Wheat Straw-Polypropylene Composites

by

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I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Composites are combinations of mainly two different components: the matrix and the filler/reinforcement. In the thermoplastic composites industry, natural fibers from agricultural crops have been emerged as alternative fillers. Crops such as wheat straw are renewable and low cost materials that, combined with thermoplastics such as polypropylene, provide engineering products with unique characteristics.

The objective of this study was to investigate the influence of processing conditions and composite formulation in the final properties of the composites. For these purposes wheat straw fibres and polypropylene (PP) were compounded in a batch mixer under a number of different thermal conditions and formulations. Fiber loading in the range from 0 to 60 wt-% was examined and the individual effects of two coupling agents (maleic anhydride modified polypropylene and maleic acid ethylene copolymer) and a lubricant were also studied. Particle size, morphology, thermal and mechanical properties and water uptake behaviour were inspected with appropriate techniques.

Wheat straw particle size distribution was studied through image analysis; distribution curves for length and width of the particles were recorded in two stages of the project: previous and after compounding the natural material with polypropylene. Morphology of wheat straw particles and wheat straw-polypropylene composites were analyzed by scanning electron microscopy (SEM). Thermal properties including melting temperature and crystallization temperature of composites and pure resin were obtained from differential scanning calorimetry (DSC) performed on the samples; percentage of crystallinity was also calculated from the heat of fusion obtained from those tests. Mechanical properties, such as flexural modulus and flexural yield strength, were accessed in a miniature materials tester. Water absorption of selected composite samples was evaluated after immersion of the samples in a water bath. Water absorption curves were used to calculate the water diffusion coefficient (diffusivity) of the composites.

Image analysis revealed the changes in the wheat straw structure due to shear forces during processing and improvement of adhesion between matrix and filler in compositions containing coupling agent. Small changes in the percentage of crystallinity of the thermoplastic phase were observed in all composites tested. Flexural tests revealed behaviour trends for the composites tested. Water uptake appeared to be a severe problem on natural fiber composites due to color fading, dimension instability and significant weight gains. Results from this work allowed the determination of some effects of processing temperature, fiber loading and use of additives on the final properties of wheat straw- polypropylene composites, thus making contributions to the scientific work that has been realized on natural fiber composites.

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Thanks to all those friends that kept me strong and happy despite of being far from home. All of you have been placed in my heart.

Dedication

I dedicate this thesis to my mother, *Ana*, who has always provided me with plenty of support and love.

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Selected Abbreviations

WS – wheat straw fibers
iPP – isotatic polypropylene
PP – polypropylene
NF – natural fibers
PE – polyethylene
EVA – ethyl vinyl acetate
LDPE – low density polyethylene
HDPE – high density polyethylene
PC – polycarbonate
PET – poly (ethylene therephtalate)
PEEK – polyetheretherketone
MA – maleic anhydride
FTIR – Fourier transform infrared
MAPP – maleic anhydride modified polypropylene
MAET – maleic acid ethylene copolymer
D – diffusivity (mm^2s^{-1})
v% – percentage in volume basis
wt-% – percentage in weight basis
M_∞ – mass uptake value at equilibrium time (gr)
t – time (h, min, s)
M – mass uptake (gr)
h – sample thickness (mm)
w – sample width (mm)
l – sample length (mm)
R – rate of crosshead motion ($mm.min^{-1}$)
L – support span (mm)
d – depth of beam (mm)
Z – rate of straining of the outer fiber ($mm.mm^{-1}.min^{-1}$)
AR – aspect ratio (unitless)
L_f – fiber length (mm, μm)
Φ – fiber width (mm, μm)
L_c – critical length of the fiber (mm, μm)
H – heat of fusion (Jg^{-1})
H° – specific heat of fusion (Jg^{-1})
Xc – percentage of crystallinity (%)
T_c – crystallization temperature (°C)
T_m – melting temperature (°C)

Chapter 1 - Introduction

Composites bring together in a single material the benefits of one or more components. These components can be organized as a matrix (continuous phase) and a filler (dispersed phase), although several other combinations are also common. It is possible to make several different composites by combining different sources of matrix and filler. The synergism promoted in the system will provide superior characteristics to this new material in relation to the individual components. Polymers are some of the most used materials in the composite industry. Both thermosettings and thermoplastics are usually employed as matrices. Combined with these matrices, fillers are commonly introduced in the systems as the second component in order to obtain a material with different characteristics from the pure matrix.

Towards the development of new materials with low-cost and high performance, natural fibers have emerged as a renewable and environmental friendly source of fillers. It is possible to combine natural fibers with different polymers to produce new classes of materials. High volume markets such as automotive panels, garbage pails, decks and furniture are some of the areas where natural fibers obtained from agricultural activities are most likely to replace inorganic fillers, thus providing low cost/high performance products. However, for both academic and industrial purpose, the wide range of thermoplastics and potential agricultural fillers and the significant diversity of combinations between these two materials lead to several questions to be investigated.

The processing conditions, the best formulation (percentage of filler in relation to the matrix) and the influence of additives in the systems are some points yet to be determined for many different combinations of matrix and natural filler. Therefore, in order to evaluate these points for a specific case, in the present work wheat straw fibres (WS) were combined with isotactic-polypropylene (iPP). For this system, a systematic study was carried out to identify a relationship between the sytem composition, its morphology and the final properties of the composites.

1.1 Motivation

Plastics derived from petroleum are used in almost every sector of the economy. However, there is a worldwide recognition that petroleum is a finite source or that its widespread use should carefully be considered. In addition, the development of new plastic resins is considered to be limited due to market acceptance; advancements in the plastic industry are now related to quality, versatility, durability and light weight of plastics, as well as technological resin improvements. In most cases new applications are driven by cost instead of property improvement. With that in mind, there are plenty of opportunities for innovations in the plastics industry.

As part of the development process in the plastics industry the global market associated with fillers has been growing significantly. Materials such as talc, mica, calcium carbonate, wood flour and fibers from different sources have been successfully employed in the plastic composite industry for almost 90 years, promoting expansion in the composite manufacture. In much of the world, wood is in short supply and forests are threatened. Despite the great advances in the forestry industry, more recently materials obtained from agricultural activities have been considered as promising alternatives for other fillers. Agro-based fibers have the potential to replace wood and inorganic fillers in certain applications.

Employment of resources available from agricultural activities in the composites industry may contribute to the economic development of rural areas promoting jobs and enhancing the non-food agricultural based economy. Only in Canada the production of wheat was around 30 million tonnes in 2004 [www.agripulp.com/econ.html#dakota], representing a large production, which requires a substantial number of workers in this field. While grain and other seeds are the main objectives of the farming activity, there is interest in developing new uses for those activities.

The choice of the fiber for composites applications depends on the availability, in which regional supply may offer a significant advantage because of savings associated with

transportation cost. Therefore, the elevated production of wheat straw in Ontario is a very attractive factor when selecting the crop material to be studied.

In order to develop economically competitive bio-composites it is necessary to understand the structural properties of filler, matrix and composite. It is well known that agricultural crops such as wheat straw have some advantages over inorganic fillers regarding properties, such as low density, biodegradability or being available from renewable resources. However, there is a general lack of information available about the conversion of agricultural by-products into novel advanced materials.

Research on the properties and processing of agricultural by-products can make possible the development of lightweight, durable biocomposites for automotive or construction applications. Full commercialization of these bioproducts is very promising. Research efforts focusing on the development of sustainable biomaterials are also a very attractive opportunity to re-invigorate the thermoplastic industry.

1.2 Objective and Scope

The main goal of this work was to carry out a study on the potential of wheat straw as a filler for polypropylene. The study focused on the effect of processing conditions on the final properties of the wheat straw-polypropylene composites. A review on previous publications about natural fiber composites was made. An experimental study was carried out to evaluate the effect of moisture, particle size distribution, compounding temperature, thermal and mechanical properties of the final composites and morphology. Wheat straw-polypropylene composites were prepared under different conditions in order to investigate the effect of those conditions on the performance of the composites. There was made no attempt to measure thermal or mechanical properties of wheat straw itself.

1.3 Document Outline

This thesis is organized in five main chapters, as follows:

Chapter 1 – introduces the reader to the thesis topic and motivation to conduct the study and gives a brief description of the document.

Chapter 2 – presents the literature review on natural fiber composites. It includes some advantages and disadvantages of natural fillers, types of polymers employed in composites, processing of natural fiber composites and main methods for characterization of those materials.

Chapter 3 – describes the materials that were employed in the experimental work; explains the methodology used for preparation of the wheat straw-polypropylene composites; and the techniques and procedures followed to access some of the final properties of the composites prepared.

Chapter 4 – presents the experimental results for processing and characterization of wheat straw, the wheat straw-polypropylene composite preparation, and the characterization and properties of those materials.

Chapter 5 – gives general concluding remarks, along with recommendations for future work.

Chapter 2 - Literature Review

2.1 Natural Fibers as Fillers

According to the American Society for Testing and Materials standard ASTM D-883, filler is a relatively inert material added to a plastic to modify its strength, permanence, work properties, or other qualities or to lower costs. Fillers can come from different sources, which can be mineral, animal or vegetable, presenting different shapes and properties. They are usually introduced in a polymeric matrix in the form of fibers or powder. Fibers can be classified in two categories: man-made (glass, carbon, metallic, nylon or ceramic) or natural (mineral, animal or plant). In this work natural fibers (NF) will be representing only plant fibers. Generally, it is accepted that fibers are materials that have aspect ratio higher than five. However, several cellulose based particulate materials, even with aspect ration lower than 5, are also called fibers because they are formed by cellulosic fibers arranged in bundles.

Until 1999 the majority of reports in the literature showed the use of wood, cellulose fibers or wood flour as fillers [Saheb and Job, 1999] obtained from plant fibers. However, due to the increasing cost of forest products around the world lignocellulosic fibers from agricultural crops are becoming a strong alternative for the production of natural fiber composites.

2.2 Lignocellulosic Fibers

Natural fibers have been studied since the 1970s, representing a reasonable source of fillers for blends, compounds or reinforced plastics [Gray, 1974]. As an alternative source of wood fiber market, lignocellulosic plants commercial activities not related to forestry have been exploited in academic research and industry lately. Figure 1 shows examples of natural fibers that can be used as filler in the plastic industry, arranged in two groups: wood and non-wood fibers.
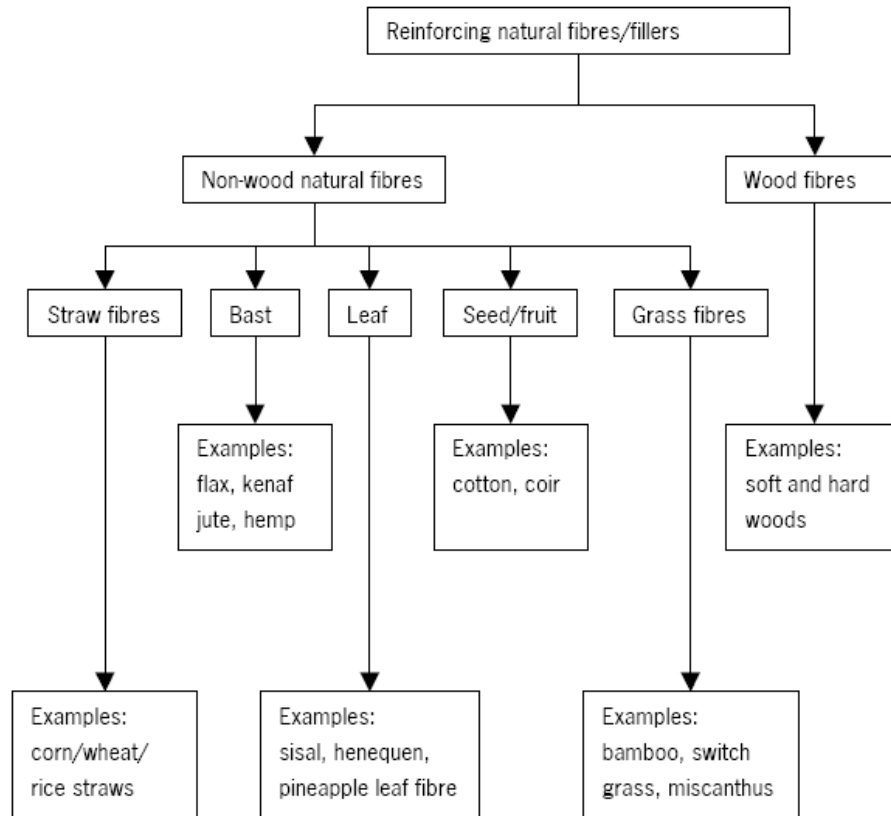
Figure 1. Organization of natural fibers that can be employed as fillers in the plastic industry [Bos, 2004].

Up to 1997, jute, flax and coir were the most popular natural fillers provided by lignocellulosic plants [Cheremisinoff, 1997]. Besides those, materials such as kenaf, hemp, sisal, abaca, banana, pineapple, bamboo and wheat straw have been studied in the past years. The availability of the agro-material in the manufacturing region is a primary concern on choosing the type of fiber to be used with plastics. In Asia, for example, bamboo is an abundant natural resource; therefore it has been extensively explored in that area.

The nature of the fiber and its physical characteristics determine the quality of the filler. Furthermore, individual fiber properties can vary depending on the source, age and history of the fiber. Chemical and physical properties are key factors to the filler performance. The chemical components of natural fibers are mainly cellulose, hemicellulose, lignin, pectin,

waxes and water-soluble substances. Generally, natural fibers contain 60-80% of cellulose and 5-20% of lignin [Saheb, 1999].

After cellulose, lignin is the second major component in most plants. It is generally accepted that fibers containing excessive amounts of lignin will present lower mechanical properties compared to those containing higher amount of cellulose than lignin. Furthermore, lignin and hemicellulose lead to low thermal stability of the crop material [Hornsby[1], 1997]. On the other hand, hemicellulose is known to contribute significantly to the strength of the fiber [Bos, 2004].

Aside the chemical composition, the physical structure of NF is of great importance; it is responsible for the mechanical properties of the filler. In the plants, the cells form crystalline microfibrils (cellulose), which connect together to form multiple layer structures, glued by the amorphous hemicellulose phase. The angle of the fibrils and the content of cellulose will determine the physical structure of the plants and therefore explain some of the mechanical behaviour presented by them.

2.2.1 Advantages of Lignocellulosic Fibers

Lignocellulosic fibers present numerous advantages over fibers from other sources: low specific gravity (resulting in transportation cost savings), non abrasiveness (allowing long life to tools, molds and dies during processing), high specific properties (such as modulus and strength), they are non brittle, easily recycled and have low cost compared to the resins. The market advantage is usually based on elements such as availability, price of the filler and performance of the final product.

To justify the superiority of lignocellulosic fibers as fillers in comparison with other fillers, the life cycle environmental performance of composites based on fillers from different sources are compared. For reasons such as lower environmental impact of production, higher fiber content that leads to a reduction of polluting base polymer content, improvement of fuel efficiency and recovering of carbon credits during the end of life incineration, natural fiber composites were considered environmentally superior in most of the applications [Joshi, 2004].

In terms of wheat straw, there are three important physical structural features that makes it an excellent natural filler for thermoplastic composite materials: a) intricate percolating pore structure of vascular bundles and central void, b) presence of microfibrils in the structure, and c) existence of polymer lignin near the surface of the straw [Malhotra, 2007].

