer:

\[
g_{rel} = \frac{g_p}{g_v}
\]

where \( g_p \) and \( g_v \) are the branching factors of the processed and virgin polymers, respectively.

Moreover, according to the work of Viebke et al. (1994), a chain scission rate can be defined as:

\[
\frac{P}{\sum n} = \frac{M_{n0}}{M_n} - 1
\]

where \( \sum n \) is the number of molecules in the neat polymer, \( P \) the difference between the number of chain scissions and the number of branchings, \( M_{n0} \) the number average molecular mass of the neat polymer and \( M_n \) the number average molecular mass of the polymer after \( P \) chain scissions.

It is also well known that the coefficient \( a \) in the Mark-Houwink (M-H) equation (Holdcroft, 1991) is a scalar related to the ‘stiffness’ of the polymer chains:
\[ [\eta] = K M_v^a \]  

(III.10)

with \([\eta]\) the intrinsic viscosity, \(K\) being a constant and \(M_v\) the viscosity average molecular mass which is usually considered to be approximately equal to the weight average molecular mass (\(M_w\)). Thus, for \(a\) around 2, the polymer molecules are considered to be rigid rods, like for aromatic polyamides, while a value of zero indicates that the polymer chains are hard spheres. For a Flory theta solvent, the value of the coefficient is around 0.5 while it is around 0.8 for a thermodynamically good solvent (Flory, 1974). In this study, 1,2,4 trichlorobenzene (TCB) was used and acted as a Flory theta solvent for the polyethylene used at 140°C.

III.4 RESULTS & DISCUSSION

III.4.1 Shear Rheology Results

Although the curves shown in Figure III.2 are close to each other, the complex shear viscosity of the samples changed slightly, especially at high shear rates. This observation suggests that the operating conditions selected were not severe enough to induce major modifications in the polymer structure. Nevertheless, Table III.3 shows that the elastic properties were modified by the processing conditions with the crossover frequency and modulus increasing with higher input energy. Since the crossover frequency is related to the average relaxation time of the polymer, higher crossover frequency (lower relaxation time) reveals a loss of polymer elasticity which can be caused by chain scissions and
weaker chain entanglements. More information can be obtained from the elongational rheology results presented next.

![Complex viscosity as a function of frequency for different samples at 160°C.](image)

**Figure III.2** Complex viscosity as a function of frequency for different samples at 160°C.
Table III.3 Crossover frequency ($\omega_c$) and modulus ($G_c$) at 160°C.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ (MJ/m$^3$)</td>
<td>68.4</td>
<td>87.0</td>
<td>174</td>
<td>238</td>
<td>356</td>
<td>451</td>
<td>617</td>
<td>932</td>
<td>1180</td>
</tr>
<tr>
<td>$\omega_c$ (rad/s)</td>
<td>1.39</td>
<td>1.20</td>
<td>1.58</td>
<td>1.24</td>
<td>1.58</td>
<td>1.87</td>
<td>1.64</td>
<td>3.06</td>
<td>2.24</td>
</tr>
<tr>
<td>$G_c$ (kPa)</td>
<td>6.32</td>
<td>6.06</td>
<td>6.86</td>
<td>6.27</td>
<td>6.73</td>
<td>7.13</td>
<td>7.04</td>
<td>8.42</td>
<td>7.98</td>
</tr>
</tbody>
</table>

III.4.2 Elongational Rheology Results

Figure III.3 presents the elongational viscosity of the samples at a strain rate of $10$ s$^{-1}$. It is clear that the general tendency is a decrease in maximum stress and elongation at break as input energy increases. In this case, the effect is more important than that reported for the shear rheological data. As presented in Table III.4, the maximum stress, which is related to the maximum elastic energy storable in the polymeric system (Wagner, 2006), decreases with increasing input energy. The same observation for the elongation at break applies. These results indicate that the polymer has shorter chains and lower chain entanglement due to the modifications in chain structure with processing.

From the elongational viscosity curves, the $\beta$ parameter was found to be higher than unity for all samples indicating that the polymer is not linear, but branched as expected. But a relation between its value and the input energy is not clear. In general, a decrease of about 15% in $\beta$ from the lowest to the highest input energy was observed revealing a decrease of
long chain branching (Nam et al., 2005). But a relation with both input power and time can lead to a better understanding. It was observed that for longer time, the $\beta$ parameter decreased with increasing input power, while for shorter time, the value increased with increasing input power. Molecular characterization should give more information about chain length and branching of the samples to explain in more details the results obtained.

**Figure III.3** Elongational viscosity as a function of time at a strain rate of $10 \text{ s}^{-1}$ for different samples.
Table III.4 Elongational rheology data for different samples.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>E (MJ/m³)</td>
<td>68.4</td>
<td>87.0</td>
<td>174</td>
<td>238</td>
<td>356</td>
<td>451</td>
<td>617</td>
<td>932</td>
<td>1180</td>
</tr>
<tr>
<td>Maximum stress (MPa)</td>
<td>2.31</td>
<td>2.5</td>
<td>2.85</td>
<td>1.94</td>
<td>2.49</td>
<td>2.53</td>
<td>1.76</td>
<td>0.96</td>
<td>1.28</td>
</tr>
<tr>
<td>Strain at break (-)</td>
<td>4.4</td>
<td>4.8</td>
<td>4.9</td>
<td>4.2</td>
<td>4.6</td>
<td>4.6</td>
<td>4.2</td>
<td>3.6</td>
<td>3.7</td>
</tr>
<tr>
<td>β coefficient</td>
<td>2.2</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.2</td>
<td>2.1</td>
<td>2.0</td>
<td>1.8</td>
<td>2.1</td>
</tr>
</tbody>
</table>

III.4.3 High Temperature Gel Permeation Chromatography data

First, the data for the neat polyethylene (virgin pellets as received) are represented in Table III.5 where Mw represents the weight-average molecular mass, Mn the number-average molecular mass, PDI the polydispersity index (Mw/Mn), Mz the Z-average molecular mass, IV the intrinsic viscosity, “M-H log K” and “M-H a” the logarithmic value of the Mark-Houwink parameter K and the Mark-Houwink exponent a, respectively. Also, BF represents the branching frequency as obtained from Eq.(III.5). These data can be considered as the reference values for the different macromolecular characteristics allowing to measure changes or degradation in comparison with each sample.
Table III.5. Molecular characteristics of the virgin LDPE (NovaPol LA-0219-A).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mw (kDa)</th>
<th>Mn (kDa)</th>
<th>PDI</th>
<th>Mz (kDa)</th>
<th>[η] (dl/g)</th>
<th>M-H Log K</th>
<th>M-H a</th>
<th>BF</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA-219-A</td>
<td>219</td>
<td>18.7</td>
<td>12</td>
<td>772</td>
<td>0.75</td>
<td>-2.77</td>
<td>0.50</td>
<td>5.28</td>
</tr>
</tbody>
</table>

The molecular data as reported in Table III.6 show for each parameter the behaviour which cannot be completely correlated using only the input energy because of small variations and no clear trend can be established. On the other hand, the values of the Mark-Houwink exponent $a$, which remained almost constant, show that the degradation process does not modify the Flory theta solvent property of the solvent used. It is also observed that the Mw was slightly changed and may explain the small changes in shear viscosity. On the other hand, changes in Mn values are more important to relate with changes in the polymer structure suggesting that thermo-mechanical strains have more influence on longer chains than shorter ones (Viebke, 1996). This implies that chain scission occurs preferentially at the extremities of the main backbone rather than in between (Guaita et al., 1990).