2.2.1.1 Recycling and Renewal

Since the last decade the problems of recycling plastic materials and utilization of renewable resources have received enormous attention from academic, industrial and governmental authorities due to both economic and environmental factors. Nowadays companies have greater focus in being "carbon neutral", improving the market for biodegradable materials such as agro-fibers. Academic contributions regarding recyclability and reprocessability of natural fiber- thermoplastic composites have been made; it was found that properties of some composites based on pineapple leaf fiber and polyethylene remained constant up to the third extrusion, decreasing marginally beyond that [George, 1995]. Therefore, it is possible to assume that natural fiber-thermoplastic composites, in addition to the biodegradability of the filler, are able to go under the recycling process without losing their main properties.

2.2.1.2 Density

Fibers provided by agro-materials present a significant low density (or specific gravity) when compared to inorganic fillers such as calcium carbonate and glass fibers. The low density of the agro-materials contributes to the use of these fillers in products directed to the automotive industry and other transportation applications, in which the weight advantages of agro-fibers are very promising concerning fuel savings. For example, for a nominal fiber loading of 25% by weight the measured density of flax straw-polypropylene and wheat straw-polypropylene composites was about 986.8 $kg.m^{-3}$ and 998.8 $kg.m^{-3}$, respectively [Hornsby[2], 1997], while the density of 25% glass fiber filled PP was 1076.0 $kg.m^{-3}$. Density of polypropylene composites containing 40% by weight of talc or mica were 1270 and 1260 $kg.m^{-3}$, respectively [Rowell, 1999]. Kenaf fiber-PP composites containing 50 wt-% of fibers presented density of 1007.0 $kg.m^{-3}$.

2.2.1.3 Specific Properties

Specific properties are calculated dividing the property by the density of the material. If we consider the low density presented by natural fibers, specific properties for these materials are most likely to present high values. Table 1 shows a comparison between some natural fibers and glass fiber. Due to low density, properties such as specific modulus presented by natural fibers are very competitive to those presented by man-made fibers, for example those made out of glass.

Table 1: Values of specific gravity, tensile strength, modulus and specific modulus of natural fibers and glass fibre. [Saheb and Jog, 1999]

Fibre	Specific Gravity	Tensile Strength (MPa)	Modulus (GPa)	Specific Modulus
Jute	1.3	393	55	38
Sisal	1.3	510	28	22
Flax	1.5	344	27	50
Sunhemp	1.07	389	35	32
Pineapple	1.56	170	62	40
Glass Fiber-E	2.5	3400	72	28

Results from previous research have shown that agro materials such as kenaf, when compounded with polypropylene, provided mechanical properties equivalent to or higher than commercial polypropylene (PP) composites based on man made fillers. For example, the specific flexural modulus of kenaf-PP was about 6.8 MPa while the values for talc-PP and mica-PP composites were 3.4 and 5.5 MPa, respectively [Rowell, 1999]. This implies that the addition of agro-fibers was able to create good mechanical results even when the density is not considered.

2.2.1.4 Cost

Crop residues after harvesting are some of the most promising readily available feedstocks for industrial applications. In United States, over 61 millions of acres of wheat straw were harvested in 1994 [Johnson, 1997]. In Canada, Ontario is the main province responsible for the

crop production; wheat is the 3rd largest Ontario crop, after corn and soybean. Each year, the wheat farming industry in this province produces 1.5 million tonnes of straw [OMAFRA, 2005]. Small amounts of the straw are currently used for animal bedding and animal feed, but the majority of the straw production is designated to the incineration (in the field) or it is simply ploughed back into the ground [Cooper, 1999].

There are five main classes of wheat grown in Ontario: they are classified according to the designation of soft or hard, spring or winter and white or red; the classes differ in characteristics of the grains and price. Considering an average annual production, one pound of wheat-straw will be in the range of $0.10 – $0.15/lb whereas inorganic fillers such as calcium carbonate and talc are in the range of $0.07 - $0.50/lb. Due to the large production of wheat straw in Ontario, the price of this crop is very competitive in this region when compared to the price of other fillers commonly used in the composites industry; which means there is a great potential of wheat-straw competing in the fillers market towards the production of low cost composites. However, additional costs related to the collection, compaction (bailing), transportation, storage and protection against fire and biological deterioration are likely to be incurred previous to the manufacturing stage.

2.2.2 Limitations of Lignocellulosic Fibers

While the advantages of natural fibers are particularly attractive to the composite industry, there are some limitations to their use. The low processing temperatures (due to deterioration of properties of the fibers when they are subjected to heat conditions), weak surface adhesion to hydrophobic matrices (natural fibers are hydrophilic materials while some thermoplastic polymers are hydrophobic, leading to an incompatibility between them) and the high moisture absorption (that decreases adhesion forces between fiber and matrix and affects the dimensional stability of final products) are some negative characteristics observed in lignocellulosic fibers.

2.2.2.1 Water Absorption

Water absorption is a severe problem presented by agro-fibers. Cellulose, one of the main constituents of cell walls of plants, contains numerous hydroxyl groups that are strongly

hydrophilic [Marcovich, 1997]. Amorphous cellulose and hemicellulose are considered to be major responsible for the high water uptake of natural fibers, since they contain numerous easyly accessible hydroxyl groups [Arbelaiz, 2005]; whereas theoretically, composites with fibers containing higher lignin content should present lower values of water uptake, since lignin is a hydrophobic compound that acts against hydrothermal degradation in fibers [Espert, 2004].

High water contents could affect the dimensional stability of the final product, narrowing the field of application of NF based composites. Some tests have been realized to obtain information about the long-term water absorption and the influence of water absorption of agro-fibers in polymeric blends [Tajvidi, 2006]; however, further understanding of different systems is still needed.

2.2.2.2 Adhesion Ability

The incompatibility between agro-materials and polymers is usually confirmed by the weak interfacial bonding observed between the two surfaces. The filler-matrix interfacial phenomenon is responsible for the stress distribution and transfer between both components, determining the mechanical and physical behaviour of composites. It is well known that polar and non-polar surfaces can only promote poor adhesion between them, leading to low strength and stiffness blends. Hornsby et al. [Hornsby[2], 1997] have found no evidence of interfacial bonding between wheat straw or flax fibers and polypropylene, verifying that materials with different surface energies do not present good interaction.

Adhesion between fibers and matrix can be attributed to four main mechanisms [Hull, 1981] which can occur at the interface, either in isolation or in combination, to produce the bond:

a) absorption and wetting, represent a physical attraction between two electrically neutral surfaces;

b) electrostatic attraction, occurs when the two surfaces have opposite charges;

c) chemical bonding, formed between chemical grouping on the fiber surface and a compatible chemical group in the matrix;

d) mechanical adhesion , observed when there is interlocking of two surfaces.

2.2.2.3 Degradation

Agents such as water, ultraviolet radiation, thermal cycling and fungal attack can promote degradation of natural plants, thus, endorsing the degradation of composites that contain natural fillers. Johnson et al. [Johnson, 1999] have tested visual and mechanical characteristics of thermoplastic-natural fiber composites after exposure to some of these agents. Degradation dependence on the loading level of filler and matrix type was reported for the tested composites [Johnson, 1999]; oxidation was the most expressive sign of the degradation of the specimens.

In general, the main degradation happens on the agro-material phase and the polymer matrix is the phase of the composites usually less affected. Temperature is the one that causes the highest deterioration of the natural fiber properties due to degradation/modification of its chemical constituents. Physical and chemical changes are likely to occur when agro-fibers are submitted to elevated temperatures during either processing or labour, hence, compromising the performance of the composite. The rate of thermal decomposition of lignocellulosic materials, for example, was reported to increase exponentially with an increase in temperature [Ichazo, 2000]. Concerning wheat straw, the onset of degradation observed for the crop fibers prepared by mechanical and chemical processes were reported to be at 217°C and 242°C, respectively [Panthapulakkal, 2006].

Research in our laboratory [Golbabaie, 2006] compared the degradation of wheat straw from the Ontario region and commercial types of cellulose and lignin; the results from degradation tests performed under two different atmospheres (air and nitrogen) are reported on Table 2. From this work it is possible to see that wheat straw, under air atmosphere, has its degradation starting at approximately 190°C. Still, wheat straw is a combination of more than one component; thermal degradation of pure cellulose or pure lignin had other onset points (Table 2). Surprisingly, weight lost for wheat straw occured at lower temperature when the material is tested under nitrogen.

Supposedly, the degradation process at lower temperatures is associated to the degradation of hemicellulose whereas higher temperature processes (280-300°C) would cause degradation of

lignin [Saheb, 1999]. Furthermore, the rate of degradation was found to be dependent on the preparation method. Such results indicate that some treatments are able to improve the thermal stability of crops like wheat straw, enhancing their suitability for processing with a large number of thermoplastics that have their melting point somewhere between 160°C and 240°C.

Table 2: Degradation temperature of commercial types of cellulose and lignin and wheat straw fibers. [Golbabaie, 2006]

Material	Degradation Temperature in Air (°C)	Degradation Temperature in Nitrogen (°C)
Cellulose source 1	274	274
Cellulose source 2	261	272
Cellulose source 3	237	234
Lignin source 1	203	194
Lignin source 2	187	200
Wheat Straw	190	180

2.3 Thermoplastics Filled With Crop Materials

Historically, cellulosic filled plastic systems have been dominated by thermosetting resin matrix systems. However, during the last two decades, emphasis has been placed on the production of cellullosic-thermoplastic composite materials. The major driving forces for this development are the potential advantages, compared with thermosetting matrix-based systems in lower cost of processing and recyclability. Research works regarding utilization of resins such as polyethylene (PE), polypropylene (PP), poly(ether amide), phenol-formaldehyde and different natural fibers are available in the literature [George, 1995; Avella, 1995; Rowell, 1997; Zárate, 2003].

Thermoplastics are among the most common polymers. They can be reversibly melted or can be dissolved in a suitable solvent [Sharples, 1966]. Advantages over other resins

(thermosetting) include low specific gravities, low cost of fabrication and favourable mechanical properties. In addition, they do not need to go under the cure stage and they can be recycled. Low density polyethylene, for example, when compounded with sisal fibers, showed better reinforcing effect than polyester, epoxy and phenol-formaldehyde compounded with the same natural material [Joseph, 1996]. The superior performance was attributed to the high matrix ductility and high strength/modulus ratio of sisal as compared to that of polyethylene matrix, in relation to the thermosetting polymers.

Furthermore, according to Van de Velde and Kiekens [Van de Velde and Kiekens, 2001], for 50v% reinforced composites, only a maximum of 5 to 10% difference in mechanical properties is to be expected when using different thermoplastic matrices. This means composite properties can be strongly dependent upon characteristics related to the filler. Regardless of the type of material, loading percentage, size, shape, chemical composition, physical properties, agglomeration, distribution of the filler in the matrix and its adhesion to the matrix are some important aspects related to the composites behaviour [Sharples, 1996]. Cost, availability, recyclability, energy use and environment impact of both filler and matrix are general market issues considered when developing a new composite.

2.4 Other Polymers Filled With Crop Materials

Polymeric resins such as epoxy, polyester and phenolic resins have been investigated as matrices for natural composites. Bos et al. [Bos, 2004] has investigated the compressive strength of unidirectional flax fiber epoxy composites. In their research, improvement of adhesion between fibers and matrix was achieved by removing the wax layer covering the fibers surface.

In a previous work, the properties of poly(ethylene-co-vinyl acetate) and sugar cane bagasse were evaluated regarding the effect of different surface treatments of the chopped bagasse [Stael, 2001]. Results suggested that EVA-bagasse composites could provide good

performance in low-density/low-strength particle boards, with advantages of being an environmentally friendly material.

Melamine-formaldehyde has been successfully used as the matrix material in natural fiber composites [Hagstrand, 2001]. This resin is suggested to be an interesting matrix due to the typically high adhesion observed, which is attributed to the possible reactions with primary OH groups in cellulose forming covalent bonds. Despite of the negative effect of the natural filler on the tensile performance of the composites, flax fiber reinforced melamine-formaldehyde was considered an attractive and competitive alternative filler when cost and density were taken into account.

2.5 Processing of Thermoplastic Composites

Thermoplastic based composites are usually produced by melt-mixing process, although they can also be produced by solution-mixing. In general, the ultimate goal of any compounding operation is usually the production of a compounded and pelletized feedstock. Pellets are suitable for use in almost any plastic processing operation, giving opportunity for the diversification of final products.

Solution-mixing processes have basically three steps. First, the matrix polymer is dissolved by a solvent at specific temperature and pressure. Second, the filler is added to the solution and they are mixed. The final step is to remove the solvent from the system. George et al. [George, 1995] employed this technique to obtain pineapple leaf fibers and polyethylene composites. It was found that fibers retained their original length after compounding, representing low amounts of damage during processing. Composites with small fiber content presented poorer mechanical properties in comparison to melt-mixed composites, which was attributed to the poor dispersion of filler in the matrix. The solution-mixing process appears as an alternative process to the composites industry; however, it is not commonly employed due to reasons such as poor final properties of the composites and solvent related problems.

As for the melt-mixing process, two types of equipment are typically employed: extruders or batch mixers. In both processes the filler is usually added to the system after the resin is melted by applied shear and temperature. The filler and resin remain inside the mixer until the particles are completely dispersed. This production process is largely preferred because of its easy operation, although the filler can be submitted to severe damage imposed by shear and temperature. Fiber damage during processing is a very important aspect because it leads to changes in fiber length, chemical or physical properties, which influences the final properties of the composites.

The reduction of fiber size is one important drawback in melt-mixing processes; therefore, it has been studied in previous works. The size reduction is attributed to the high shear forces and temperature that the filler undergoes during processing. George et al. [George, 1995] analyzed the fiber breakage occurred during processing a blend of pineapple leaf fibers and polyethylene at different rotor speeds. According to the fiber size distribution curves obtained, it was found that higher rotor speeds cause severe damage to the filler (reduction in their length) while low rotor speeds produced composites with low mechanical properties due to poor dispersion of fiber in the matrix.

Regarding the effect of processing conditions, high temperatures are likely to promote degradation of the agro-materials, thus changing their characteristics as fillers. Another problem related to compounding is the difference in bulk density of the two components (matrix and filler), which may bring problems in the feed step of the process. Bulk density issues can be simplified by selecting a lignocellulosic component with a bulk density as close to the thermoplastic component as possible, however, this action would minimize the low density advantage of natural fibers [English, 1997].

2.5.1 Chemical Modification of Fibers and Additives

Properties of polymeric composites are significantly influenced by interfacial interactions between matrix and filler. To improve the adhesion of NF and the polymer matrix, fiber treatment prior to compounding and additives have been studied lately. After the treatment, the surface energy of the fibers, closely related to their hydrophilicity, is increased to a level much

closer to the surface energy of the hydrophobic materials (thermoplastics). Thus, a better wettability and a higher interfacial adhesion are obtained between the two components.

The drying process previous to compounding is one of the most important aspects for processing NF. Drying decreases the amount of water present in the fiber's surface, which is responsible for weak interactions between filler and matrix. Additionally, pores and voids will appear in the matrix because of the evaporation of water during the process, thereby lowering the visual and mechanical quality of the composites.

Besides the basic and traditional drying process, employed in almost 100% of the compounding processes, physical and chemical methods can be used to optimize the fibers surface towards a higher compatibility to the matrix. Physical treatments will change the structural arrangement of the fibers while chemical treatments will modify the chemical composition of the fiber surface by reacting groups to the surface. In general all chemical treatments follow the same principle, the introduction of chemical groups that can react with hydroxyl groups present in the cellulose (NF) [Espert, 2003].