In order to explain in more detail the results obtained, processing time and input power were found useful to better understand what is happening during the degradation process. According to the work of Scaffaro and coworkers (Scaffaro et al., 2009), there is a competition between chain scission and chain branching due the formation of macroradicals while processing. Chain scission is mainly promoted by higher chain
mobility (high shear rate and high temperature), while chain branching is enhanced by lower chain mobility (lower shear rate and lower temperature). In processing, time can amplify or reduce one of these two phenomena. Figure III.4, which represents the scission rate as obtained by Equ.(III.9), allows explaining the effect of each parameter (time or input power) on the samples. Two regions can be observed. At shorter time, a transition occurs from a predominance of chain scission at lower input power to chain branching at higher input power. On the other hand, for longer time, a transition from the predominance of chain branching at lower input power to chain scission at higher input power is observed. The influence of time is either to promote chain mobility by scission or to reduce chain mobility through increasing chain branching, leading to chain scission again. On the other hand, at lower input power, a transition from a predominance of chain scission at shorter time to chain branching at longer time is observed, while at higher input power, a transition from a predominance of chain branching at shorter time to chain scission at longer time period occurs. In this case, the input power has the same role than time confirming the existence of the transition region where the competition between chain scission and branching is neutral (dynamic balance). This situation can explain the fact that samples with the similar input energy exhibit different molecular properties and also the fact that samples especially situated close to this neutral region can exhibit some molecular properties higher than the virgin polymer. Although the branching frequency for all samples is larger than that of the unprocessed polymer, samples in the neutral region present the highest branching frequency values. This can be explained by macro-radicals created and reacting to increase the number of chain branching on shorter backbone chains.
The relative branching factors for samples are represented in Figure III.5. As for the chain scission rate, a combination of input power and time better reflect the behaviour of the different samples. The branching factor being related to intrinsic viscosity, the more the polymer is branched, the lower is the branching factor. Thus, Figure III.5 also indicates that all the samples are more branched than the virgin polymer and the relative branching factor of samples increased with both time and input power suggesting that the input energy is the predominant parameter influencing changes in branching factors.
Table III.6 Molecular characteristic of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E</th>
<th>Mw</th>
<th>Mn</th>
<th>PDI</th>
<th>Mz</th>
<th>[η]</th>
<th>M-H Log K</th>
<th>M-H a</th>
<th>BF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(MJ/m³)</td>
<td>(kDa)</td>
<td>(kDa)</td>
<td>(-)</td>
<td>(kDa)</td>
<td>(dl/g)</td>
<td>(dl/g)</td>
<td>(-)</td>
<td>(-)</td>
</tr>
<tr>
<td>C-A-A</td>
<td>68.4</td>
<td>206</td>
<td>15.3</td>
<td>13.72</td>
<td>715</td>
<td>0.707</td>
<td>-2.915</td>
<td>0.52</td>
<td>8.59</td>
</tr>
<tr>
<td>A-A-A</td>
<td>87.0</td>
<td>215</td>
<td>14.2</td>
<td>15.50</td>
<td>792</td>
<td>0.716</td>
<td>-2.780</td>
<td>0.50</td>
<td>7.44</td>
</tr>
<tr>
<td>A-B-A</td>
<td>174</td>
<td>178</td>
<td>16.8</td>
<td>10.61</td>
<td>707</td>
<td>0.707</td>
<td>-2.864</td>
<td>0.52</td>
<td>9.56</td>
</tr>
<tr>
<td>B-C-A</td>
<td>238</td>
<td>223</td>
<td>17.1</td>
<td>13.67</td>
<td>853</td>
<td>0.720</td>
<td>-2.940</td>
<td>0.53</td>
<td>10.9</td>
</tr>
<tr>
<td>B-A-C</td>
<td>356</td>
<td>194</td>
<td>17.3</td>
<td>11.61</td>
<td>700</td>
<td>0.690</td>
<td>-2.959</td>
<td>0.53</td>
<td>9.43</td>
</tr>
<tr>
<td>A-B-B</td>
<td>451</td>
<td>192</td>
<td>19.6</td>
<td>9.84</td>
<td>683</td>
<td>0.695</td>
<td>-3.055</td>
<td>0.55</td>
<td>10.8</td>
</tr>
<tr>
<td>B-C-B</td>
<td>617</td>
<td>188</td>
<td>19.4</td>
<td>9.71</td>
<td>680</td>
<td>0.674</td>
<td>-2.978</td>
<td>0.53</td>
<td>12.6</td>
</tr>
<tr>
<td>C-C-C</td>
<td>932</td>
<td>215</td>
<td>12.3</td>
<td>17.48</td>
<td>962</td>
<td>0.681</td>
<td>-2.735</td>
<td>0.48</td>
<td>7.32</td>
</tr>
<tr>
<td>A-C-C</td>
<td>1180</td>
<td>189</td>
<td>14.7</td>
<td>13.03</td>
<td>744</td>
<td>0.659</td>
<td>-2.925</td>
<td>0.52</td>
<td>7.48</td>
</tr>
</tbody>
</table>
Figure III.4 Chain scission rate as a function of input power (J) and time.
Figure III.5 Relative branching factor as a function of specific power (J) and time.
III.5 CONCLUSIONS

Usually, investigations of polymer properties after processing aim at establishing relations between macroscopic properties and degradation. In this work, it was shown that polymer degradation in a batch mixer can lead to complex situations making the behaviour of the polymer under different processing conditions more complex than simply the phenomenon of chain scission based on input energy or global thermo-mechanical strains applied to the system. The formation of macro-radicals better explains why the polymer chains under specific conditions can lead to the predominance of branching or chain scission.

The samples analysed in this study showed that elongational rheological properties are more sensitive to changes in polymer structure than shear properties indicating that long chains branching are more affected than the main backbones in any degradation process. Decrease of the maximum stress in elongation reached 66% from the highest to the lowest maximum stress, while elongation at break decreased up to 27%.

Changes in the macromolecular properties (molecular mass distribution and chain structure) revealed the necessity to consider a minimum of two parameters (time and input power) to better understand the predominance of branching or chain scission. While $\text{Mw}$ slightly changed in the range studied, $\text{Mn}$ changed substantially (up to 37%). The branching factor, related to the intrinsic viscosity, was shown to be more affected by the input energy.
In order to predict the properties of a polymer subjected to a degradation process, this work establishes that the main obstacle is to know if predominance is towards branching or chain scission under specific processing conditions. By using parameters such as input energy, input power and time, it was possible to explain how thermo-mechanical strains affected the polymer structure during processing. Nevertheless, more works should be conducted to better quantify the competition between chain branching and chain scission under other conditions like presence of additives, reinforcements and for polymers blends.
Chapter IV
Rheological Properties of Polypropylene/Hemp Fibre Composites*

RÉSUMÉ

Cette étude consiste en l'analyse de l'effet des fibres de chanvre sur les propriétés rhéologiques en cisaillement et en élongation du polypropylène (PP). Les paramètres étudiés sont la concentration de fibre de chanvre (0-30%) et de l'agent couplant, ainsi que celle du polypropylène greffé d’anhydride maléique (MAPP) (0-0.6%). La rhéologie en cisaillement a révélé que la teneur en fibres influençait principalement les propriétés à faibles taux de cisaillement comme la contrainte maximale et la viscosité du plateau newtonien, tandis que l'addition d'agent couplant influençait principalement les propriétés à moyen et fort taux de cisaillement comme le temps de relaxation, l'indice de fluidité et le paramètre de Yasuda. D'autre part, les résultats obtenus en rhéologie élongationnelle ont révélé un comportement dit ‘rhéo-fluidifiant’ avec un accroissement de la consistance et une diminution du taux d’élongation à la rupture avec l'augmentation de la concentration en fibres. L’ajout du MAPP, ayant pour effet d’améliorer la compatibilité des fibres avec le polymère, a par ailleurs révélé un effet plastifiant influençant significativement les propriétés rhéologiques.
ABSTRACT

This study investigates the effect of hemp fibres on the shear and elongational rheologies of polypropylene (PP). The parameters studied were hemp content (0-30%) and maleic anhydride polypropylene (MAPP) addition (0-0.6%). Shear rheology revealed that fibre content mainly influences low shear rate properties like yield stress and zero-shear-viscosity, while coupling agent addition mainly influences intermediate to high shear rate parameters like relaxation time, power-law index and Yasuda parameter. On the other hand, elongational rheology results showed a strain-softening behaviour of the composites with increasing consistency and decreasing strain at break as fibre concentration increases. MAPP addition is also shown to improve the fibre-polymer compatibility, but at the same time produces a plasticizing effect having a significant effect on rheological properties.

* Twite-Kabamba Eddy, Mechraoui Ahmed and Rodrigue Denis, Polymer Composites, 30(10), 1401-1407 (2009).
IV.1 INTRODUCTION

Although several studies investigated the mechanical and morphological properties of natural fibre/polymer composites in the solid state (Julson et al., 2004; Lu et al.; 2005; Bledzki et al., 1998), almost nothing can be found on their complete rheological characterization: i.e. shear and elongational rheology in the melt state. Even less information can be found for natural fibre composites (Mobuchon et al., 2005; Li and Wolcott, 2004 and 2006). Similarly, as the foaming of polymer composites is gaining in interest (Schut, 2001; Aranguren et al., 2007; Bledzki et al., 2005), it becomes highly important to characterize their rheological behaviour in both shear and elongation while processing the material in its melt state. This rheological information will be useful to better control the final morphology of composite foams under specific processing conditions, especially when natural fibre are used.

In the past, studies on fibres like jute (Basu et al., 1992), maple (Hristov et al., 2007), coconut (Leblanc et al., 2006), sisal and pineapple (Mishra et al., 2004), flax and cotton (Steller, 2005) have been reported. Unfortunately, mostly shear rheology (melt state) and mechanical properties (solid state) have been reported. The growing interest in producing stronger materials and new applications like automotive and building industries were the driving force. Furthermore, the use of natural fibres instead of glass fibres is very attractive because they have lower cost, lower specific weight, higher specific stiffness and tenacity. Furthermore, they are renewable resources with biodegradable characteristics, good thermal and acoustic insulations and higher electrical resistance (Mohanty et al., 2005; Bledzki and
They also have a major impact on the environment by being recyclable. Nevertheless, natural fibres have some disadvantages, which mainly consist in their poor fire and moisture resistance and high variability. They also require lower processing temperatures, which limit their applications.

Among all the available natural fibres, hemp is known for its superior strength, durability, and resistance to rot (Mohanty et al., 2005). Hemp has a low amount of lignin which is the organic glue binding the plant cells. For this reason, hemp treatment is more environmentally friendly since less bleaching with strong chemicals like chlorine is needed before the fibres can be used. In composite formulation, hemp is twice stronger than common wood (Kane, 2007) and hemp-based products are biodegradable (Mohanty et al., 2005). These reasons clearly justify the use of hemp as reinforcement in the plastic composite industry. In a previous study (Mechraoui et al., 2007), the mechanical and morphological properties of these composites have been reported. The present paper constitutes a continuing effort in understanding the relations between properties, composition and processing of natural fibre composites.

For the moment, very few papers reported on the elongational rheology behaviour of polymer composites in the melt state. Unfortunately, none of them concerned natural fibre composites. The most important ones are summarized here to understanding the behaviour of composites in both elongational and shear deformations.
Takahashi and coworkers (Takahashi et al., 1999) investigated the elongational properties of low density polyethylene (LDPE) blended with glass bead, glass flake, glass fibre and talc. They found that the strain-hardening properties of LDPE decreased with filler addition in the following order: glass beads, glass flakes, talc and glass fibres, the latter even exhibiting strain-softening. They explained this behaviour by the damping function and the relaxation spectrum defined via the Bernstein-Kearsley-Zapas (BKZ) model and also the degree of recovery. They concluded that decreasing strain-hardening properties up to a point where strain-softening occurs was related to stronger damping and smaller degree of recovery influenced by smaller particles and larger aspect ratio of the fillers, all of which reducing composite’s elasticity. Even though their results were limited to very small strain rates between 0.0041 and 0.34 s⁻¹, they reported that strain-softening can occur.

On the other hand, the effect of coupling agent addition in composites has been studied. Hristov and Vlachopoulos (Hristov et al., 2007) investigated the effect of different coupling agents (maleated polyethylene: Polybond 3009, Polybond 3109 and Coesive F30) on the rheological properties of high density polyethylene (HDPE) of different molecular mass (MW) and molecular mass distributions (MWD). In their case, HDPE was filled with maple wood flour. Using rotational and capillary rheometers combined with Scanning Electron Microscopy (SEM) for morphological analysis, they found that low MW and narrow MWD HDPE led to larger viscosity increase with wood flour addition. They also showed that the presence of coupling agents led to significant interfacial adhesion improvement as confirmed by SEM analysis and affected the pressure drop as well as the wall shear stress.
Nevertheless, their investigation did not study the plasticizing effect of the coupling agent and did not report any elongational properties.

Finally, since fibre concentration is the main parameter controlling the performances of a composite, Guo and coworkers (Guo et al., 2005) investigated the rheological properties of linear low density polyethylene (LLDPE) filled with E-glass fibres. In this case, a much wider range of shear rates \(10^{-4}\) to \(10^4\) s\(^{-1}\) and higher filler concentrations (up to 60\%wt.) was used. The results were analyzed with a modified FENE-P model by introducing fibre-fibre interactions and coupling between fibre orientation and polymer chains conformation. Two parameters were found important: the fibre-fibre interaction coefficient known also as the Folgar-Tucker constant and the polymer-fibre coupling factor. Both values were strongly dependent on the filler volume fraction and shear rate: increasing the filler concentration led to increased viscosity and pressure drop. Once again, these results were limited to shear deformations without coupling agent.

From our previous work (Mechraoui et al., 2007), the mechanical and morphological properties of hemp/polypropylene composites were reported. It was found that the optimum coupling agent was maleic anhydride polypropylene (MAPP) at a concentration of 2\%wt (fibre basis). Using the same materials and conditions, an investigation is presented here on the shear and elongational rheology of these composites. This information is highly important in order to understand how the structure of the blend in the melt state can influence the final morphology of the composites under specific processing conditions.
IV.2 EXPERIMENTAL

IV.2.1 Materials

The same materials as our previous work were used (Mechraoui et al. 2007). The polymer was polypropylene (Pro-Fax PF-814) from Basell (Canada) with a density of 902 kg/m$^3$ and a melt flow index of 3.0 g/10 min (230°C/2.16 kg). Hemp fibres were provided by Stermergy Canada) with an original staple length of 10 mesh. The fibres were sieved upon arrival and a narrower range of sizes was used. Fibre size distribution was measured by optical microscope and image analysis. The original distribution was a length (L) of 942 ± 170 µm and a diameter (D) of 257 ± 61 µm, giving an average L/D ratio of 3.6. To modify the PP/hemp interface, maleic anhydride polypropylene (MAPP) was added as a coupling agent: Licomont AR 504 in a wax form supplied by Clariant (Canada). The MAPP used has an acid value of 35-45 mg KOH/g with an average molecular mass of 12 kg/mol.

Before blending, the fibres were first dried at 105°C for 24 h to eliminate moisture. The composites were then compounded at different weight ratios (10, 20 and 30%wt.) in an internal batch mixer (Haake, Rheomix) at 40 rpm and 175°C for 15 min to obtain well dispersed materials. While processing, the polymer was introduced first and then the coupling agent until the mixing torque reached a constant value (generally after 2 min). At this point, hemp fibres were introduced for a total mixing time of 15 min. The compound was then compression moulded at 200°C under 3 tons of pressure for 5 min in moulds having dimensions of 140 x 140 x (1 or 2) mm. To determine the fibre size distribution after processing and moulding, the samples were dissolved in trichlorobenzene and filtered.
The results gave $L = 775 \pm 110 \, \mu m$ and $D = 280 \pm 41 \, \mu m$, for an average $L/D$ ratio of 2.7. Due to mixing and compression moulding, the fibres are assumed to be randomly distributed in the plane (orthotropic).

Table IV.1 presents the different compositions used in this study. All the concentrations are given as weight percent. When MAPP was added, 2%wt. based on fibre content was used except for the neat PP where a total of 0.2%wt. was added.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Hemp content (% wt.)</th>
<th>Presence of MAPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-H30-MAPP</td>
<td>30</td>
<td>yes</td>
</tr>
<tr>
<td>PP-H30</td>
<td>30</td>
<td>no</td>
</tr>
<tr>
<td>PP-H20-MAPP</td>
<td>20</td>
<td>yes</td>
</tr>
<tr>
<td>PP-H20</td>
<td>20</td>
<td>no</td>
</tr>
<tr>
<td>PP-H10-MAPP</td>
<td>10</td>
<td>yes</td>
</tr>
<tr>
<td>PP-H10</td>
<td>10</td>
<td>no</td>
</tr>
<tr>
<td>PP-MAPP</td>
<td>0</td>
<td>yes</td>
</tr>
<tr>
<td>PP</td>
<td>0</td>
<td>no</td>
</tr>
</tbody>
</table>
IV.2.2 Shear Tests

A parallel plate geometry on an ARES rheometer (Rheometric Scientific) was used for shear characterization. The tests were made on disc samples of 25 mm in diameter at a gap of 1.5 mm and a temperature of 180°C. This temperature was selected because it corresponds to the usual die temperature used for producing polyolefin composites and foams (Li and Wolcott, 2006; Kamal et al., 1984). Two test modes were used: dynamic oscillatory and transient measurements. The dynamic oscillatory mode tests were made at a strain of 5% which corresponds to the linear viscoelastic zone. For transient tests, a deformation rate of 0.03 s\(^{-1}\) was selected for a period of 150 seconds and to apply Trouton’s law (Li and Wolcott, 2004), three times these transient values were used.

IV.2.3 Elongational Tests

To perform uniaxial elongation deformation, the SER-HV-A01 model of the SER Universal testing Platform from Xpansion Instruments was used (Sentmanat, 2004; Sentmanat et al., 2005). The SER unit is a dual windup extensional fixture and elongational data were obtained by measurement of the transient elongational viscosity after application of a constant strain rate. The tests were also performed at a temperature of 180°C on rectangular samples with dimensions of 17 x 10 x 1.2 mm. Due to transducer sensibility limits, rheological measurements were performed in the range of available deformation rates which was between 0.1 and 10 s\(^{-1}\). Data treatment was performed according with standard definitions as described in a previous work (Twite-Kabamba and Rodrigue, 2008). The parameters are defined as:
- The stress ($\sigma$) as the product of the elongational viscosity ($\eta_E$) with the strain rate ($\dot{\varepsilon}$):

$$\sigma = \eta_E \dot{\varepsilon} \quad \text{(IV.1)}$$

- The strain $\varepsilon$ as the product of time ($t$) with strain rate ($\dot{\varepsilon}$):

$$\varepsilon = t \dot{\varepsilon} \quad \text{(IV.2)}$$

The elongational power-law model is defined as:

$$\sigma_E = M \dot{\varepsilon}^N \quad \text{(IV.3)}$$

where $\sigma_E$ is the elongational stress, $M$ is the elongational consistency and $N$ is the elongational power-law index. From Equation (IV.3), the elongational viscosity ($\eta_E$) is computed as:

$$\eta_E = M \dot{\varepsilon}^{N-1} \quad \text{(IV.4)}$$

Tait's equation (Rodgers, 1993) was used to estimate PP density at the test temperature ($180^\circ$C) as shown in Table IV.2 (neglecting the effect of MAPP on density).
Table IV.2 PP/Hemp density (kg/m$^{3}$) at 25 and 180°C.

<table>
<thead>
<tr>
<th>Samples</th>
<th>25°C</th>
<th>180°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-H30</td>
<td>1050</td>
<td>955</td>
</tr>
<tr>
<td>PP-H20</td>
<td>979</td>
<td>891</td>
</tr>
<tr>
<td>PP-H10</td>
<td>909</td>
<td>828</td>
</tr>
<tr>
<td>PP</td>
<td>905</td>
<td>764</td>
</tr>
</tbody>
</table>

IV.3 RESULTS and DISCUSSION

IV.3.1 Dynamic Shear Results

The complex viscosity curves are represented in Figure IV.1. As expected, the complex viscosity increases with hemp concentration in the composite. On the other hand, the effect of MAPP addition is more complex. It reinforces the interactions between the fibre and the polymer, but also plasticizes the polymer matrix. Therefore, a competition between both effects occurs as reported by Han and co-workers for silane and titanate coupling agents on polyolefin composites based on calcium carbonate, glass beads or glass fibres (Han, 1978 and 1981). For small MAPP amount (0.2%) (PP-MAPP), the level of viscosity decrease at low frequency (0.1 rad/s) is about 30%. This plasticizing effect can also be observed at low hemp content by looking at the behaviour of PP-H10-MAPP. The composite without MAPP (PP-H10) has a higher viscosity meaning that MAPP molecules rest almost entirely
in the PP matrix and not only at the PP/hemp interface. As the amount of hemp increases, the reinforcing effect becomes stronger. At 20% hemp, a balance seems to occur and both effects compensate each other leading to a similar viscosity with and without MAPP addition. At higher hemp content (30%), the viscosity for composite with MAPP is higher than without. This effect (reinforcing and plasticizing) was reported for different kinds of coupling agent and natural fibre (different concentrations). It was suggested that the optimum concentration of coupling agent should be carefully chosen for each fibre concentration (Lu et al., 2005; Han, 1981).