Several methods have been reported in the literature, such as steam explosion [Avella, 1995], silane treatment [Hornsby[1], 1997], acetylation [Espert, 2003] and fungal retting [Sain and Panthapulakkal, 2006].

Hornsby et al. [Hornsby[1], 1997] have found that the silane treatment had little or no effect in improving the fibers adhesion to the matrix. The acetylation of cellulose fibers led to a lower percentage of crystallinity of the composites, diminishing the quality of the material [Espert, 2003] while for sisal fibers it changed considerably the thermal stability of the fibers [Albano, 1999]. On the other hand, a steam explosion process [Avella, 1995] and fungal retting [Sain and Panthapulakkal, 2006] treated fibers showed good results compared to non-treated fibers, improving the composites' properties.

Furthermore, chemical and mechanical fiber preparation methods are likely to change the chemical composition of the fibers. Wheat straw treated by chemical pulping, for example, exhibited 62% less hemicellulose and 70% less lignin after treatment. When comparing the two

methods, chemically processed fibers are 32% richer in cellulose compared to the mechanically processed fibers [Panthapulakkal, 2006].

2.5.2 Coupling Agents

Plenty of publications describe the chemical modification by coupling methods as a very efficient treatment to improve adhesion forces between matrix and filler. This method requires a third material that has properties that are intermediate between fibers and polymer. The mechanism involves a chemical reaction between the fibers surface and the coupling agent (third material introduced in the system), promoting covalent bonds between filler and matrix. Maleic anhydride (MA) has been used for this purpose by several research groups [Avella, 1995; Gassan and Bledzki, 2000; Caufield, 1999; Sanadi, 2001; Rowell, 1999; Chen, 1998; Mi, 1997]. This chemical is usually inserted in the systems through maleic anhydride grafted copolymers (polypropylene copolymer, polyethylene copolymer, etc.). Two properties of maleated copolymers that could influence their effectiveness as coupling agents for natural fibre/thermoplastic composites are molecular weight (affects entanglement with the matrix chains) and acid number (determines the functionality present in the coupling agent) [Arbelaiz, 2005].

To assure the actual contribution of coupling agents to the composite properties, the reaction between coupling agents and hydroxy groups present on the fibers surface was investigated. Avella et al. [Avella, 1995] presented an FTIR spectrum of a natural fiber composite containing maleic anhydride modified polypropylene. The cyclic anhydride band disappearance could be observed after the thermal activation of the system, confirming the reaction between the additive and fibers.

Research about the effects of fiber-matrix adhesion on the materials' behavior under fatigue or impact loadings was reported by Gassan and Bledzki [Gassan and Bledzki, 2000]. Significant increase in dynamic modulus, reduction of stiffness and increase in fatigue limits were observed in polypropylene/jute-fibers composites with higher fiber-matrix adhesion quality (MA-PP treated). A comparison between PP/kenaf fiber blends with and without MA coupling agent was made by Caulfield et al. [Caulfield, 1999]. According to the authors, MA raised the

softening temperatures and enhanced the impact properties of the composites considerably, indicating a better adhesion between polymer and kenaf fibers in the presence of coupling agent.

In addition to the surface adhesion improvements, coupling agents are suggested to be also capable of influencing filler distribution in the matrix. Distribution of bamboo fibers was investigated in composites containing 50 to 60 wt-% of filler in two host materials: polypropylene and maleic anhydride modified polypropylene (MAPP). A better filler distribution was observed in composites containing MAPP, suggesting that this coupling agent is able to enhance the filler distribution [Chen, 1998]. Maleic anhydride concentration influence in mechanical properties, such as tensile strength, was also tested in 50 wt-% bamboo fiber composites. Remarkable increases in the tensile strength with MA content up to 0.12% and continuous improvement in the strength with contents up to 0.25 wt-% were recorded. Besides the surface adhesion, in the reaction between maleic anhydride and fibers, polar carboxylic groups of the maleic acid firmly bond to OH groups present in the fibers' surface, thus reducing the hygroscopicity of the composites [Marcovich, 1998].

2.6 Characterization and Properties of Composites

Different plants provide fibers with different physical and chemical characteristics, thus different suitability is expected for compounding with thermoplastics and composites manufacturing. It is possible to determine some fibers' characteristics and evaluate their quality as fillers by testing composites based on these fibers.

The properties observed are those related to the performance of the final products. Thermal and mechanical properties, thermal degradation and morphology of the blends are features typically investigated.

2.6.1 Filler/Fiber Loading

Filler loading (both volume and weight fraction) plays an important role in determining the final characteristics of composites. Research in natural fiber composites has reported loadings in the range from 0 to 60% by weight of fiber in thermoplastic matrices; 60% generally represents the upper loading limit of filler. Despite of that, Sanadi et al. [Sanadi, 2001] described a composite up to about 90 to 95 percent by weight of fiber in polypropylene. In addition, a new material with 85% by weight of kenaf and PP-MAPP was successfully processed (compression molding), presenting high stiffness as a final property. Investigations in this area report physical properties comparable to commercial composites based on glass or wood fibers for composites containing 50 wt-% of fibers in a polymeric matrix.

The amount of fiber present in composite systems usually influences properties such as water absorption, stiffness, strength and elongation. It is well known that the higher the percentage of natural fibers in a composite the higher is the capacity of the material to absorb water. Furthermore, failure strain, as well as the tensile energy absorption, is decreased as the loading of fibers is increased. On the other hand, an improvement in the flexural and tensile strength, tensile energy absorption, failure strain and un-notched Izod impact strength were observed when a very small amount of fibers (0.5%, weight basis) was added to a polymer matrix [Rowel, 1999].

2.6.2 Size and Orientation of the Filler

Another important factor related to the final properties of composites is the size of the fillers. Fibers' length and length/width ratio are main features in determining the filler distribution in the matrix as well as mechanical properties of the composites. Fibers less than 50mm long are generally accepted to be short fibers, whereas fibers greater than 50mm long are regarded as continuous fibers [Cheremisinoff, 1997].

Besides the fibers' size, orientation of fibers relative to one another has significant influence on the properties of the final product [Hollaway, 1994]. It is possible to find three different arrangements of fibers when they are dispersed in a matrix; two of them are considered ordinary. Fibers can be aligned longitudinally or in the transverse direction of the product

length. This alignment usually occurs when the composite system is submitted to high shear forces in the direction of the product length or perpendicular to that. Besides the aligned possibilities, randomly oriented fibers is the third possibility. Due to processing conditions, fibers oriented in the longitudinal direction or randomly are frequently observed in commercial products.

Maximum strength and reinforcement are achieved along the direction of fiber alignment in longitudinally oriented composites. Reinforcement is almost nonexistent in the composites where the fibers are aligned in the transverse direction (perpendicular to the flow direction). Randomly oriented composites present properties in-between these two extremes [George, 1995].

The effect of fiber length and orientation in some polymeric composites was studied by George et al. [George, 1995]. According to the authors, there is a critical fiber length (L_c) that is required for the fiber to develop its fully stressed condition in the matrix. Fiber debonding from the matrix will occur when the fiber is shorter than its critical length while a high composite strength and breaking of the composites under stress are likely to be seen when the fibers length is greater than the critical length. Short pineapple-leaf-fibers showed an optimum performance for the length of 6mm. The highest enhancements in strength and modulus were observed when the fiber length was increased from 2 to 6 mm; although, when the fiber length was increased to 10mm, the tensile strength and modulus were almost unaffected. Some difficulties were also mentioned regarding processing 10 mm long fibers. Concerning the orientation, longitudinally oriented pineapple-leaf fiber composites showed, in general, better mechanical properties than transversely and randomly oriented composites.

2.6.3 Thermal Degradation of Crop
Fiber degradation is an important issue related to natural fiber composites. Degradation in natural fibers can be observed by the darkening of the fibers, usually associated to the pyrolysis and oxidation of the components due to exposure to high temperatures. The thermal degradation of the fibers usually starts at about 240°C, depending on the chemical composition of the plant.

Thermal degradation has been observed in sisal and jute fibers. At 210°C, sisal fibers appeared much darker compared to their original color while jute fibers turned from yellow to dark brown at 240°C [Grande and Torres, 2005]. Thus, the former type of fiber showed a higher degradation temperature, according to the authors [Grande and Torres, 2005], probably due to the amount of cellulose and lignin in the plant. When processing was conducted by extrusion, an increase in the screw speed also contributed to darkening the fibers. In addition, degradation of sisal fiber composites was observed to give out serious odour that could persist for a long time [Fung, 2003].

Degradation of the fibers leads to brittleness and poor mechanical integrity of thermoplastic composites; therefore, it is important to establish the maximum temperature that each agro-fiber can be submitted to without depreciating physico-chemical properties when employed as filler.

2.6.4 Hydrophilicity of Crop

Agricultural crop materials are usually hydrophilic, which is opposite to the majority of thermoplastic materials, which are hydrophobic. When exposed to moisture, agro-fibers are likely to absorb water; the absorption capacity depends on several factors. Tajvidi et al. [Tajvidi, 2006] reported that fiber content, shape of the natural filler (flour or fiber) and chemical composition (amount of cellulose, hemicelluloses and lignin) were factors affecting the water absorption behaviour.

The opposite nature of filler and matrix can also result in difficulties to disperse the reinforcing material in the major component. Clumps can be formed during processing, leading to poor dispersion quality of the filler in the matrix and therefore irregular properties along the product [Rowell, 1997]. Furthermore, an increase in the composite moisture content may cause a decrease in the adhesion forces between filler and matrix, decreasing final mechanical properties of the composite such as tensile strength and tensile modulus [Johnson, 1999; Caulfield, 1999].

It is possible to investigate the water absorption behaviour of natural fiber composites by simple immersion experiments. The relationship between time and amount of water absorbed by a certain composite will determine its ability to pick up moisture.

2.6.5 Mechanical Properties

The individual properties of matrix and filler are important issues when evaluating mechanical properties of the composites. According to Joseph et al. [Joseph, 1996], mechanical performance of fiber reinforced plastic composites depends mainly on three factors: (a) strength and modulus of the fiber, (b) strength and chemical stability of the resin, and (c) effectiveness of the bond between resin and fibers in transferring stress across the interface. In fact, mechanical behaviour of composite materials is governed by the synergy between fibers and matrix.

George et al. [George, 1995] compared pineapple fibers with sisal and jute fibers. Among the composites filled with these natural fibers, the one containing pineapple fibers presented the highest elongation at break values. The superiority of pineapple fiber based composites was attributed to the high cellulose content of the natural filler; therefore, one can conclude that nature of the filler has strong influence in determining composites' final properties.

Furthermore, parameters such as fraction and orientation of filler, fiber aspect ratio and fiber-matrix adhesion must be taken into consideration when assessing mechanical tests. The presence of additives such as coupling agents can enhance the adhesion between the two phases of the composite. Therefore, the effect of this type of compatibilizer on mechanical behaviour of different composites has been researched; yet, several combinations of filler and matrix are still to be investigated. Moreover, the effect of coupling agents can be beneficial, prejudicial or none, depending on the final property evaluated [Rijsdijk, 1993]. For instance, flax straw-PP composites grafted with maleic anhydride, presented significant increase in tensile yield strength, attributed to the fiber-matrix interaction promoted by the functionalized polymer [Hornsby, 1997].

Composites are usually evaluated from flexural, tensile, compression or impact tests. However, the properties to be evaluated are normally related to the application field of the final product. Tests that are easy to carry out, that are relatively straightforward and that can provide easy qualification of the material are usually preferred.

2.6.6 Filler Morphology Previous to Compounding

Morphology of external and internal structures of fillers can be investigated with image analysis. Internal structure of agro-materials presents interesting features for composite purposes such as the porous structure, which makes the materials very light. Emphasis on the structure of wheat straw was given in another work from our laboratory in collaboration with the Department of Plant Agriculture at University of Guelph [Golbabaie, 2006]. Figures 2 and 3 are scanning electron micrographs of cross sections of wheat straw as raw material; both images show the physical structure of wheat straw. Externally, the stems of wheat straw are cylindrical structures, separated at intervals by nodes. The stem structure observed in Figure 2 has an outer epidermis, a cellular inner region and a central void [Panthapulakkal, 2006]. A closer view to the cellular structure of wheat straw is shown in Figure 3.
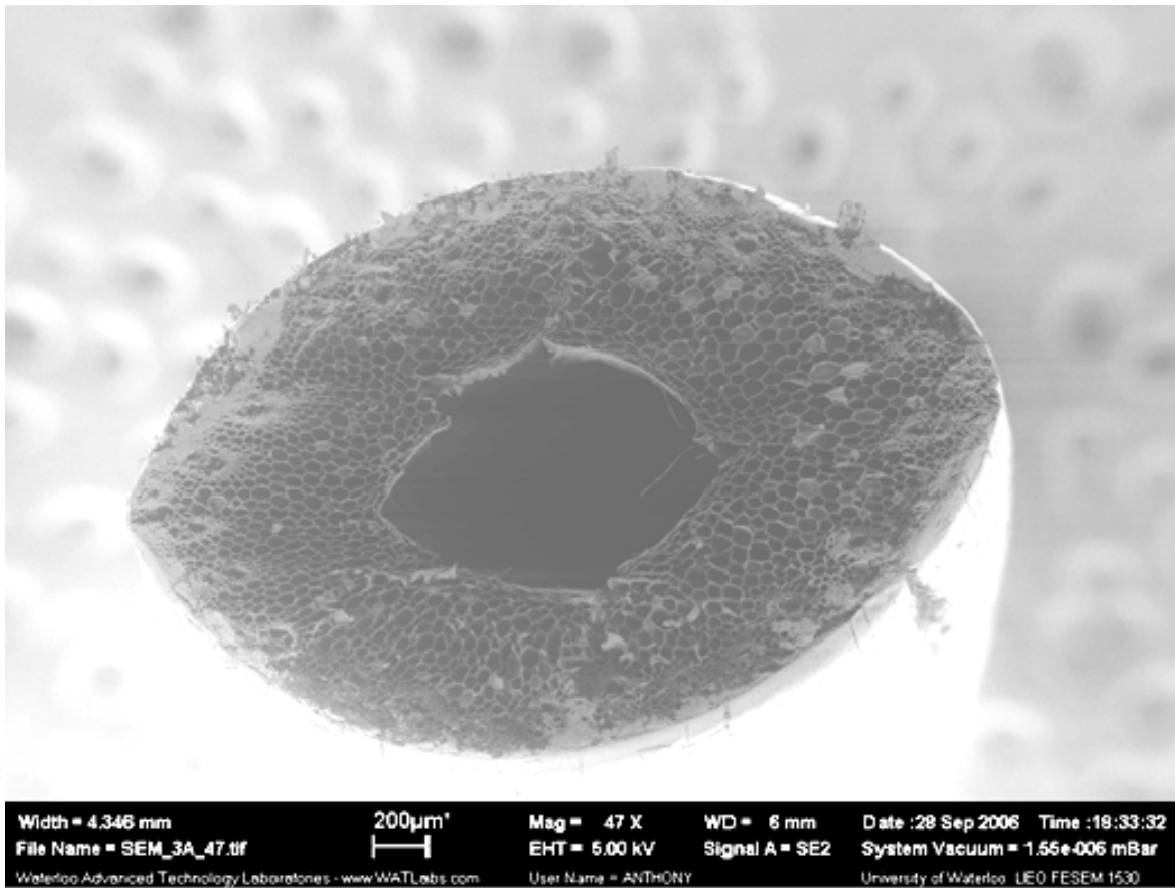
Figure 2: Electron micrograph of wheat straw [Golbabaie, 2006]. Mag. (x 47)