![Figure IV.1](image_url)  
*Figure IV.1* Complex shear viscosity ($\eta^*$) as a function of frequency at 180°C and 5% strain for different compositions of PP/Hemp/MAPP.
Figure IV.1 also indicates that a yield stress may be present for composites where its value increases with hemp content (Utracki and Fisa, 1982; Beery et al., 1992). This phenomenon is well known and can be described by a modified Carreau-Yasuda model to include yield stress (Naderi et al., 2007):

\[ \eta_{(\omega)} = \frac{\sigma_0}{\omega} + \eta_0 \left[ 1 + \left( \lambda \omega \right)^a \right]^{(n-1)/a} \]  

(IV.5)

where \( \sigma_0 \) is the yield stress, \( \eta_0 \) is the zero shear viscosity, \( \lambda \) is a material time constant, \( a \) is the Yasuda parameter and \( n \) is the power-law index.

As shown in Table IV.3, both yield stress and zero shear viscosity increase with hemp concentration. An interesting observation is an inversion of the trend around 20% hemp. Below this hemp content, MAPP addition decreased \( \sigma_0 \) and \( \eta_0 \) while at higher hemp content it increased them. It is believed that for a critical hemp concentration (20% here), the reinforcing effect of MAPP is stronger than its plasticizing effect due to higher amount of MAPP molecules present at the fibre-polymer interface and less molecules lying around in the polymer matrix.
Table IV.3 Modified Carreau-Yasuda model parameters for PP/Hemp/MAPP composites (180°C).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_o$ (kPa)</th>
<th>$\eta_o$ (kPa.s)</th>
<th>$\lambda$ (s/rad)</th>
<th>$\alpha$ (-)</th>
<th>$n$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-H30-MAPP</td>
<td>2.07</td>
<td>8.53</td>
<td>0.265</td>
<td>0.780</td>
<td>0.426</td>
</tr>
<tr>
<td>PP-H30</td>
<td>1.45</td>
<td>7.96</td>
<td>0.320</td>
<td>0.848</td>
<td>0.445</td>
</tr>
<tr>
<td>PP-H20-MAPP</td>
<td>0.535</td>
<td>9.29</td>
<td>0.141</td>
<td>0.533</td>
<td>0.274</td>
</tr>
<tr>
<td>PP-H20</td>
<td>0.673</td>
<td>8.33</td>
<td>0.165</td>
<td>0.560</td>
<td>0.308</td>
</tr>
<tr>
<td>PP-H10-MAPP</td>
<td>0.073</td>
<td>4.09</td>
<td>0.122</td>
<td>0.554</td>
<td>0.320</td>
</tr>
<tr>
<td>PP-H10</td>
<td>0.165</td>
<td>6.61</td>
<td>0.177</td>
<td>0.570</td>
<td>0.329</td>
</tr>
<tr>
<td>PP-MAPP</td>
<td>0</td>
<td>2.45</td>
<td>0.152</td>
<td>0.563</td>
<td>0.406</td>
</tr>
<tr>
<td>PP</td>
<td>0</td>
<td>3.58</td>
<td>0.531</td>
<td>0.667</td>
<td>0.487</td>
</tr>
</tbody>
</table>

On the other hand, the presence of MAPP decreased the values of $\lambda$, $\alpha$ and $n$ for any hemp concentration reflecting again its plasticizing effect at intermediate ($\lambda$ and $\alpha$) and high ($n$) shear rates. These parameters are related respectively to the onset of shear-thinning or to the relaxation time ($\lambda$), to the width of the transition region between the zero-shear-rate region and the power-law region ($\alpha$), as well as to the degree of shear-thinning (melt strength loss) at high shear rate ($n$) (Pinarbasi and Liakopoulos, 1995).
Figure IV.2 presents the elastic ($G'$) and loss ($G''$) moduli of the samples. From these curves, the crossover frequency ($\omega_c$) and the crossover modulus ($G_c$) can be obtained and their values are reported in Table IV.4. It can be seen that the crossover frequency increases with hemp concentration indicating a decrease in the average relaxation time ($\lambda_w = 1/\omega_c$). From the neat PP to PP-H30-MAPP, the decrease is about 40%. The presence of MAPP enhances this decrease with the exception of PP-H20-MAPP for which the effects of MAPP seem to be negligible within experimental uncertainty. Increasing crossover frequency with hemp addition, with or without MAPP, reveals a loss of elasticity of the composites, the fibres being more rigid than polymer macromolecules (Steller, 2005). Similarly the crossover modulus increases with hemp concentration in the composite. From the neat PP to the PP-H30-MAPP, the increase is about 230%.
Figure IV.2 Storage (closed symbols) and loss (open symbols) moduli as a function of frequency at 180°C and 5% strain for different compositions of PP/Hemp/MAPP.
Table IV.4 Crossover frequency \( \omega_c \) (rad/s) and crossover modulus \( G_c \) (kPa) for different compositions of PP/Hemp/MAPP composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>With MAPP</th>
<th>Without MAPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-H30</td>
<td>82.2 / 79.0</td>
<td>65.4 / 65.5</td>
</tr>
<tr>
<td>PP-H20</td>
<td>59.1 / 57.4</td>
<td>60.2 / 54.1</td>
</tr>
<tr>
<td>PP-H10</td>
<td>81.9 / 36.6</td>
<td>58.5 / 43.9</td>
</tr>
<tr>
<td>PP</td>
<td>98.7 / 27.9</td>
<td>59.2 / 23.8</td>
</tr>
</tbody>
</table>

IV.3.2 Transient Shear Results

Figure IV.3A shows the transient shear viscosity \( (\eta_S^+) \) for different PP/Hemp/MAPP compositions following a step in shear rate from 0 to 0.03 s\(^{-1} \). From these curves, a similar behaviour as presented in Figure IV.1 for the complex viscosity is observed: the plasticizing effect of MAPP is decreasing with increasing hemp content. At a fixed strain rate, the composite need more time to achieve the steady state value indicating that the fibre-polymer interactions are more important and more time is needed before reaching the equilibrium state (Mechraoui et al., 2007; Guo T., 2005).
As reported in several works (Guo T., 2005; Araki et al., 2005), the transient shear viscosity of fibre/polymer blends reveals the effect of fibre orientation. A kink in the composite curves is observed but not in neat PP as illustrated in Figure IV.3B. This kink may indicate a transition between a multidirectional fibre orientation and fibres mostly oriented in the flow direction. This phenomenon has also been shown by Guo (2005). Their transient shear data of Thermotropic Liquid Crystalline Polymer (LCP) were confirmed by optical microscopy during the test showing that the effect is related to the orientation of lamellar crystals. Based on our results, the strains at which the kink occurs are reported in
Table IV.5. Further investigations for better understanding of this phenomenon would be needed. Nevertheless, a minimum is observed here at the critical concentration of 20%.

Figure IV.3B Illustration of the kink in the transient shear viscosity ($\eta_s^+$) vs. frequency curves at 180°C and 0.03 s$^{-1}$. 
Table IV.5 Strain (%) at which the kink occurs for different compositions of PP/Hemp/MAPP composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>With MAPP</th>
<th>Without MAPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-H30</td>
<td>1.32</td>
<td>1.29</td>
</tr>
<tr>
<td>PP-H20</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>PP-H10</td>
<td>0.90</td>
<td>0.75</td>
</tr>
</tbody>
</table>

IV.3.3 Elongational Results

It is well known that common polypropylene does not exhibit much strain-hardening during an elongational test (Sebastian and Dearborn, 1983; McCallum et al., 2007). Trouton’s law (Li and Wolcott, 2004) is often verified and it is the case here as presented in Figure IV.4 which reports the elongational viscosity of neat PP showing no strain-hardening. On the other hand, all the composites exhibit strain-softening mainly due to the orientation and concentration of hemp fibres which are responsible for the weak melt elasticity. Elongational softening can also be explained by stronger damping and smaller degree of recovery (Takahashi et al., 1999). Figure IV.5 shows that strain-softening increases with increasing elongation rates. The effect of hemp and MAPP contents is discussed next.
Figure IV.4 Transient viscosity ($\eta_s^*$) as a function of time for neat PP at 180°C and different strain rates. The line represents Trouton’s law obtained from shear transient data.
Figure IV.5 Elongational viscosity ($\eta^*$) as a function of time for PP-H30-MAPP at 180°C and different strain rates.

At a strain rate of $10 \text{s}^{-1}$, the effect of hemp concentration is illustrated in Figure IV.6 which represents the elongational viscosity as a function of time for different compositions of PP/Hemp/MAPP. As shown in Table IV.6, the maximum stress increases and the strain at break decreases with increasing hemp content. From the neat PP to the PP-H30-MAPP, the increase in maximum stress is about 30% while the strain at break decreased around 65%. Here again, the effect of MAPP depends upon the reinforcing or plasticizing effects since an inversion also occurs around 20% hemp.
Figure IV.6 Elongational viscosity ($\eta^*$) as a function of time at 10 s$^{-1}$ for different compositions of PP/Hemp/MAPP at 180°C.
Table IV.6 Maximum stress and strain at break for PP/Hemp/MAPP composites at 10 s\(^{-1}\).

<table>
<thead>
<tr>
<th>Samples</th>
<th>With MAPP</th>
<th>Without MAPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-H30</td>
<td>97.6 / 1.0</td>
<td>93.2 / 1.1</td>
</tr>
<tr>
<td>PP-H20</td>
<td>84.7 / 1.2</td>
<td>84.5 / 1.3</td>
</tr>
<tr>
<td>PP-H10</td>
<td>77.1 / 1.5</td>
<td>81.3 / 1.4</td>
</tr>
<tr>
<td>PP</td>
<td>-</td>
<td>75.1 / 2.9</td>
</tr>
</tbody>
</table>

At a strain of 0.5, which represents a strain before the overlap between the composite curves with and without MAPP, the elongational viscosity as a function of strain rate is presented in Figure IV.7, while Table IV.7 reports on the power-law parameters (Twite-Kabamba and Rodrigue, 2008) as obtained from Equations (IV.1-4). From neat PP to PP-H30-MAPP, the consistency index \( M \), which is related to melt strength, increased by 240%. The addition of hemp slightly decreased the power-law index \( N \). Lower power-law index values indicate higher melt strength decreases with increasing strain rates. The presence of MAPP in the composites decreased even more the power-law index.
Figure IV.7 Elongational viscosity ($\eta'_E$) as a function of strain rate for different compositions of PP/Hemp/MAPP at 180°C and $\epsilon = 0.5$. 
<table>
<thead>
<tr>
<th>Sample</th>
<th>$M$ (kPa.s$^N$)</th>
<th>$N$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-H30-MAPP</td>
<td>28.2</td>
<td>0.56</td>
</tr>
<tr>
<td>PP-H30</td>
<td>23.8</td>
<td>0.63</td>
</tr>
<tr>
<td>PP-H20-MAPP</td>
<td>18.9</td>
<td>0.68</td>
</tr>
<tr>
<td>PP-H20</td>
<td>18.3</td>
<td>0.70</td>
</tr>
<tr>
<td>PP-H10-MAPP</td>
<td>14.3</td>
<td>0.69</td>
</tr>
<tr>
<td>PP-H10</td>
<td>14.8</td>
<td>0.70</td>
</tr>
<tr>
<td>PP</td>
<td>8.20</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table IV.7 Elongational power-law parameters ($M$, $N$) for PP/Hemp/MAPP composites (180°C).
IV. 4 CONCLUSION

In this study, the rheological properties in both shear and elongation have been reported for PP/Hemp/MAPP composites in the melt state. From the results obtained, several conclusions can be drawn.

Under shear stress, increasing hemp concentration increased the crossover modulus ($G_c$) and frequency ($\omega_t$) of the composites without MAPP, while the presence of MAPP enhanced the values except for the 20%wt composite (PP-H20-MAPP). Using a modified Carreau-Yasuda model, the yield stress and the zero shear viscosity increased with hemp concentration and the effect of MAPP was to decrease the values of the parameters in the power-law region ($\lambda$, $a$ and $n$).

Under elongational stress, the composites exhibit a strain-softening behaviour indicating a loss of elasticity. Increased hemp content leads to higher values of the consistency index and the maximum stress which can be related to the rigidity and the orientation of the fibres in the flow direction.

Finally, the presence of MAPP was found to be the origin of two competing effects: matrix plasticizing and fibre/polymer adhesion enhancing. The balance between both effects determines the final behaviour of the composite. In our case, a critical hemp concentration of 20% was found to represent a balance between both effects under the conditions studied.
Chapter V

Properties of Recycled LDPE/Birch Fibre Composites*

RÉSUMÉ

Cette étude examine les propriétés d'un matériau composite de fibres de bois/plastique soumis à un processus de recyclage. En particulier, on étudie l'influence des fibres sur le degré de dégradation du matériau. À cette fin, le polyéthylène de basse densité (LDPE) a été choisi comme matrice et la fibre de bouleau jaune comme renfort. Jusqu'à 10 générations de recyclage ont été effectuées sur une ligne d’extrusion sous des conditions maintenues constantes. Pour chaque génération, des analyses thermiques, rhéologiques et morphologiques ont été réalisées en combinaison avec des analyses macromoléculaires incluant la distribution de poids moléculaires du LDPE. Les résultats ont révélé que la cristallinité du composite augmentait avec le nombre de régénération, tandis que la viscosité en cisaillement diminuait avec le nombre de recyclage. La rhéologie en élongation a également révélé un comportement dit ‘rhéo-épaississant’ pour le polymère et un comportement dit ‘rhéo-fluidifiant’ pour le composite. De l'analyse morphologique, un coefficient de sévérité de la dégradation a été défini pour caractériser l'impact des conditions d'opération sur la longueur des fibres. Enfin, les analyses macromoléculaires ont montré que le poids moléculaire moyen en nombre (Mn) a été plus sensible que le poids moléculaire moyen en masse (Mw) au processus de recyclage. Le taux de branchement relatif, ainsi que le taux de branchement, ont également été modifiées par l'effet du recyclage en présence ou non de fibres de bois.
ABSTRACT

This study investigates how the properties of a wood polymer composite are modified by recycling, especially how the presence of fibres modify polymer degradation. To this end, low density polyethylene was selected as the matrix and yellow birch fibres as the reinforcement. The effect of recycling was simulated via closed-loop reprocessing of the material up to ten times under constant extrusion conditions. For each generation, thermal, rheological and morphological measurements were combined with macromolecular investigations including the complete molecular mass distribution of the polymer. The results revealed that polymer crystallinity increased with the number of composite regeneration, while the zero-shear viscosity decreased with recycling. Elongational rheology also revealed that the behaviour of the polymer changed from strain hardening to strain softening for the composite. From the morphological analysis, a degradation severity coefficient was defined to characterize the impact of operating conditions on fibre length. Finally, macromolecular investigations showed that the number-average molecular mass (Mn) was more affected than the weight-average molecular mass (Mw). The relative branching factor and the branching frequency were also modified by the effect of reprocessing with and without the presence of wood fibre.

*Eddy Twite-Kabamba, Zineb Fassi Fehri and Denis Rodrigue, accepted in Progress in Rubber, Plastics and Recycling Technology (2010).
V.1 INTRODUCTION

The importance of composites based on natural fibres is growing every day with the number of new applications found for these materials. Their low cost, lower densities and availability combined to their interesting mechanical properties give them advantages over classical composites based on glass fibre in terms of sustainable development. Indeed, fibres from cotton, flax, hemp, sisal, jute, agave, kenaf or any vegetal are now used at industrial scale in areas such as automotive, aeronautic and home appliances (Mohanty et al., 2005). In order to expand the use of natural fibres in manufacturing new composite materials, wood fibre is one readily available source. As a special case, yellow birch fibres usually encountered in pulp and paper industries (Law et al., 1999; Seisto and Poppius-levlin, 1997), can be used due to their availability. The most interesting characteristics of these fibres are lower cost and good moisture resistance. They are also ecological and recyclable. For the moment, polymer composites based on yellow birch fibres are generally used in building and furniture (www.craftsman-style.info).

Although natural fibre based composites production and studies are still increasing, the recycling of these composites is much less investigated. Since the materials produced today will reach their end of life in the near future, the recycling of these materials must be studied in order to reach sustainability of resources and lower material accumulation (Boffat, 1996).

Several studies on composite materials based on natural fibre are available, especially on mechanical and morphological properties (De Arcaya et al., 2009; Hristov and
Vlachopoulos, 2007; Leblanc et al., 2006; Mishra et al., 2004; Mechraoui et al., 2007). Unfortunately, very few of them focused on their recycling. Moran and coworkers (Moran et al., 2007) investigated the effect of multiple extrusion cycles (up to 5 cycles) on the mechanical properties of polypropylene/natural fibre composite. The natural fibre used was flax at a concentration of 20 wt%. It was shown that thermo-mechanical degradation caused by processing induced polymer chain scissions and decrease fibre dimensions, especially fibre length. This combined effect was responsible for higher elastic modulus and lower strength in both flexural and tensile tests. The authors supposed that the main parameter affecting composite properties was the mixing quality and the fibre modulus instead of fibre aspect ratio and/or fibre diameter. They also concluded that polymer crystallinity was not modified. Each composite also had good impact performance and exhibited acceptable mechanical response especially for the elastic modulus which was higher than neat polypropylene for all generations. They concluded that recycled composite materials based on natural fibres can be used for industrial applications, with good results when using a compatibilizer. On the other hand, Gosselin and coworkers (Gosselin et al., 2006) investigated the mechanical properties of composites based on recycled polyolefins (HDPE/PP in a ratio of 85/15) reinforced with yellow birch fibres (up to 40 wt%). Using injection moulding, they produced composites and composite foams with azodicarbonamide (ACA) as a blowing agent (up to 1.5 wt%). Their results showed that using a coupling agent up to 10 wt% (maleic-anhydride-polypropylene, MAPP) led to significant increase of both specific complex moduli (modulus per unit weight) in flexion and torsion with birch fibre content. Their results also showed that the specific Young's moduli in tension increased with fibre concentration with an optimum around 20-30 wt%,
while the elongation at break increased at low fibre concentration, but decreased with foaming (density reduction) and MAPP addition.

Based on the limited amount of information available on natural fibre composite recycling, the aim of this study is to determine how natural fibre composites can be reused as a sustainable material regarding to their behaviour in the recycling process. A focus is made here on low density polyethylene (LDPE)/yellow birch fibre composites. Although the main characterizations are on rheological and molecular properties of the materials, thermal and morphological analyses are also presented. The investigation includes up to ten extrusion cycles for both the polymer matrix and the composite to determine the effect of wood fibres in the recycling process. In order to limit the experimental work, only one fibre concentration (15% wt.) was used.

V.2 MATERIALS and EXPERIMENTAL

V.2.1 Materials

Yellow birch fibres, with a bulk density of 670 kg/m³, were provided as a residue of Canadian wood industries. The fibres were sieved upon arrival and dried (100°C for 24 h) to reduce moisture. The fibre sizes, as measured by optical microscopy, had length (L) of 1110±420 μm with a diameter (D) of 320±140 μm, giving an average L/D ratio of 3.5. As the matrix, low density polyethylene (Novapol-LA-0224-A) from Nova Chemicals with a density of 924 kg/m³ and a melt index of 2.3 (190°C/2.16 kg) was used.
V.2.2 Composite processing

A co-rotating twin-screw extruder (Haake Rheomex TW-100) was coupled with a cylindrical die (1.5 mm in diameter with L/D=1), a cooling water bath (room temperature) and take-off rolls to collect the extruded strand (draw speed of 4 cm/s). The temperature profile in the extruder was set to 110°C in the feeding zone, 140°C in the compression zone, 170°C in the metering zone and 150°C at the die. The extrusion screw speed was constant at 40 rpm giving a flow rate of 0.55 kg/h. The composite strands were finally pelletized and ready to be reintroduced in the extruder under the same processing conditions. This closed loop recycling of the material was repeated up to ten times to follow the matrix and fibre degradation with processing. As a base for comparison, the polymer matrix alone followed the same processing treatment to determine the effect of adding fibres in recycling a thermoplastic resin.