Width = 1.016 mm	20μm*	Mag = 200 X	WD = 6 mm	Date :28 Sep 2006 Time :18:37:15
File Name = SEM_3B_200x.tif	⊢	EHT = 5.00 kV	Signal A = SE2	System Vacuum = 1.49e-006 mBar
Waterloo Advanced Technology Laboratories - www.WATLabs.com		User Name = ANTHONY		University of Waterloo LEO FESEM 1530
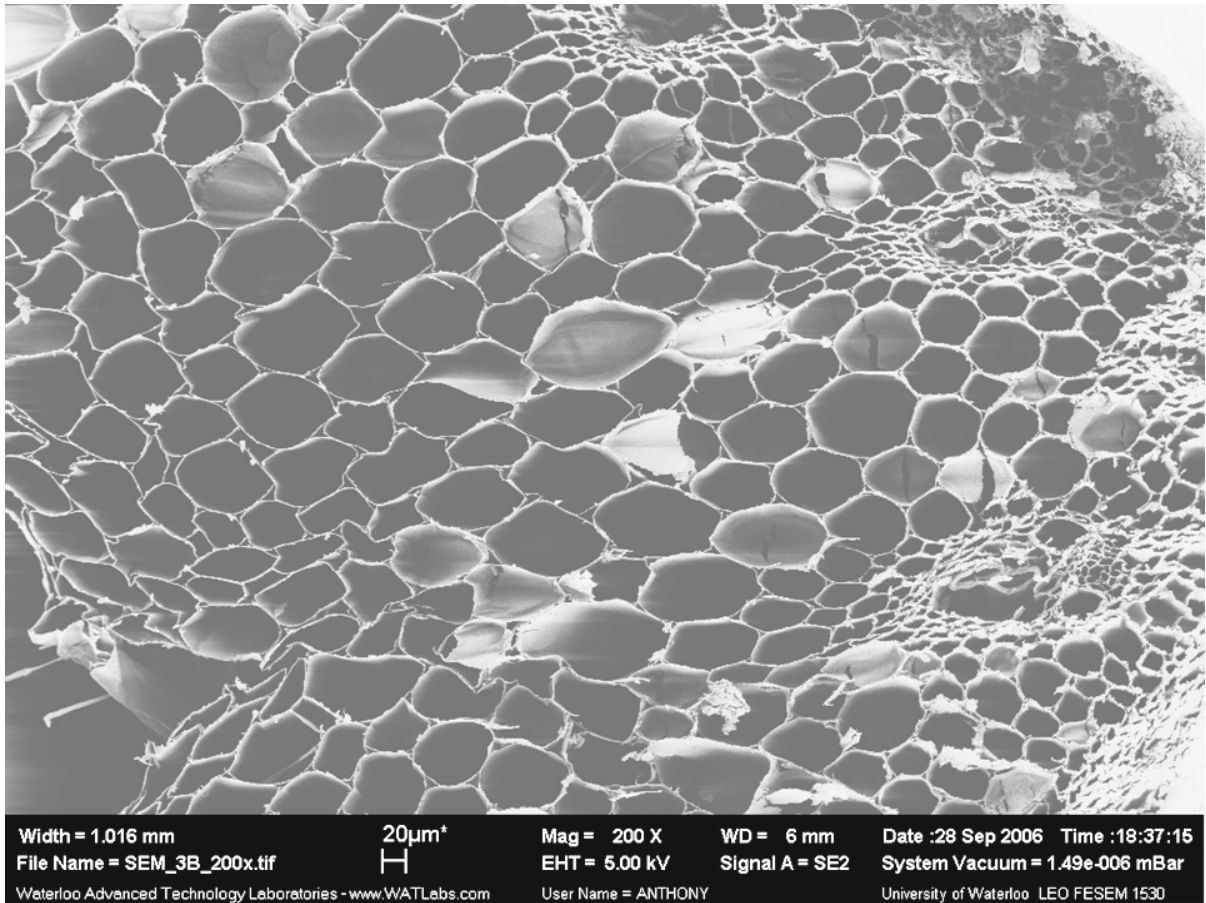
Figure 3: Electron micrograph of wheat straw internal cellular structure [Golbabaie, 2006]. Mag. (x 200)

Figure 4 represents the internal view of the longitudinal hollow section of wheat straw. In this micrograph it is possible to see several microfibrils. Those microfibrils have diameters in the range of 2 to less than 1 μm and lengths of several microns.
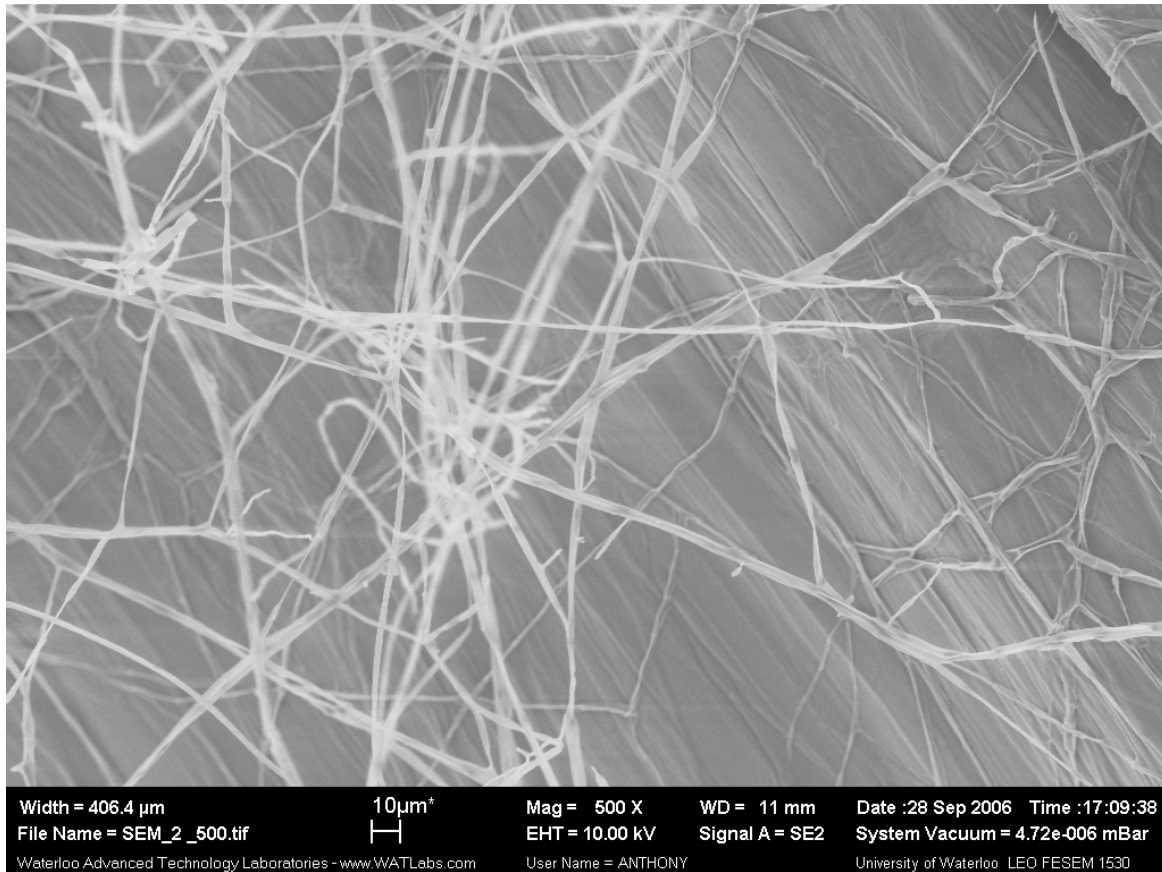
Figure 4: Electron micrograph of wheat straw – microfibrils present in the central void [Golbabaie, 2006]. Mag. (x 500)

A wheat straw particle after grinding is shown in Figure 5. It is possible to notice that the grinding process promotes minimum damage to the wheat straw. During the grinding process, the straws were chopped in small particles without affecting extensively the surface structure of the material; therefore, one can say that the chemical composition of the external epidermis remains the same as the material before grinding.

Figure 6 is a closer look to the wheat straw particle shown in Figure 5. The presence of microfibrils in the structure of the crop is easily observed after the grinding process, when these microfibrils apparently come out of the internal part (central void). According to the micrograph, some microfibrils have dimensions of about 300 nm and 5000 nm as diameter and length, respectively.
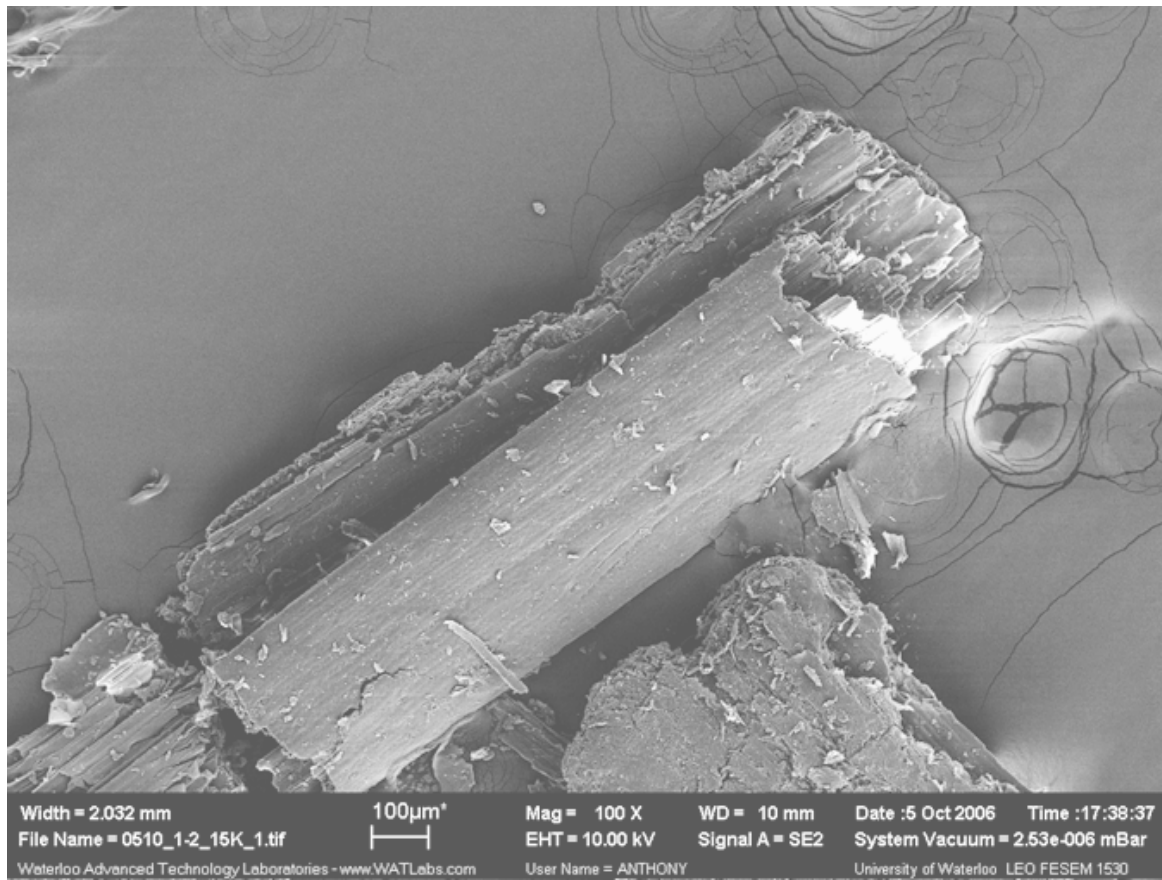
Figure 5: Electron micrograph of wheat straw particle after grinding [Golbabaie, 2006]. Mag. (x 100)
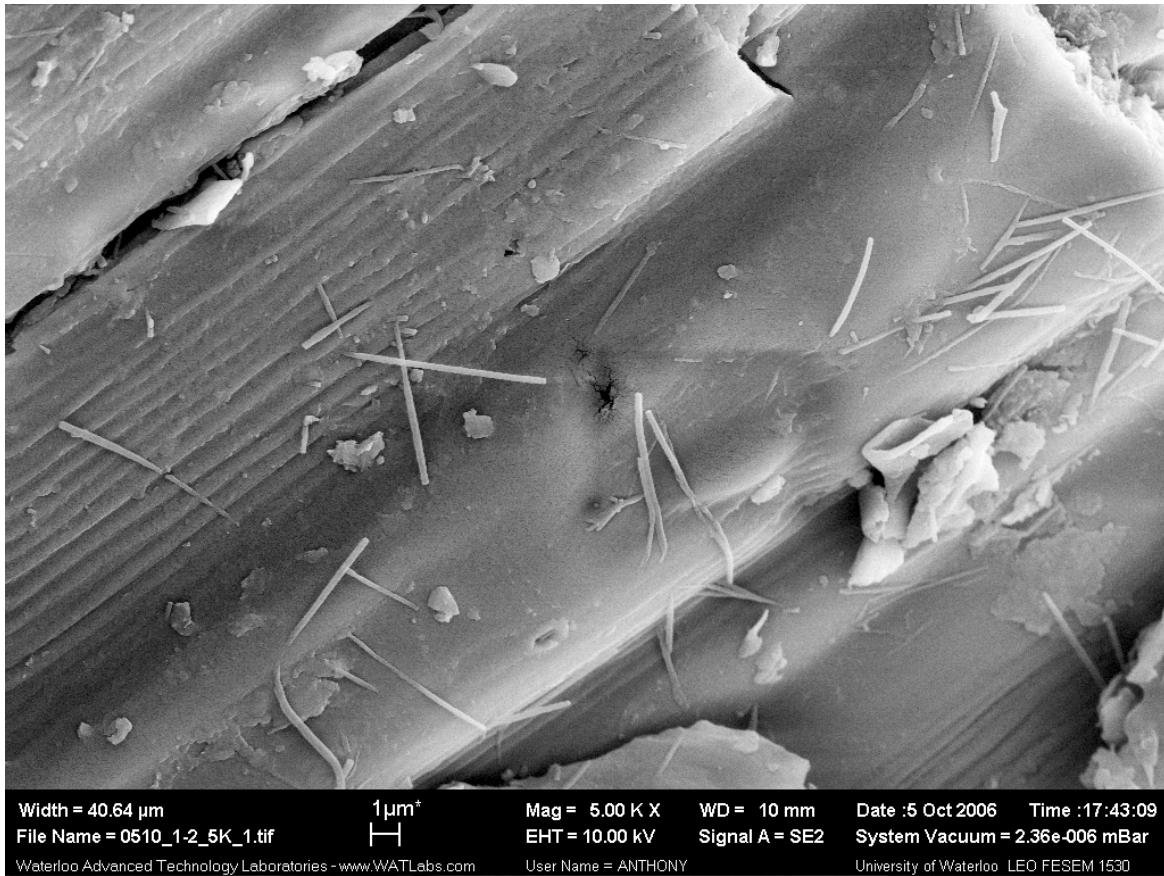
Figure 6: Electron micrograph of wheat straw particle after grinding - closer view [Golbabaie, 2006]. Mag. (x 5000)

2.6.7 Surface Interaction and Filler Characterization After compounding

The arrangement of the particles and their interaction with the polymeric matrix after compounding are of great relevance for the quality of the composites. Different degrees of reinforcement can be achieved by the addition of natural fibers to different polymers due to the different adhesion strength between matrices and fibers. Moreover, the interaction between the two phases is mainly responsible for stress transfer and encapsulation of the fiber, which have huge impact on the mechanical properties and water absorption, respectively.

The surface interaction between the two components in a composite is usually investigated with fiber pull out tests and electron micrographs. The pull out test can tell how well the fiber

is attached to the matrix, while in the micrographs it is possible to observe the specimen with high magnification, making it easier to examine its morphology.

Generally, there is some extent of filler damage during the compounding process, which may change the final properties of the composite. The modifications in the fibers surface and size are mainly caused by shear stresses together with temperature degradation effects (in the melt-mixing process). To analyze the alteration on the fibers' size, shape and surface due to damage caused during processing, natural fibers can be extracted from the polymeric matrix with a solvent. An extraction technique, combined with optical or electron microscopy is a suitable method used to evaluate the effects of the processing conditions in the morphology of the filler.

Chapter 3 - Materials and Methods

3.1 Materials

Wheat straw (WS) was obtained from the region of Ontario-CA. The variety was Pioneer 25R47, and it was grown by a local farmer near Aberfoyle and harvested in late July, 2005. The base resin used was a low melt flow, impact resistant copolymer polypropylene (PP2407-01, supplied by A. Schulman Inc.). The density was 0.9 g/cc (ASTM D792) and the melt flow rate was 1.5 g/10min (230°C, ASTM D1238), according to the supplier. Antioxidant Irganox 1010 (Ciba Inc.) was added in all the experiments (except one) at the rate of 0.5 wt-% based on polymer weight. Two coupling agents were tested in this study, both from DuPont. The fist one, Fusabond MD-353D, is a maleic anhydride modified polypropylene (MAPP); the second one, Fusabond W PC-576D, is a maleic acid ethylene copolymer (MAET). A commercial amine based lubricant, Glycolube WP 2200 (Lonza Inc.), was also tested in these experiments. Base resin and additives were used as supplied. The solvent used during the extraction experiments was xylene (supplied by EMD Chemicals Inc.).

3.2 Grinding and Drying

Prior to compounding, the wheat straw material was prepared with the use of a mill. Wheat straws were cut into 5-6cm long pieces and passed through a stainless steel rotary cutter – Thomas-Wiley Laboratory Mill Model 4 – running at 800rpm with a 32 mesh Tyler separating screen (opening size 0.5mm). The feed aperture was localized on the top of the rotary cutter. The ground wheat straw was collected after the separating screen on the bottom of the equipment. The process was conducted continuously, with pauses of 15 minutes every hour, for five consecutive hours. After five hours, the process was stopped and re-started the next day. This procedure was adopted due to slight increases in temperature detected in the mill after long periods of work.

Once the wheat straw was ground, the particles were separated into beakers for drying. Each beaker contained the amount of ground material sufficient to prepare one batch of WS-polypropylene composite. The beakers were left inside an air circulating oven at 110°C for around 10 hours previous to compounding. After drying, the humidity of the wheat straw was approximately 0.5 wt-%.

3.3 Compounding

Wheat straw fibers were blended with copolymer polypropylene in a batch mixer with two internal screws - roller rotors (Haake Fisons Rheocord 90 - Folio Industries Inc.). The blends were prepared at constant speed of 40 rpm. For specifics formulations, three different processing temperatures were used. Every 200 g batch of mixture was carried out in the same way: first the polymer was fed into the mixer and melted, second the additives were added, and finally the fibers were added (taken from the oven after the drying period). The mixing time was about 15 min for each batch. The torque curves for the internal mixer and the temperature profiles in the mixing chamber were recorded as a function of time for each experiment.

3.4 Extraction

In order to evaluate the damage to the fibers due to processing, after compounding WS fibers were extracted from the composites. A precise amount (around 2 grams) of composite was immersed inside a 150-mesh stainless steel wire bag (as suggested in the ASTM D2765-01) in boiling xylene for 24 hours. During this period, the solution in the round bottom flask was replaced by fresh solvent about 3 times; at each time, the solution was passed through a paper filter in order to collect the fines that came out from the wire bag.

Xylene was discharged properly; the paper filters and the wire bag containing fibers were dried, at room temperature, inside a fume hood chamber, for 24 hours. Fibers from both the filters and the wire bag were deposited in the same container.

3.5 Characterization

3.5.1 Particle Size Analysis

Particle size distribution of the wheat straw fibers was measured by software for image processing and analysis - Scion Image (Windows). In brief, this software digitalizes images as a two dimensional array of pixels ranging from 0 (white) to 256 (black). To proceed with the analysis, thresholding is used to segment the image into objects of interest and background on the basis of gray level. All pixels equal to or greater than a single threshold level are displayed in black and all other pixels (background) are displayed in white. Features in black were counted and measured by scanning across the image.

To obtain the images, fibers were well spread on a thin glass slide, so that they were not touching each other. The observations were made under a stereomicroscope (Leica MZ6) with use of two illumination techniques: transmitted light and incident light (or reflected light). The magnification of the images was x10, at which it was possible to visualize a large number of fibers at the same time. Images were recorded with a digital camera (Sony AVC-D5). Comparison between both illumination techniques confirmed that the image to be analyzed by the software (transmitted light technique) was a real representation of the particles size.

Length and width of the fibers were obtained from the length of major axis and length of minor axis, respectively, of the best fitting ellipse drawn by the image analysis software for each particle available in the field of view of the microscope. To analyze the particles, the software automatically counts and measures the objects of interest by scanning across the image. When a boundary of an object is found the program draws an ellipse that best fits the object and then redraws the dark object in a different gray level, so that it becomes invisible to the scanning process. For each sample, three different digital pictures were used in this analysis. To obtain the dimensions of the major and minor axis in millimetres, an object with known length was

used in the calibration procedure; the known distance was measured in pixels (from the digital picture) and according to that there was a scale relating pixels and millimetres.

Figure 7 is an illustration of the procedure used to measure the length (major axis) and diameter (minor axis) of the fibers.
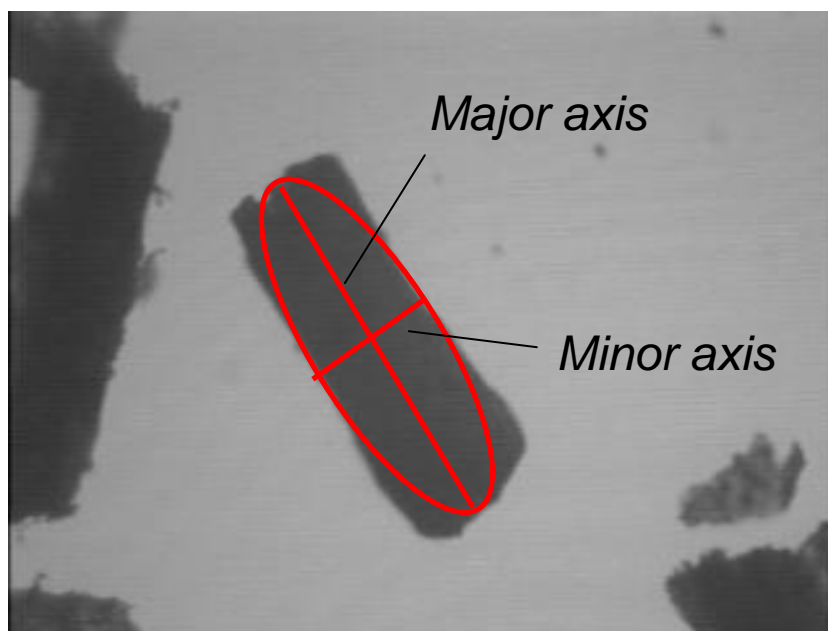
Figure 7: Example of the ellipse drawn by the image analysis software on a single fiber.

3.5.2 Morphology

The morphology of wheat straw fibers and composites where observed in three different phases: a) after grinding (before compounding), b) after compounding, and c) after extraction of the polypropylene matrix. After grinding the internal structure of the wheat straw, the particle size distribution and aspect ratio were evaluated. Then, after compounding, the shape, size and arrangement of the particles in the composites, as well as fibre matrix adhesion, were investigated. The third observation was made over the fibers extracted from composites. All those observations where carried out using the scanning electron microscope LEO SEM with field emission Gemini Column. Samples were fixed to aluminium stubs with double sided conductive tape. The composite samples where immersed in liquid nitrogen for 3 minutes. Then, the frozen samples where broken in half, thus providing two cross sections of fractured surfaces that were also fixed in stubs with double-sided conductive tape. All samples were

sputter coated with gold to improve electrical conductivity on the surface (gold layer 8-10 nm thick).

3.5.3 Thermal Properties

Differential scanning calorimetry (DSC) was carried out in a DSC model Q10 from TA. For the DSC analysis, a film of each sample was prepared by heating around 1g of the sample at 180°C for 2 minutes and pressing it for 3 minutes under 3000 psi. The films were cooled down at ambient temperature; no temperature control or quenching was applied.

The thermal analysis procedure for each sample (about 4-5 mg weight) was as follows: samples were heated from 40°C to 210°C (run I). After achieved this temperature, samples were kept at 210°C for 5 minutes in order to promote thermal equilibrium and erase any trace of crystallinity or thermal history. Then, samples were cooled to 40°C using a scan rate of 10°C/min; after achieved 40°C, they were kept in this temperature for 5 minutes. Finally, the sample was submitted to another heating cycle from 40°C to 210°C (10°C/min rate) (run III). Thermal analysis of the additives and natural fibers were also realized in order to better understand the results presented by the composites.

3.5.4 Water Absorption

Due to the hygroscopic behaviour of agro-materials, the wheat straw fiber composites were tested for the incorporation of water. The water absorption test was carried out based on the ASTM D570-98 specification. Analysis were performed on specimens prepared by compression molding. To prepare the bars, the same procedure was followed for all the composites: first the material was heated at 200°C for 10 minutes in order to achieve a completely molten state. After that, the composite material was pressed to 10000 pounds in the mold for 3 minutes, thus producing molded bars 63.35 mm long, 12.75 mm wide and 3.3 mm thick.

Two specimens of each formulation were selected and dried in an air circulating oven for 1 hour at 108 ± 0.5°C. Following the drying stage, the specimens were allowed to cool down inside a dissecator (8% of relative humidity), weigh to a precision of 0.001g and then

immersed in deionised water at 23 ±1°C. Such weight is called here conditioned weight (see Equation 1).

After 4 h of immersion in water, the amount of water absorbed by each specimen was measured. The bars were removed from water, patted dry and weigh to a precision of 0.001g. The same measurement procedure was realized after 9h of immersion in w ater and then at different immersion times. During the entire experiment period (90 consecutive days), the water temperature was maintained constant at 23 ± 1°C. The water was changed every week. After the experiment was finished, images of the samples immersed in water and test bars not immersed in water were recorded with a camera (Canon EOS Digital Rebel XTi).

The amount of water absorbed by each composite was calculated by the following equation:

$$increase\,in\,weight\,(\%) = \frac{wet\,weight - conditioned\,weight}{conditioned\,weight} \qquad (1)$$

3.5.5 Mechanical Properties

The mechanical behaviour of composites is of great importance in determining the final application for the engineered materials. However, there are several mechanical properties that are interesting in most fields of composites application. Thus, it is necessary to decide which properties are going to be evaluated in each case.

Flexural tests based on specification ASTM D790-03 procedure A were performed on the composite materials and the pure resin using a miniature materials tester – MiniMat 2000 with a load cell of 200 N. The specimens preparation followed the roughly the same procedure described in the preparation of specimens for the water absorption experiment. However, instead of drying the samples for one hour, the specimens were submitted to a controlled thermal treatment using convection oven to promote a uniform thermal history for all samples. This treatment consisted of heating the bars from room temperature (approximately 25°C) to 140°C. After 5 minutes at constant temperature (annealing at 140°C), a cooling rate of 10°C/min was applied to the system, decreasing the temperature down to 25°C. The annealing

occurs when the polymer is submitted to a temperature below the melting point (and above the glass transition temperature) at which the polymeric chains can move slowly, thus forming additional crystallites [Harding, 1988]. The thermal treatment also assures that all samples will present exactly the same thermal history previous to performing the flexural tests, avoiding any influence in the data collected. Once this treatment was finished, the specimens were conditioned at $23 \pm 2°C$ and $50 \pm 5\%$ of relative humidity for at least 48 hours before testing, as suggested in the standard specification.

Three molded bars were then cut in half along the specimen's length, which produced six test specimens for each sample. At least five specimens for each sample were tested. The tested bars measured approximately 31.5 mm x 12.75 mm x 3.3 mm. The exact dimensions were measured using the digital calliper and used for calculation of the results.

The approximate support span-to-depth ratio is 5:1. The rate of crosshead motion is calculated specific to each specimen using Equation (2):

$$R = ZL^2 / 6d \qquad\qquad (2)$$

where:

R = rate of crosshead motion, mm/min;

L = support span, mm;

d = depth of beam, mm; and

Z = rate of straining of the outer fiber, mm/mm/min = 0.01 (in accordance to procedure A).

Chapter 4 - Results and Discussion

In this chapter, results obtained from each analysis technique employed in this work are presented and discussed individually; however, it is clear that many of these results are interrelated. Further discussion regarding the overall performance of the composites in relation to each variable analyzed is summarized at the end of this section.