V.2.3 Thermal analysis

A Perkin Elmer DSC 7 was used to carry out differential scanning calorimetry (DSC) analysis to determine the melting and crystallization temperatures, as well as their respective enthalpy. All the samples were heated from 60°C to 150°C and cooled down from 150°C to 60°C after a holding time of 2 minutes at 150°C. The temperature ramps were performed at 10°C/min.
V.3 RHEOLOGY

V.3.1 Shear Rheology

From the extruder pellets, rectangular samples were compression moulded via a hydraulic press (Carver Laboratory Press Model C). The moulding conditions were a heating time of 5 min at 150°C and a cooling time of 5 min under a pressure of 3 tons. A parallel plate geometry on an ARES rheometer (Rheometric Scientific) was used to study the rheological properties of the materials under shear. The tests were made on disc samples of 25 mm in diameter with a gap of 1.5 mm. Measurements were done in the dynamic oscillatory mode using a strain of 3% to stay in the linear viscoelastic zone for both the composites and polymer matrix. Different temperatures (140, 160 and 180°C) were selected to build a rheological master curve using the time-temperature superposition principle, which also enables to determine the flow activation energy ($E_a$) given by an Arrhenius (Collier et al., 2006) relation (Eq. V.1):

$$a_T = \exp \left[ \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (V.1)$$

where $a_T$, $E_a$, $R$, $T$ and $T_0$ are the temperature shift factor, the flow activation energy, the universal gas constant, the given temperature and the reference temperature respectively.

The chosen reference temperature was 160°C and the data were fitted at this reference temperature to the Carreau-Yasuda viscosity equation (Eq. V.2):
\[ \eta(\omega) = \eta_0 \left[ 1 + (\lambda \omega)^a \right]^{(n-1)/a} \]  

(V.2)

where \( \eta_0 \) is the zero shear viscosity, \( \lambda \) is a material time constant, \( a \) is the Yasuda parameter and \( n \) is the power-law index.

V.3.2 Elongational Rheology

The SER-HV-A01 model of the SER Universal testing Platform from Xpansion Instruments (Sentmanat et al., 2005) was used for uniaxial elongation tests. The SER unit is a dual windup extensional fixture and elongational data were obtained by measurement of the transient elongational viscosity after application of a constant strain rate. The tests were carried out at a temperature of 150°C on rectangular samples with dimensions of about 17 x 10 x 1.2 mm. In the limits of the transducer sensibility and for the reason of more clarity of figures, rheological measurements were only carried out at the higher strain rates and data treatment was done as described in previous works (Twite-Kabamba and Rodrigue, 2008; Twite-Kabamba et al., 2009). The parameters reported in this study are the maximum stress and the strain at break.

V.3.3 Morphological Investigations

To determine the fibre size distribution after each generation, the pellets were dissolved in 1,2,4-trichlorobenzene (TCB) at 140°C. The solution was then filtered to extract the fibres
which were dried before measuring their sizes by means of an optical stereo-microscope (Olympus SZ-PT). Image analysis was done via the Image Pro-Plus software.

V.3.4 Macromolecular Investigations

To quantify the degradation of the polymer matrix, its molecular mass distribution (MWD) was characterized. The data were obtained with an approximate error of 5%, via gel permeation chromatography (GPC) on a Model 350 High Temperature Triple Detector Array (HT-TDA) from Viscotek (Malvern Company). This equipment includes a Differential Refractive Index (RI) detector, a four-capillary Differential Viscometer detector and a Low Angle Light Scattering (LALS) detector. The solvent was 1,2,4-trichlorobenzene (TCB) stabilized by 2,6-Di-tert-butyl-4-methylphenol. The data were obtained at a flow rate of 1.00 ml/min at 140°C. Two PL gel columns made from styrene divinyl benzene copolymer particles with a diameter of 10 μm and a length/internal diameter of 300/75mm were used. The sensitivity range of the HT-GPC was comprised between $10^4$ and $10^7$ Da in Mw. Polymer concentration of the samples was between 2 and 4 mg/ml and calibration was made with two polystyrene (PS99K and PS280K) and one polyethylene (PE1475) standards in the same range of concentration. By using the OmniSec GPC software, several parameters were calculated: the number average molecular mass (Mn) and the weight average molecular mass (Mw) to get the polydispersity index (PI = Mw/Mn). Also, determination of branching and branching frequency was based on the Zimm-Stockmayer model (Eq.V.3) for a Random, Tri-Functional Monodisperse polymer as (Drott, 1977):
\[ g_M = \left[ \left( 1 + \frac{B_M}{7} \right) \frac{1}{2} + \frac{4B_M}{9\pi} \right]^{-1/2} \]  

(V.3)

where \( g_M \) is the ratio of intrinsic viscosity (IV) of a linear and branched polymer and \( B_M \) is the number of branches. The calculations were done using the PE1475 standard as the linear reference, a structure factor of 0.75 and a repeat factor of 14 000.

It is also known from the work of Zimm and Stockmayer (Zimm and Stockmayer, 1949) that the radius of gyration of a long chain branched macromolecule (\( R_b \)) is smaller than that of a linear macromolecule (\( R_l \)) containing the same number of repeating units. The ratio of the radii, \( g = \frac{R_b}{R_l} \) is called the branching factor. The authors developed formulae for the value of \( g \) for various branched and cyclic polymer molecules. The ratio of the intrinsic viscosity of a long-chain branched polymer \([\eta]_{br}\) to that of a linear polymer \([\eta]_l\) of the same molar mass can be calculated according to (Eq.V.4):

\[ \frac{[\eta]_{br}}{[\eta]_l} = g^\varepsilon \]

(V.4)

where \( \varepsilon \) is a constant experimentally determined by Foster and coworkers (Foster et al., 1980) to be 0.75 for long chain branched polyethylene with tri-functional branching points. In this study, we defined the relative branching factor as the ratio of the branching factor of the polymer or composite over the value of the virgin polymer (no processing).
V.4 RESULTS and DISCUSSION

V.4.1 Thermal Analysis Results

First, the crystallinity of the samples was studied. The crystallinity degree (Eq. V.5) was estimated as:

\[
\chi_c = \frac{H_m}{H_m^*} \times 100
\]  

(V.5)

where \( H_m \) is the melting enthalpy, \( \chi_c \) is the crystallinity degree, and \( H_m^* \) is the melting enthalpy of 100% crystalline polyethylene taken as 288 J/g (Luyt and Hato, 2005). Table V.1 shows that the melting point of the different generations remains between 111°C and 113°C for the polymer, and between 112°C and 115°C for the composites, which can be considered to be almost constant within experimental uncertainty. On the other hand, the crystallinity degree of the polymer does not show significant changes, but the composites display some changes with the number of generations. The presence of fibres does not improve crystallite formation and growth at first and crystallinity decreases. Furthermore, for the first generations (from the first to the 6th), the composite crystallinity rate decreases in comparison with that of polymer because crystallite growth is limited by the presence of fibres impeding long polymer chains mobility. But for later generations (from 8th to 10th), trans-crystallinity (Berzin et al., 2001) due to the presence of increasing number of small fibres and smaller polymer chains (due to the breaking of fibres and long polymer chains with the number of regeneration) seems to occur. This trans-crystallinity is responsible of the increasing of crystallinity degree of those generations.
Table V.1. Thermal properties of the recycled polymer matrix / recycled composites.

<table>
<thead>
<tr>
<th>Generation (-)</th>
<th>Melting temperature (°C)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Polymer / Composite</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>111.8 / -</td>
<td>26.9 / -</td>
</tr>
<tr>
<td>2</td>
<td>112.8 / 112.0</td>
<td>28.6 / 20.4</td>
</tr>
<tr>
<td>4</td>
<td>113.4 / 113.1</td>
<td>29.0 / 21.5</td>
</tr>
<tr>
<td>6</td>
<td>111.7 / 111.4</td>
<td>29.5 / 23.8</td>
</tr>
<tr>
<td>8</td>
<td>112.9 / 115.0</td>
<td>30.9 / 31.1</td>
</tr>
<tr>
<td>10</td>
<td>111.8 / 114.3</td>
<td>29.8 / 30.4</td>
</tr>
</tbody>
</table>

V.4.2 Rheological Results

V.4.2.1 Shear Rheology

The Carreau-Yasuda viscosity model was used to describe the rheological behaviour of the different generations of polymer and composite. Typical viscosity curves are presented in Figures V.1-2 and the fitting parameters (For Eq.V.2) are reported in Tables V.2-3.
Figure V.1. Complex viscosity of selected polymer generations as a function of frequency at 160°C.
Figure V.2. Complex viscosity of selected composite generations as a function of frequency at 160°C.

The Arrhenius relation (Eq.V.1) was used to calculate with a correlation coefficient ($R^2$) of 0.998, the flow activation energy ($E_a$) represented in Table V.2 for selected generations of polymer and composite. Higher the flow activation energy is, lower is the temperature dependence of viscosity. From Table V.2, the regeneration process decreases the flow activation energy meaning that the increase of the temperature dependence of viscosity occurs. From the second generation to the tenth generation, a decrease of about 24% in the case of polymer and of about 30% in the case of composite was observed. On the other hand, an increase from the polymer to the composite at least of 30% was observed at each
regeneration indicating that the fibre presence reduces the dependence temperature of viscosity.