4.1 Filler Particle Size Distribution

After grinding, the particle size distribution of WS fibers was measured as described elsewhere in this work. Fig. 8 *a* and *b* are examples of the digital images recorded with the use of a microscope and two illumination techniques, incident light and transmitted light, respectively.
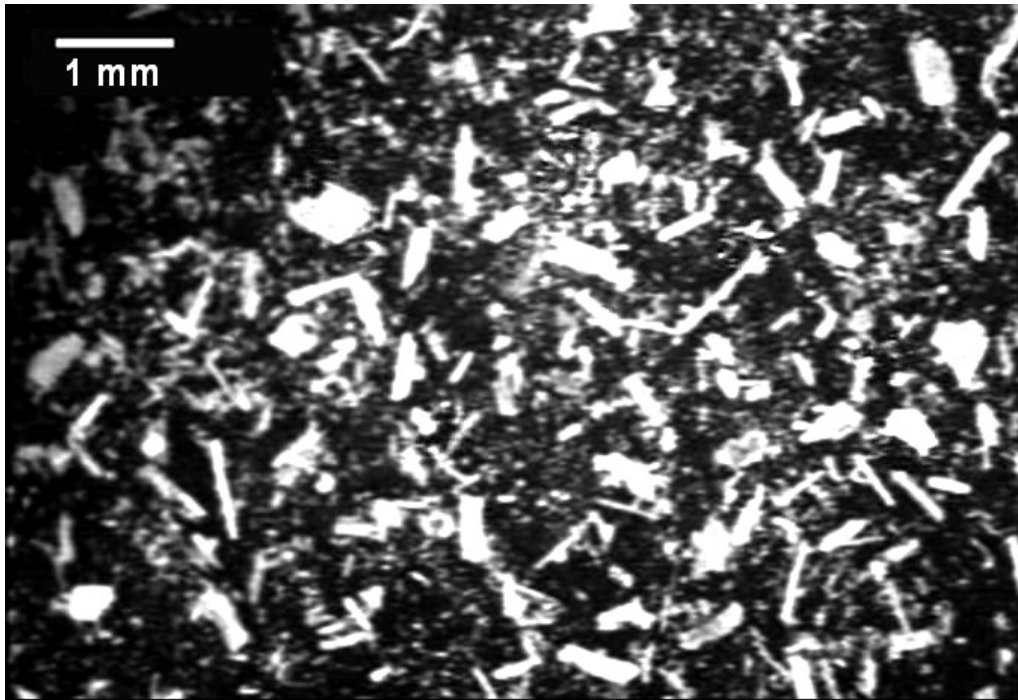
(a)
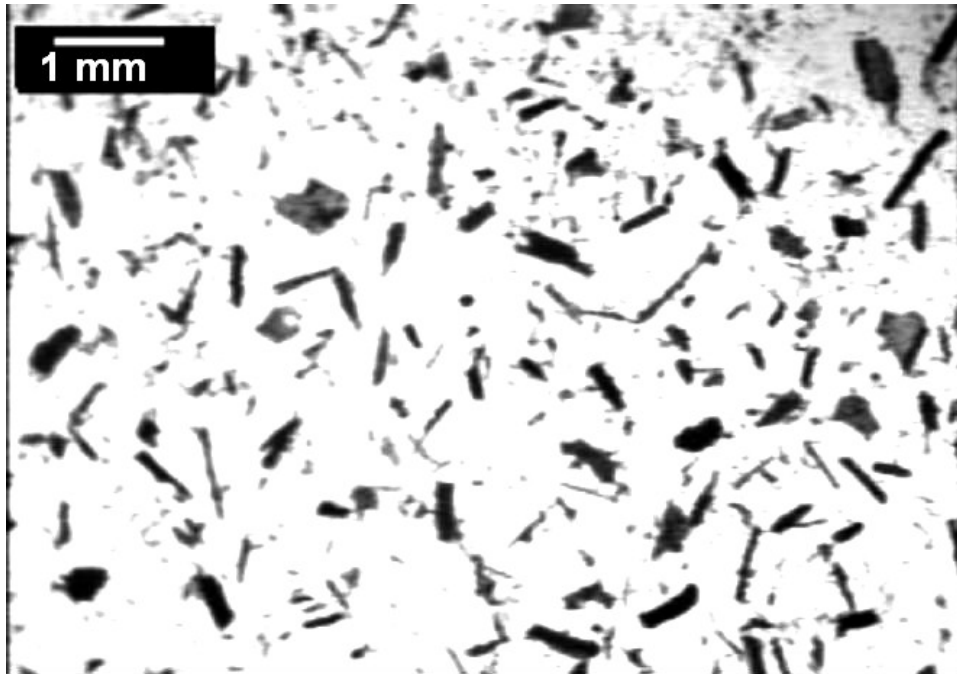
(b)

Figure 8: Wheat straw fibers, (a) transmitted light, (b) reflected light.

Results for WS fibers size distribution previous to compounding are shown in Fig. 9 and Fig. 10.
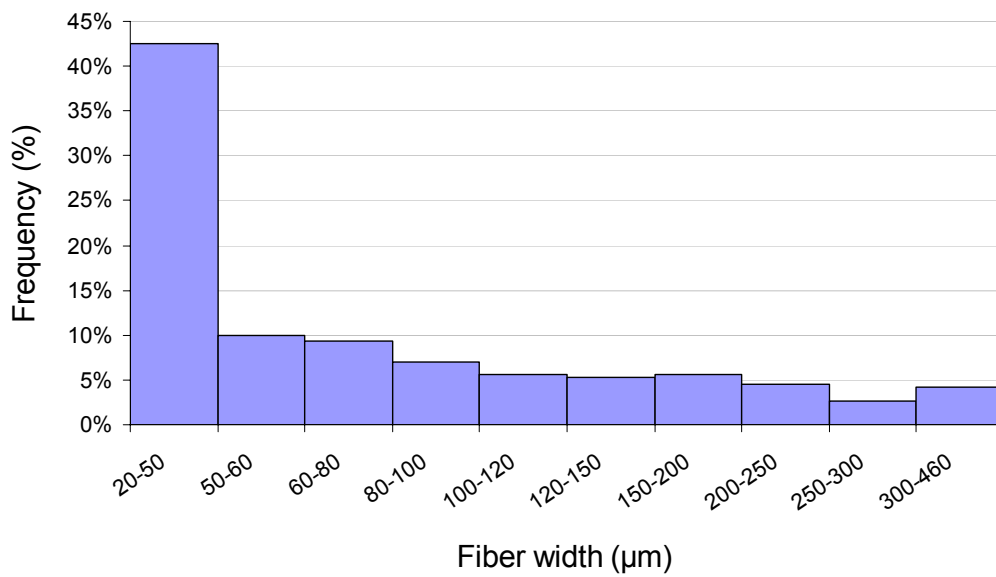
Figure 9: Wheat straw fiber width distribution.
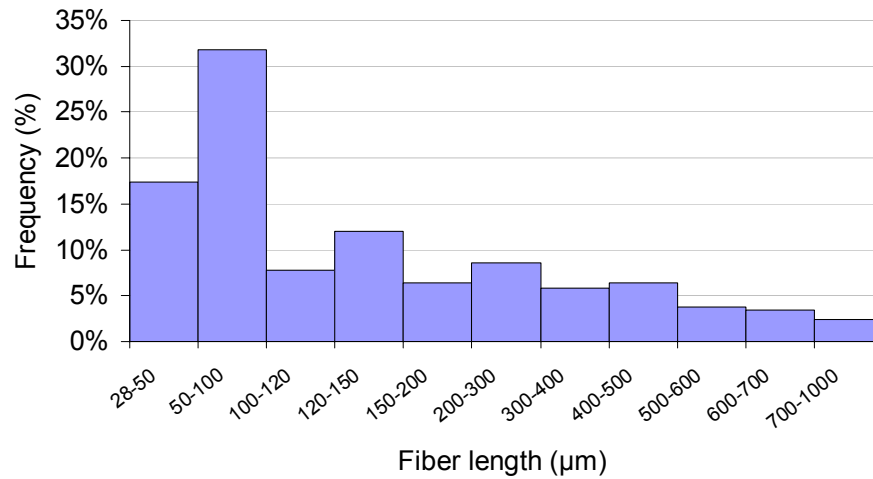
Figure 10: Wheat straw fiber length distribution.

Values of fiber width are in the range of 20-460 microns with approximately 60% of the fibers exhibiting a width lower than 80 microns, while values of fiber length are in the range of 28-1000 microns with approximately 50% of the fibers shorter than 100 microns. The ground wheat straw presents also a distribution of aspect ratios (AR) (AR=L_f/φ, where L_f and φ are fiber length and width, respectively). Particles were found to have aspect ratio from 1 to 9. The average AR observed for wheat straw after grinding was of 2, thus they can be mostly considered short fibers or particles. Figure 11 shows the aspect ratio distribution.
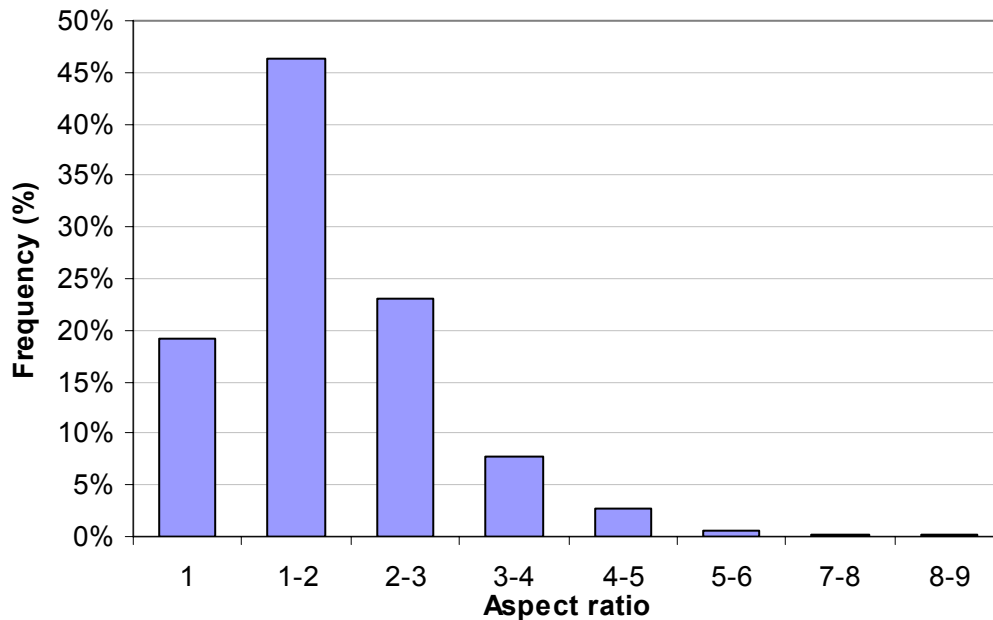
Figure 11: Wheat straw aspect ratio distribution.

Fiber length has an important effect over mechanical properties of composites. It is well known that as the aspect ratio of the fibers decreases, the efficiency of the fibers in stiffening and reinforcing the matrix decreases. Supposedly, the length of the fibers should be at least equal to the critical length (L_c) for effective stress transfer from the matrix to the fiber, which depends on the bonding strength between fiber and matrix [Nielsen and Landel, 1994]. The critical length varies from fiber to fiber and from system to system and it usually depends on such factors as the relative moduli of the two phases, the strength of the interfacial bond, the shear strength of the matrix and the tensile strength of the fiber. Despite that, it was observed in sisal-low density polyethylene that excessive fiber lengths decreased tensile properties of the composite, suggesting better properties for composites with fillers that do not overcome the critical length [Joseph, 1996]. The same behaviour was observed in some thermoset sisal composites, where tensile and flexural strengths decreased with the increase in fiber length. Those results were attributed to the fiber-to-fiber contact in the system. According to Zárat et al. [Zárat, 2003], longer fibers tend to bend or curl during molding, causing a reduction in the effective fiber length.

4.2 Compounding Process

The formulation of the wheat straw-polypropylene composites prepared in the batch mixer is reported in Table 3 (related to processing temperatures), Table 4 (related to filler loading) and Table 5 (related to additives).

Table 3: Formulation of WS-polypropylene composites prepared for comparison of processing temperature.

Sample #	% Fiber	% PP	Temperature (°C)
1	30	70	230
2	50	50	230
3	30	70	190
4	50	50	190
5	30	70	160
6	50	50	160

All samples contained antioxidant.

Table 4: Formulation of WS-polypropylene composites prepared for comparison of filler loading.

Sample #	% Fiber	% PP	Temperature (°C)
11	0	100	190
7	10	90	190
8	20	80	190
3	30	70	190
9	40	60	190
4	50	50	190
10	60	40	190

All samples contained antioxidant.

Table 5: Formulation of WS-polypropylene composites prepared for comparison of additives effects.

Sample #	% Fiber	% PP	% MAPP	% MAET	% Lubricant	Temperature (°C)
3	30	70	-	-	-	190
16	30	70	-	-	-	190
17	30	70	-	-	3	190
18	30	70	2	-	-	190
19	30	70	-	2	-	190

All samples but 16 contained antioxidant.

The torque in the mixer was measured during the melt-mixing process. A comparison between different processing temperatures for compositions prepared with 50 wt-% of WS and different contents of WS for composites prepared at 190°C are shown in Figures 12 and 13, respectively.
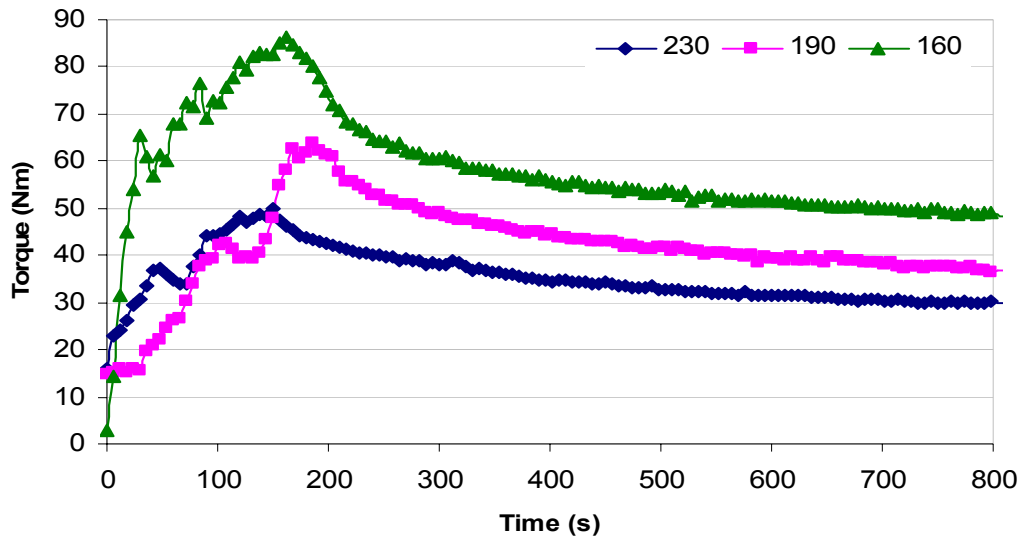
Figure 12: Torque curves for wheat straw composites containing 50 wt-% fibers at 160°C, 190°C and 210°C.
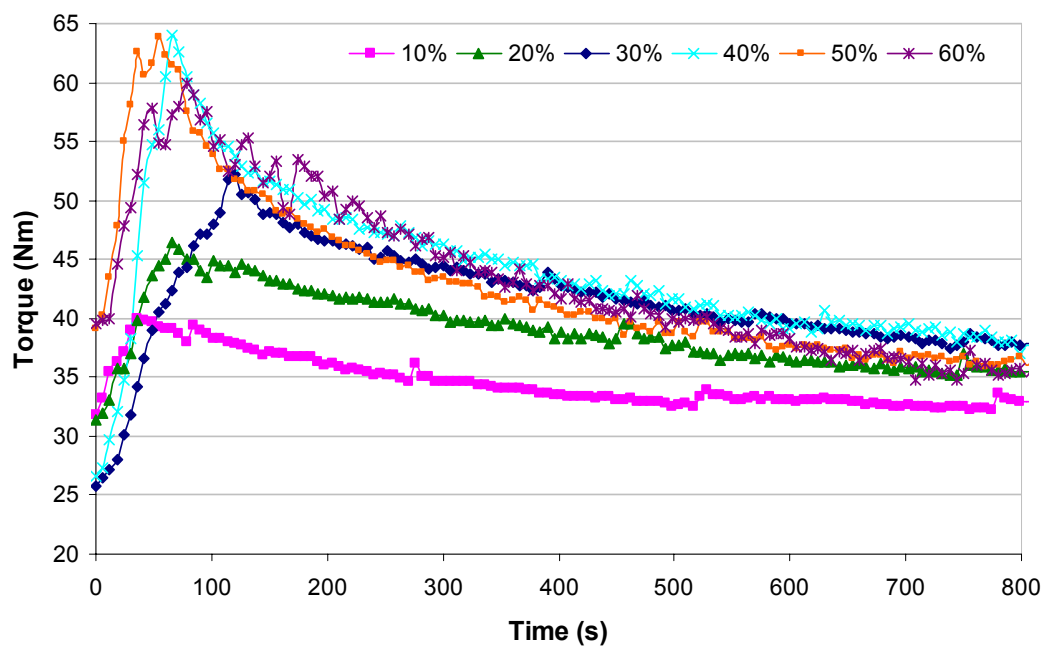
Figure 13: Torque curves for wheat straw composites processed at 190°C containing 10, 20, 30, 40, 50 and 60 wt-% of fibers.