Table V.2. Flow activation energy ($E_a$) of selected generations of polymer/composite

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_a$ (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generation-2</td>
<td>56.33/78.62</td>
</tr>
<tr>
<td>Generation-6</td>
<td>50.57/67.49</td>
</tr>
<tr>
<td>Generation-10</td>
<td>42.74/55.26</td>
</tr>
</tbody>
</table>

Table V.3 shows for the polymer matrix, that the zero shear viscosity decreases with the number of generation, indicating that the polymer structure is changing, mostly due to lower chain entanglements related to chain break. From the first to the tenth generation, $\eta_0$ decreased by 30%. The other parameters (Berzin et al., 2001) related respectively to the onset of shear thinning or the time relaxation ($\lambda$), the width of the transition region between the zero-shear-rate region and the power-law region ($a$), as well as the degree of shear-thinning at high shear rate ($n$) did not display significant differences between each generation. This indicates that the main modification in the polymer is in chain entanglement (low shear zone) rather than main backbone chain breaking (high shear rates) according to the specific operation conditions used in the extruder.
Table V.3. Carreau-Yasuda parameters for the polymer matrix / the composites

<table>
<thead>
<tr>
<th>Generation</th>
<th>$\eta_o$ (kPa.s)</th>
<th>$a$</th>
<th>$\lambda$ (s/rad)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (virgin)</td>
<td>20.9/-</td>
<td>0.76/-</td>
<td>3.88/-</td>
<td>0.42/-</td>
</tr>
<tr>
<td>2</td>
<td>19.3/34.6</td>
<td>0.81/0.54</td>
<td>4.02/4.70</td>
<td>0.43/0.39</td>
</tr>
<tr>
<td>4</td>
<td>18.4/30.8</td>
<td>0.76/0.51</td>
<td>3.85/4.47</td>
<td>0.44/0.40</td>
</tr>
<tr>
<td>6</td>
<td>17.1/28.4</td>
<td>0.79/0.56</td>
<td>4.13/4.34</td>
<td>0.42/0.39</td>
</tr>
<tr>
<td>8</td>
<td>16.8/24.2</td>
<td>0.86/0.58</td>
<td>4.37/4.26</td>
<td>0.45/0.41</td>
</tr>
<tr>
<td>10</td>
<td>14.7/19.7</td>
<td>0.83/0.61</td>
<td>4.57/3.93</td>
<td>0.43/0.42</td>
</tr>
</tbody>
</table>

For the composites, the parameters of the Carreau-Yasuda model are also shown in Table V.3. The zero-viscosity of the composites is higher than that of the polymers due to the presence of fibre, but the difference decreases with regeneration; the value is about 80% higher for the first generations and decreases down to 35% for the tenth generations. Similarly, the other model parameters ($\lambda$, $a$ and $n$) are in general lower than those of the polymer because of fibre rigidity decreases elasticity and fluidity of the material. Nevertheless, although the values did not change for all composite generations, unlike in the polymer case, indicating that the fibres are more important in controlling the shear
rheology of the composites. It is interesting to see that decreasing fibre length has an impact on $\lambda$ which is related to the relaxation time of the material. The more fibre length decreases, the more time relaxation decreases, indicating that composite elasticity at constant fibre concentration increases with decreasing fibre size (Takahashi et al., 1999).

**V.4.2.2 Elongational Rheology**

As shown in Figure V.3, the expected strain hardening behaviour was exhibited for the low density polyethylene matrix alone. It is clear that elongational viscosity slightly decreased with recycling. Table V.4 reported on the maximum stress and the strain at break of the LDPE. From the second to the tenth generation, the decrease in maximum stress was about 26% and the strain at break did not change.
Figure V.3. Elongational viscosity of selected polymer generations as a function of time for a strain rate of 10 s$^{-1}$ and a temperature of 150$^\circ$C.

Table V.4. Maximum stress (MPa) and Strain at break (-) of selected polymer generations under elongational rheology tests.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum stress (MPa)</th>
<th>Strain at break (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generation-2</td>
<td>1.63</td>
<td>4.3</td>
</tr>
<tr>
<td>Generation-6</td>
<td>1.47</td>
<td>4.3</td>
</tr>
<tr>
<td>Generation-10</td>
<td>1.19</td>
<td>4.2</td>
</tr>
</tbody>
</table>
On the other side, the composites exhibited strain softening as shown in Figure V.4. This behaviour is related to the presence of wood fibres which have very low elasticity (Twite-Kabamba et al., 2009). In this case, the maximum stress was almost three decades lower than its neat polymer matrix and the decrease from the second to the tenth generation was about 46% as shown in Table V.5. Once again, the strain at break did not change with regeneration, but the values are much lower indicating lower melt elasticity (Takahashi et al., 1999).

![Elongational viscosity of selected composite generations as a function of time at a strain rate of 10 s⁻¹ and a temperature of 150°C.](image)

**Figure V.4.** Elongational viscosity of selected composite generations as a function of time at a strain rate of 10 s⁻¹ and a temperature of 150°C.
Table V.5. Maximum stress (kPa) and Strain at break of selected composite generations under elongational rheology tests.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum stress (kPa)</th>
<th>Strain at break (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generation-2</td>
<td>2.10</td>
<td>2.0</td>
</tr>
<tr>
<td>Generation-6</td>
<td>1.86</td>
<td>2.0</td>
</tr>
<tr>
<td>Generation-10</td>
<td>1.13</td>
<td>2.1</td>
</tr>
</tbody>
</table>

V.4.3 MORPHOLOGICAL RESULTS

As presented in Figure V.5, fibre length significantly decreased with the number of regenerations. In general, more degradation was observed in the first generation and the value tends to level off after the 6th generation. On the other hand, fibre diameter, as shown in Figure V.6, was more stable with a very small decrease with the number of generations.
Figure V.5. Fibre length as a function of regeneration. The line represents the fit to Eq.(V.6) with the parameters of Table V.6.
Figure V.6. Fibre diameter as a function of regeneration.

The results of Figure V.6 may indicate that elongational strains in the extruder were almost entirely transferred to the matrix, meanwhile the shear strains were acting on the wood fibre to cause break-up. This can explain the exponential decrease of fibre length because longer fibres have more possibilities to break. To modify changes in fibre length, the use of a coupling agent may improve the transfer of shear stress to the matrix (Gosselin et al., 2006). From the data of Figures V.5-6, the L/D ratio of the fibres should have the same behaviour as the fibre length with the number of generations due to the very weak changes in fibre diameter. The results also indicate that without coupling agent addition, there is an optimum fibre size for stress transfer between the matrix and the fibres under given process conditions. Based on Figure V.5, a negative exponential law as proposed by Twite and
coworker (Twite-Kabamba and Rodrigue, 2008) is used to estimate fibre length decrease as (Eq.V.6):

\[
\frac{L - L_\infty}{L_0 - L_\infty} = e^{-\alpha N}
\]

where \(N\) is the number of generations, \(L\) the fibre length, \(L_0\) the initial fibre length and \(L_\infty\) the minimum fibre length after an infinite number of generations. The parameter \(\alpha\) is called the degradation severity coefficient and was determined using the non-linear regression package of SigmaPlot software. The values for each parameter are reported in Table V.6 for the conditions tested.

<table>
<thead>
<tr>
<th>(L_0) ((\mu m))</th>
<th>(L_\infty) ((\mu m))</th>
<th>(\alpha)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1117</td>
<td>236</td>
<td>0.262</td>
<td>0.999</td>
</tr>
</tbody>
</table>

A relation between the processing conditions and the final material's properties should be possible. In this case, the degradation severity coefficient \((\alpha)\) can estimate how fast the process modifies or degrades the composite properties. Thus, higher \(\alpha\) values correspond to faster fibre length degradation with the number of generations. For a given composite and under specific processing conditions (temperature profile, flow rate, screw speed, etc.), the value of \(\alpha\) could be determined. Since only one set of condition was used here, it is not
possible to propose a relation of this kind, but more work is under way and the results will be reported in a future paper. Nevertheless, since fibre concentration was maintained constant here, fibre degradation produced higher specific surface area between the matrix and the fibre is created. Furthermore, reprocessing the material causes better mixing and both factors increased the total contact area between the polymer and the fibre. This fact should lead to better stress transfer in both shear and elongation. This should also lead to better homogeneity of the composite and may improve the properties although the fibre aspect ratio (L/D) decreases (Kalaprasad et al., 2004). Both phenomena are in competition and the final properties of the composites are a balance between several parameters related to processing, composition and morphology.

V.4.4 Macromolecular Investigations

First, the GPC data for the virgin polyethylene, which served as the matrix for both composite and polymer regeneration, are represented in Table V.7. These data can be considered as the reference values for the different macromolecular characteristics allowing to determine any changes or degradation related to processing.

<table>
<thead>
<tr>
<th>LDPE</th>
<th>M_w (kDa)</th>
<th>M_n (kDa)</th>
<th>PI</th>
<th>M_z (kDa)</th>
<th>[η] (dl/g)</th>
<th>Rh (nm)</th>
<th>BF (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NovaPol 0224-A</td>
<td>185.1</td>
<td>18.5</td>
<td>10</td>
<td>534.6</td>
<td>0.72</td>
<td>11.1</td>
<td>27.46</td>
</tr>
</tbody>
</table>
In Table V.7, $M_w$ represents the weight-average molecular mass, $M_n$ the number-average molecular mass, $\Pi$ the polydispersity index, $M_z$ the Z-average molecular mass, $IV$ the intrinsic viscosity, $R_h$ the hydrodynamic radius and $BF$ is the branching frequency.