The torque curves were recorded from the point when the fibers were added to the polymer already melted until the value was constant (uniform flow conditions). Around one minute was spent to complete the addition of WS to the melted polypropylene in each experiment. It is apparent in the graphic comparing processing temperatures (Figure 12) that the lower the temperature the higher the torque required to promote mixing between filler and matrix.

Interestingly, Glasser et al. [Glasser, 1999] found no significant influence in torque for different loadings of acetylated Yellow poplar fibers in cellulose acetate butyrate at 204°C.

In Figure 13, the maximum torque in the beginning of the experiment was quite different from sample to sample. Composites containing 40 and 50 wt-% of fibers showed the highest torque in the beginning of the mixing. For the maximum filler loading (60 wt-%) the curve appeared to be very irregular. This is probably because of the weak interaction between fibers and matrix

due to the low content of polymer in the system. The material was irregular and breakable during mixing.

A relationship between torque and fiber-matrix interaction was also suggested by Glasser's group [Glasser, 1999]. An increase in torque during melt processing was attributed to a large interfacial surface area in the mixture, which promotes resistance to deformation during processing. This phenomenon was also observed in the experiments reported here.

In Figure 14 it can be seen that samples containing coupling agents presented slightly higher torques when compared to the sample without any additive. Furthermore, the composite containing lubricant presents the lowest torque, thus confirming the positive effect of lowering the density of the molten polymer.
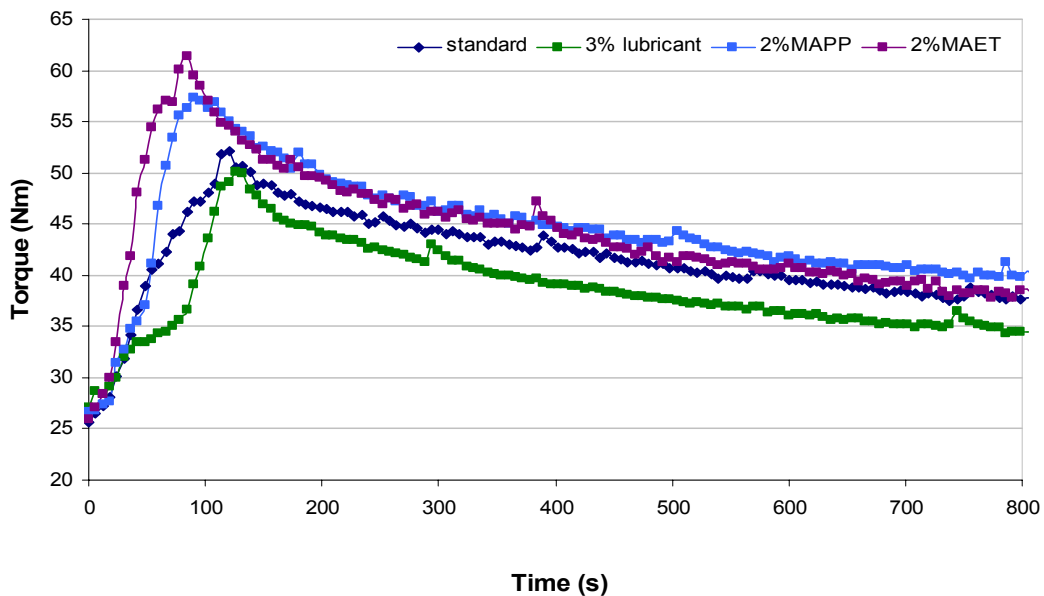
Figure 14: Torque curves for wheat straw composites processed at 190°C containing 30 wt-% of fibers without additives, containing lubricant, MAPP and MAET.

4.3 Filler Particle Size Distrib`ution After Compounding

Wheat straw fibers were extracted from composites to investigate the effects of thermal and mechanical degradation during the compounding. The extraction was carried out at approximately 150°C, for compositions containing 30 wt-% of natural fibers, processed at 160°C, 190°C and 230°C. The distributions of width and length for WS recovered by extraction are shown in Figures 15 and 16, respectively. The aspect ratio of WS particles after the extraction is presented in Figure 17.
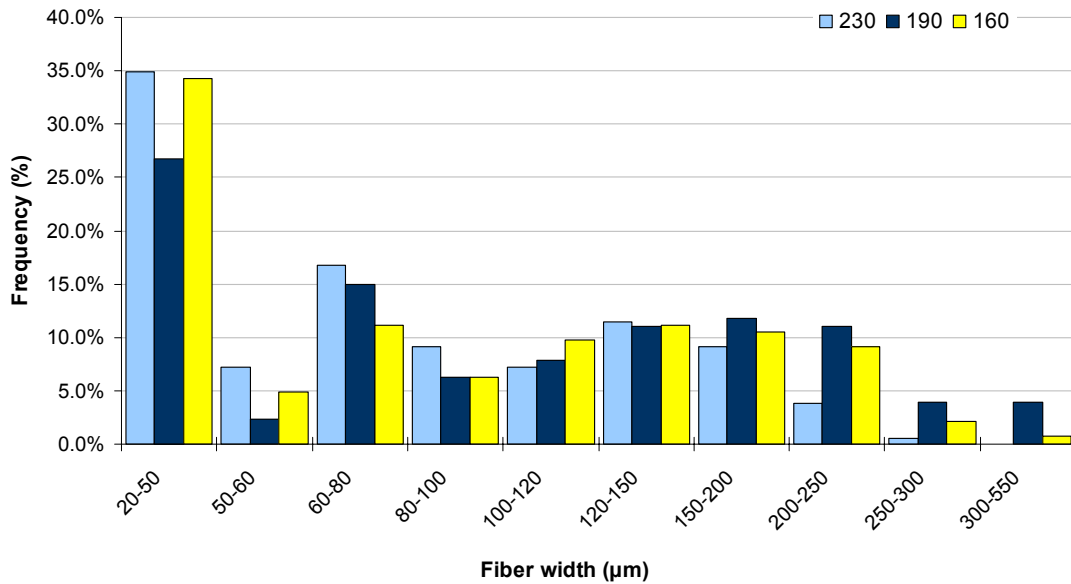
Figure 15: Wheat straw fiber width distribution after extraction for samples processed at 160°C, 190°C and 230°C.
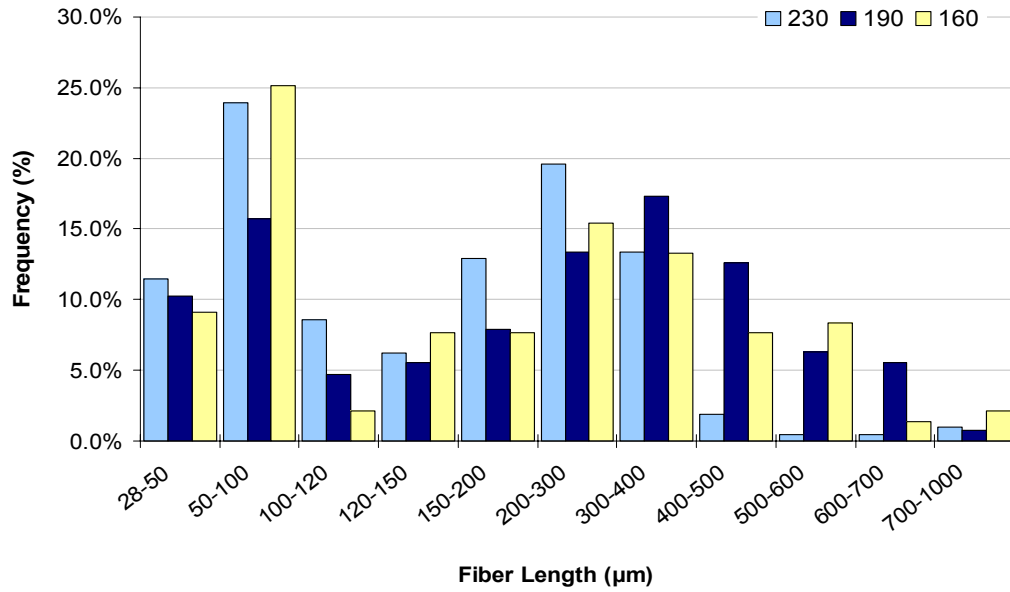
Figure 16: Wheat straw fiber length distribution after extraction for samples processed at 160°C, 190°C and 230°C.
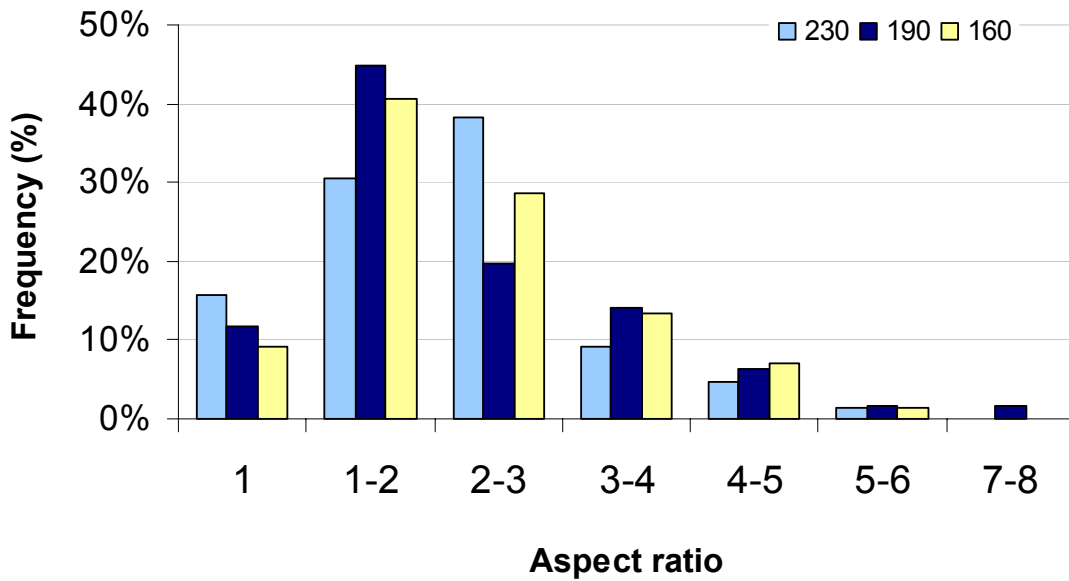
Figure 17: Wheat straw aspect ratio distribution for samples processed at 160°C, 190°C and 230°C.

Fiber breakage during processing is a very important pattern because it can affect the final properties of the composites due to fiber length changes. The reduction in fiber size is attributed to the attrition and temperature that fibers undergo during processing. Fibers can be broken into smaller particles if the hydrodynamic forces exceed the fibre strength and/or the cohesive forces between the individual fibres [Arbelaiz, 2005]. Also, it is possible that during the extraction experiments, due to thermal treatment, WS fibers can degrade at some extent. In the present work the extraction temperature was below all compounding temperatures investigated.

Major thermal degradation of lignocellulosic fibers is expected to occur at temperatures above 190°C [Golbabaie, 2006], temperature above the one at which the fibers were extracted. Therefore, degradation caused by solvent extraction was not considered an issue in the present work; however, further investigation (such as microscopic analysis) would probably give more concrete results about the extent of the changes in the fibers caused by extraction.

Although fiber analysis based on extraction technique has been mentioned by different authors (Glasser, 1999; George, 1995; Hornsby, 1997), this technique was found to provide some interesting results.

By comparing Figures 15-16 (extracted, after compounding) to Figures 9-10 (after grinding, before compounding) it is possible to verify that, surprisingly, the length distribution obtained for the fibers before compounding presented higher frequency of small particles (fines) comparing to the frequency obtained for the material after compounding. As it can be seen in the Figures 10 and 16, before compounding the amount of fibers with length in the range from 28 to 100 microns was about 50%; after compounding the amount of fibers with length in this range was about 25%. A reasonable explanation is that after extraction a large amount of fine fibers remained in the solvent solution or adhered to the paper filter; i.e., the part of the sample was lost. Thus, the length of those fines was not considered in the particle size distribution analysis, misleading the results.

Comparing results from extraction of fibers processed at three different temperatures, compounding at 230°C led to a slightly lower frequency of long particles and higher frequency of medium length particles. In other words, fibers were broken in smaller lengths during blending process conducted at high temperature, probably due to thermal degradation. According to Grande and Torres [Grande and Torres, 2005] when temperature is increased, fiber attrition is more relevant, increasing size reduction. Fibers extracted from the composite prepared at 160°C also presented quite large frequency of fibers with lengths between 50 and 100 microns. In this case, the breakage of the fibers is attributed to the low viscosity of the system and therefore high forces acting on the fibers. Further investigation on the fibers is required to identify which one, temperature degradation or shear forces, is the major cause of damage and fiber breakage.

George et al. [George, 1995] studied the effect of processing temperature on pineapple leaf fiber composites. Their results showed a decrease in mechanical properties at higher temperatures due to degradation of fibers and poor dispersion. The fiber breakage was attributed not so much to the attrition forces (since the viscosity of the polymer is low at this temperature) but to the degradation of the fibers at high temperature.

In spite of the fact that in the present work extent of fiber damage was investigated only regarding the effect of processing temperature, it was found in the literature that the original fiber length of natural fibers can be drastically decreased when a higher fiber content is introduced in the system

Due to the small change in the average length of the fibers, the aspect ratio was also slightly affected. The aspect ratio distribution after extraction presented values between 1 and 8; the average aspect ratio was 2. It was expected that the average aspect ratio of WS fibers after compounding would be lower than the fibers prior to compounding; however, the average ratio in both cases was the same. This result can be attributed to the fine fibers that were lost during filtration and therefore not measured.

It was reported in the literature that the reduction in the aspect ratio was around 30% when the fiber content was raised from 20 to 60 wt-% in the case of short flax fibers [Arbelaiz, 2005]. In addition, the processing time is another point to be taken into consideration. It is expected that higher damage levels would be found when processing times are longer.

4.4 Morphology

The morphology of the wheat straw-polypropylene (WS-PP) composites and the wheat straw particles were analyzed using scanning electron microscopy. With the use of this analytical technique it is possible to observe the damage caused in the fibers' surface due to processing and the surface interaction between wheat straw particles and polymer. Micrographs of several wheat straw-PP composite samples are shown in Appendix A. Figure 18 is a representative image of the damage on the fibers' surface. It shows the modifications on the fiber's surface, probably caused by shear forces during processing the mixture of 30 wt-% WS fibers in PP at 190ºC. In this image, some parts of the structural walls of the wheat straw were peeled off (arrows indicate the points where part of the surface was pelled off). These features are modifications that the filler undergoes during the melt-mixing process.

The surface interaction between filler and matrix in composites with different formulations is observed in Figures 19 and 20. In both micrographs of freeze fracture surfaces it is noticeable that there is a good interaction between filler and matrix; i.e., the surfaces of matrix and filler touch each other and no voids are observed between the two materials (arrows 1 and 2 indicate points of good adhesion between the surfaces). The good adhesion in both cases is attributed to the presence of coupling agent based on maleic anhydride, MAET and MAPP (Figs. 19 and 20 respectively).

The micrograph shown in Figure 19 also shows the internal vascular bundles slightly smashed during processing, becoming flatter after that. These deformed bundles are indicated by arrows (3 and 4) in the Figure 19.