As expected, the molecular mass distribution of the polymer matrix was modified by the thermo-mechanical history of the material and the results are presented in Figures V.7-10. The first observation is that changes in the molecular mass distribution are small due to low energy input for processes done at a laboratory scale. In our case, the weight average molecular mass ($M_w$) in Figure V.7 changed slightly with regeneration, while Figure V.8 showed that the number average molecular mass ($M_n$) decreased continuously from the first to the 10th generation. Overall, the decrease was of 17% and 4% for the polymer matrix and the composite respectively in $M_w$ and a decrease of 30% in $M_n$ for both composite and polymer matrix from the first to the tenth generation. These results indicated that chain scission occurred mainly on the molecules having the longest chains which led to a greater change in $M_n$ than in $M_w$ (Viekbke et al., 1996). Furthermore, the average decrease in $M_w$ is around 10%, while it was around 15% for $M_n$ from polymer to composite for all regenerations. Most of this reduction could be attributed to the presence of birch fibre which increased mechanical stresses (higher viscosity) in processing. Thus the presence of fibre enhanced polymer chains scission during the process.

From the work of Strömberg and Karlsson (2009), polymer degradation in any process could lead to the formation of macro-radicals which could interact with each other producing new branchings or even new cross-linkings. This could explain, as shown in Figures V.9 and V.10, the results for the relative branching factor and the branching frequency as a function of number of generation. In these Figures, the composites exhibited
lower relative branching factor and higher branching frequency than the polymer alone. If there were no significant differences between each regenerations of polymer or composite, the decrease of relative branching factor for all composite regenerations was about 21% less than for the neat polymer, while the branching frequency increased by about 36% between the neat polymer and the composite for all regenerations. This indicated that the fibre, in its role to promote chain scission in reprocessing, enhanced the production of macro-radical allowing chain branching to occur (Hamielec et al., 1991).

Figure V.7. Weight-average molecular mass (M_w) as a function of generation number for the polymer and composite.
Figure V.8. Number-average molecular mass ($M_n$) as a function of generation number for the polymer and composite.
Figure V.9. Relative branching factor as a function of generation number for the polymer and composite.
Figure V.10. Branching frequency as a function of generation number for the polymer and composite.

In our case, the macromolecular investigation showed the effect of wood fibres on the polymer matrix degradation process under given operating conditions. The main observation was that the fibres contributed significantly to chain breaking and therefore modified all properties of the material especially number-average molecular mass, branching factor and branching frequency. Nevertheless, more work is under to determine the effect of other parameters like fibre content, fibre type and processing conditions to get a more complete picture of the situation.
V.5 CONCLUSION

From this investigation, the properties of yellow birch fibres/low density polyethylene composites were studied during a recycling process. Using ten passes in a closed-loop extrusion process under fixed operating conditions, differences were observed between the neat polymer and the composite.

First, thermal characterizations allowed to detect the phenomenon of trans-crystallinity due to the fibre presence and its role to promote crystallinity.

Second, the shear rheological properties revealed that while the zero shear viscosity of the neat polymer decreased by about 30% from the first to the tenth regeneration, the value for the composite decreased by 40%. As expected, fibre addition increased the zero-shear viscosity of the composites in comparison with the polymer for every generation. This increase was about 80% for the first generations and drops to 35% for the last generation. It was also found that the other parameters of the Carreau-Yasuda viscosity model were not significantly influenced for both polymer and composite. It was also mentioned the effect of fibre presence on the dependence temperature of viscosity: the fibre presence increased the flow activation energy of more than 30%. On the other hand the regeneration process decreased the flow activation energy of about 24% for the polymer and of about 30% for the composite.
Third, the elongational rheology investigations revealed a major difference between the neat polymer and the composite. A strain-hardening behaviour was obtained for the neat polymer which strength decreased by about 26% from the first generations to the last generation. On the other hand, a strain-softening behaviour was obtained for the composite with a decrease of about 46% from the first generations to the last generation. It was also observed the maximum stress of the composite was almost three orders of magnitude lower than the neat polymer, while no significant changes in the strain at break was observed for both polymer and composite.

Fourth, the morphological investigations revealed that the fibre diameter was not affected by regeneration, but fibre length decreased with recycling up to the sixth generation while the value levelled off. The results obtained allowed to establish a negative exponential law to predict the decrease of fibre length generation number through the introduction of a degradation severity coefficient. This lumped parameter was used to characterize the impact of all operating conditions (complete thermo-mechanical history) on final fibre size.

Finally, the macromolecular characterization through GPC clearly showed a decrease of the number-average molecular mass, which was more affected than the weight-average molecular mass. The decrease was of 17% and 4% for the polymer matrix and the composite respectively in Mw and of 30% in Mn for both composite and polymer matrix from the first to the tenth generation. The fibre presence had the effect to decrease further the polymer by about 15%. The branching factor and the branching frequency were also
investigated. The results revealed a branching factor increase of about 36% from the polymer to the composite for all regenerations, and a branching frequency decrease of about 21% from the polymer to the composite for all regenerations, meanwhile no significant change was observed between each regeneration for both polymer and composite. It was also shown that the presence of wood fibres coupled with the thermomechanical energy introduced by the reprocessing of the material enhanced the production of macro-radicals, which led to higher branching frequency and lower relative branching factor. Although interesting results are presented here, work needs to be done to get more information of the quantitative effect of each parameter on the final properties of the recycled wood/polymer composite.
Chapter VI

General Conclusions and Recommendations

This thesis provided a better understanding on how a polymer loses its performances during degradation or recycling, and pointed out changes in melt and macromolecular properties, which are directly related to their solid properties.

Two kinds of materials were studied and led to different conclusions for each one:

A. For polymer foams, elongational rheology was found to be a good tool to predict the foamability of polymer with parameters like the Strain Hardening Factor (SHF) or the Strain Hardening Ratio (SHR). Decreases in foamability were detected by increased cell size, which can be attributed to cell coalescence. The degradation process could be modeled by an exponential law to express the decrease of cell density. Parameters like the foamability lost coefficient related to the operation conditions can better characterize the severity of the degradation process during the recycling. Furthermore, it was shown that foaming increases the thermo-mechanical strains on the polymer matrix while processing. On the other hand, the polymer degradation was studied to better understand the macromolecular changes occurring during the degradation process. In the batch mixer and under specific processing conditions, the polymer exhibited a competition between chain scission and chain branching induced by the production of macro-radicals. Parameters such as power and energy inputs allowed to investigate the predominance of chain scission or chain branching, while elongational rheology described the predominant role of
long chains branching which were more affected in the degradation process. This investigation established how complex is the phenomenon and the challenges to build an accurate and comprehensive model to predict the degradation degree of plastic materials submitted to the recycling process.

B. For composites based on natural fibre, rheological investigations of PP/Hemp/MAPP composites revealed some interesting aspects of the role of coupling agent and fibre concentrations. Shear rheology exhibited a competition between matrix plasticizing effect and fibre/polymer adhesion enhancing requiring investigations on an optimum ratio concentration between coupling agent and fibre contents for a given matrix in the mixing process. Elongational rheology displayed a strain softening behaviour induced by weaker composite elasticity. In both shear and elongational rheologies, the higher was the fibre concentration, the higher were the properties such as yield stress, zero shear viscosity, as well as maximum stress and consistency index which are related to fibre rigidity and orientation.

On the other hand, recycling of yellow birch fibres/LDPE composites was studied and rheological and macromolecular properties were investigated. The fibre presence in shear rheological tests revealed an effect on the zero shear viscosity and the flow activation energy: both decreased with the number of regeneration and remained higher than those of neat polymer submitted to the same recycling process. Meanwhile, a strain hardening behaviour was observed for the neat polymer and the fibre presence induced a strain softening behaviour in elongational rheology investigations. In both shear and elongational rheologies, an increased loss of properties was obtained for the composites. The macromolecular properties were more affected by a decrease of the number-average molecular mass than the weight-
average molecular mass with the number of regeneration. Other parameters such as
the branching factor and the branching frequency were also investigated and
revealed the effect of fibre presence on the production of macro-radicals. As for
rheological investigations, macromolecular properties strongly changed in presence
of fibre. Also, the recycling process played a significant role on fibre size: a
negative exponential law was found to predict the decrease of fibre length with the
number of regeneration by introducing a degradation severity coefficient which is
related to the process conditions applied.

This thesis remains as a first step toward an efficient recycling process for both polymer
foams and composites. For polymer foams, due to the huge number of polymers, blowing
agents, nucleating agents and others additives used in different ways to foam the polymers,
more investigations are needed for a better understanding of the degradation process and to
know exactly how to predict the behaviour for different operating conditions. When
established, the competition between chain branching and chain scission is the next step
needing explanation; i.e. how to predict and quantify the predominance of chain scission
for a given degradation process under specific operating conditions. Also, investigations of
the melt state properties of recycled polymer foams aim at correlating the solid state
properties such as mechanical and morphological properties to macromolecular and
rheological properties. The challenge is to find accurate relationships despite of polymer,
blowing agent and nucleating agent types, operating conditions. There are certainly
interactions between each parameter here.
For polymer composites based on natural fibres, future works have to investigate different kinds of natural fibres under different operating conditions and types of processes. Nowadays, investigations are focused on new combinations of polymers and natural fibres because they are still trying to develop new materials like hybrids, but recycling is just beginning for many of them. This thesis was the first step and gave some interesting ways to improve recycling of natural fibre composites. Rheological properties can be used as a tool to improve expected performance such as mechanical properties: how to improve bonding between polymer and fibres, mixing time of composites and finding the optimal concentration of additives such as coupling agents. Like for polymer foams, composites based on natural fibres have to be more investigated for a deeper understanding of the degradation process for both polymer matrix and reinforcing fibres in a recycling process. This will enable to establish more accurate models allowing the prediction of the melt state properties and macromolecular behaviours during recycling or degradation processes. Also, to establish accurate correlations between solid state properties, such as mechanical properties, and melt state properties by using degradation models from rheological and macromolecular properties remains the challenge for the future.

Finally, the degradation of polymer foams and composites was studied at a laboratory scale. Validation of the models at larger scales must be done for more industrial applications where degradation is not only due to more severe operating conditions, but also environmental conditions and impurities.
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