Furthermore, from Figure 20 it can be pointed that forces between the filler and matrix were stronger than the ones along the wheat straw structure, so that when the fracture surface was originated, the fiber was broken instead of the being pulled out of the matrix. It can be seen in the micrograph that the structure of the wheat straw was broken (as indicated by arrows 1 and 2), while the surfaces remained attached to the matrix (as indicated by arrows 3 and 4). The good interaction between the surfaces can promote the strength of the material, becoming more suitable for engineering applications.
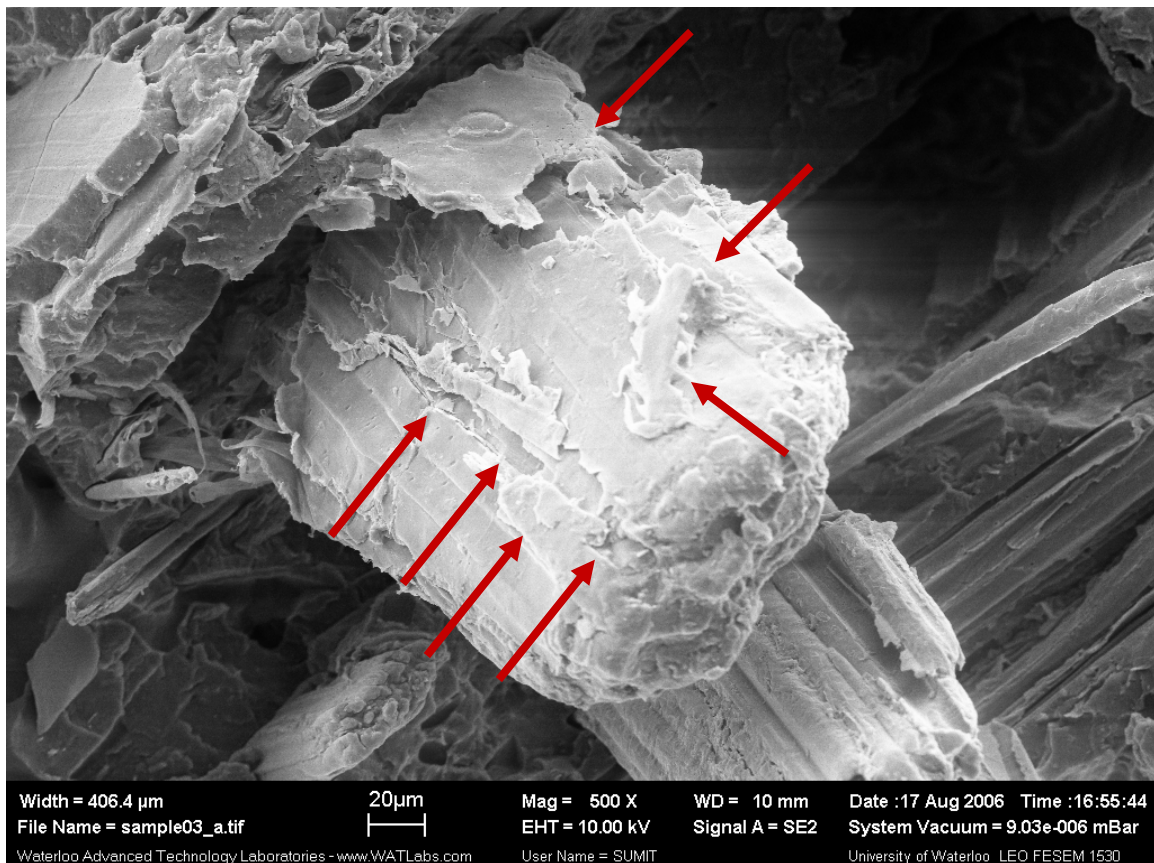
Figure 18: Fracture surface of WS-PP composite: wheat straw particle damage after compounding at 190ºC. Mag. (x 500)
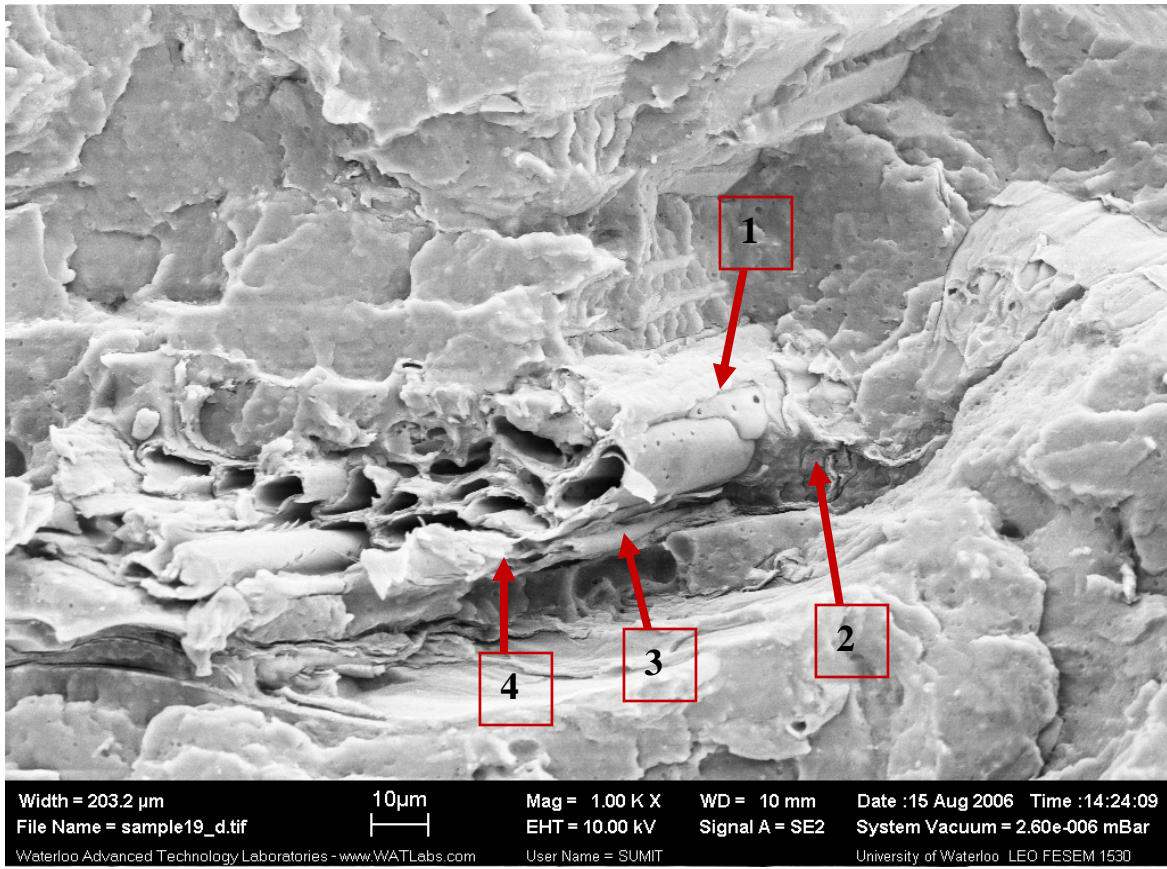
Figure 19: Fracture surface of WS-polypropylene composite containing 30 wt-% of fibers and MAET. Mag.(x 1200)
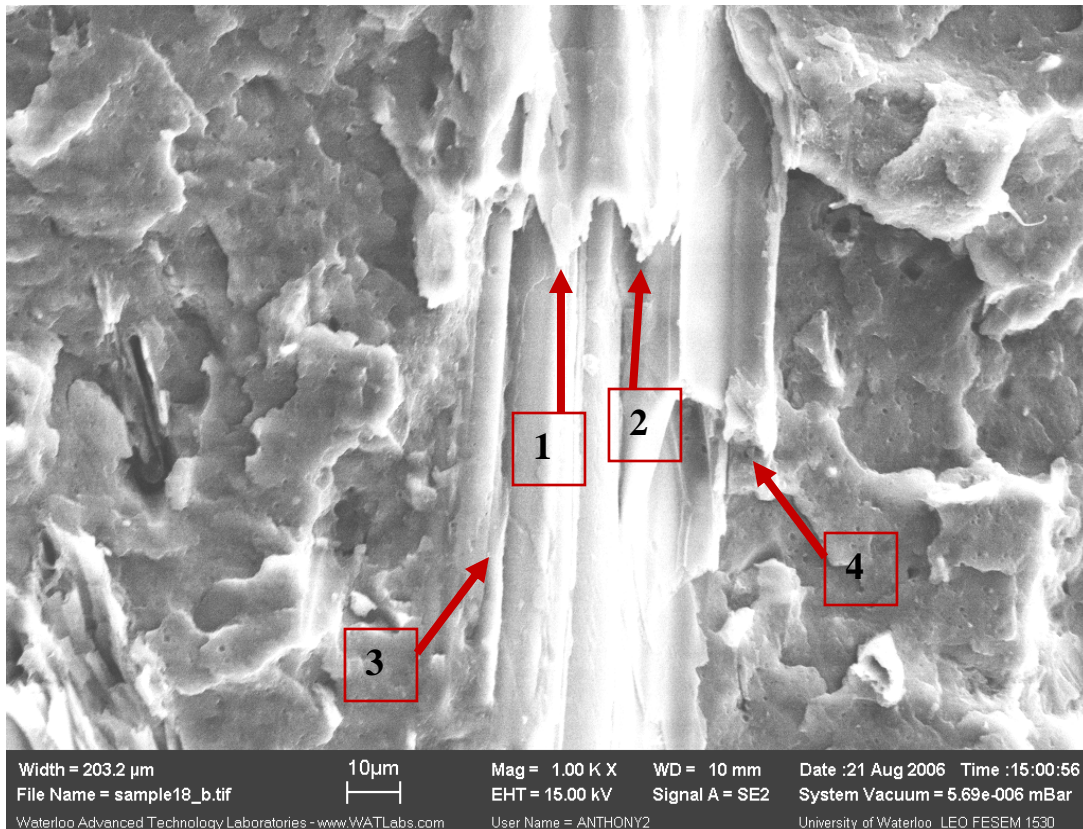
Figure 20: Fracture surface of WS-polypropylene composite containing 30 wt-% of fibers and MAPP. Mag. (x 1000)

The morphology of the composite prepared at high temperature (230ºC) is observed in Figure 21. Numerous voids can be noticed in this surface. Those voids can be attributed either to the evaporation of water and other volatile components in the fibers chemical structure or to the fiber pull out that occurred during the generation of the surface. At high temperature volatile substances present in the natural fibers can evaporate; therefore, the irregular surface is very likely to be caused by the evaporation phenomenon during processing. Bigger openings are then attributed to the fiber pull out.

The presence of gaps in the interface of filler-matrix is a very strong indicator that fibers were not well attached to the polymeric matrix. According to Hornsby et al. [Horsnby[2], 1997], the appearance of gaps between the phases arises as a consequence of the large volumetric contraction during melt cooling and solidification of the polymer. Similar morphology is observed in composites prepared at low temperatures (160ºC), as shown in Figure 22. It is

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valid to remember that the composites in both Figures 21 and 22 do not contain additives in their formulation, which increases the probability of fiber pull out due to the weak fiber surface interaction with the matrix. Probably some of the voids observed in Figure 22 arise from evaporation of water and volatiles, however, extensive evaporation due to degradation of the wheat straw is not considered in this case. A large number of holes resulting from the fiber pull-out was also reported by Rana et al. [Rana, 1998] for samples of an uncompatibilized system while considerably less holes and many broken fiber ends, embedded in the polymer matrix, were evidenced in compatibilized systems.

Width = 2.032 mm	100μm	Mag = 100 X	WD = 10 mm	Date :11 Oct 2006 Time :17:09:21
File Name = sample1_a1.tif	⊢┤	EHT = 10.00 kV	Signal A = SE2	System Vacuum = 3.43e-006 mBar
Waterloo Advanced Technology Laboratories - www.WATLabs.com		User Name = PAULA		University of Waterloo LEO FESEM 1530
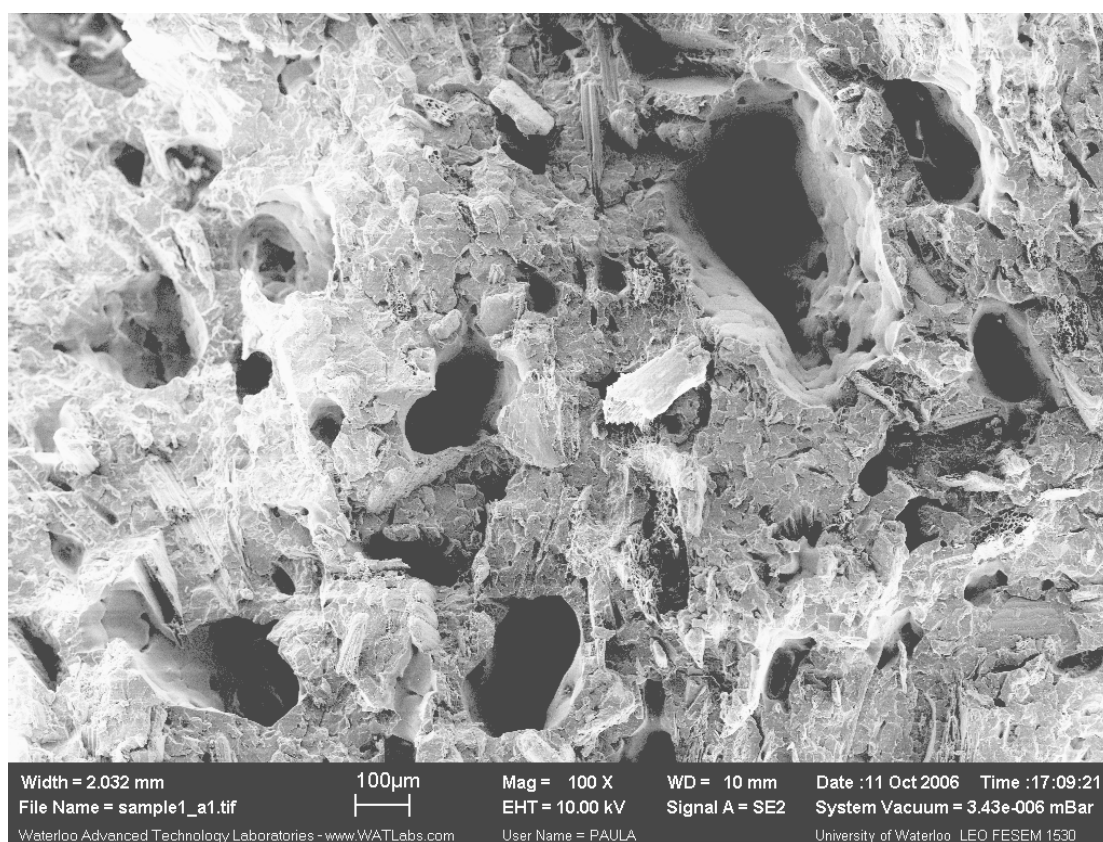
Figure 21: Fracture surface of WS-polypropylene composite containing 30 wt-% of fibers and processed at 230ºC. Mag. (x 500)

Width = 406.4 µm | 10µm | Mag = 500 X | WD = 9 mm | Date :11 Oct 2006 | Time :16:54:32
File Name = sample5_b2.tif | ⊢⊣ | EHT = 10.00 kV | Signal A = SE2 | System Vacuum = 4.45e-006 mBar
Waterloo Advanced Technology Laboratories - www.WATLabs.com | | User Name = PAULA | | University of Waterloo LEO FESEM 1530
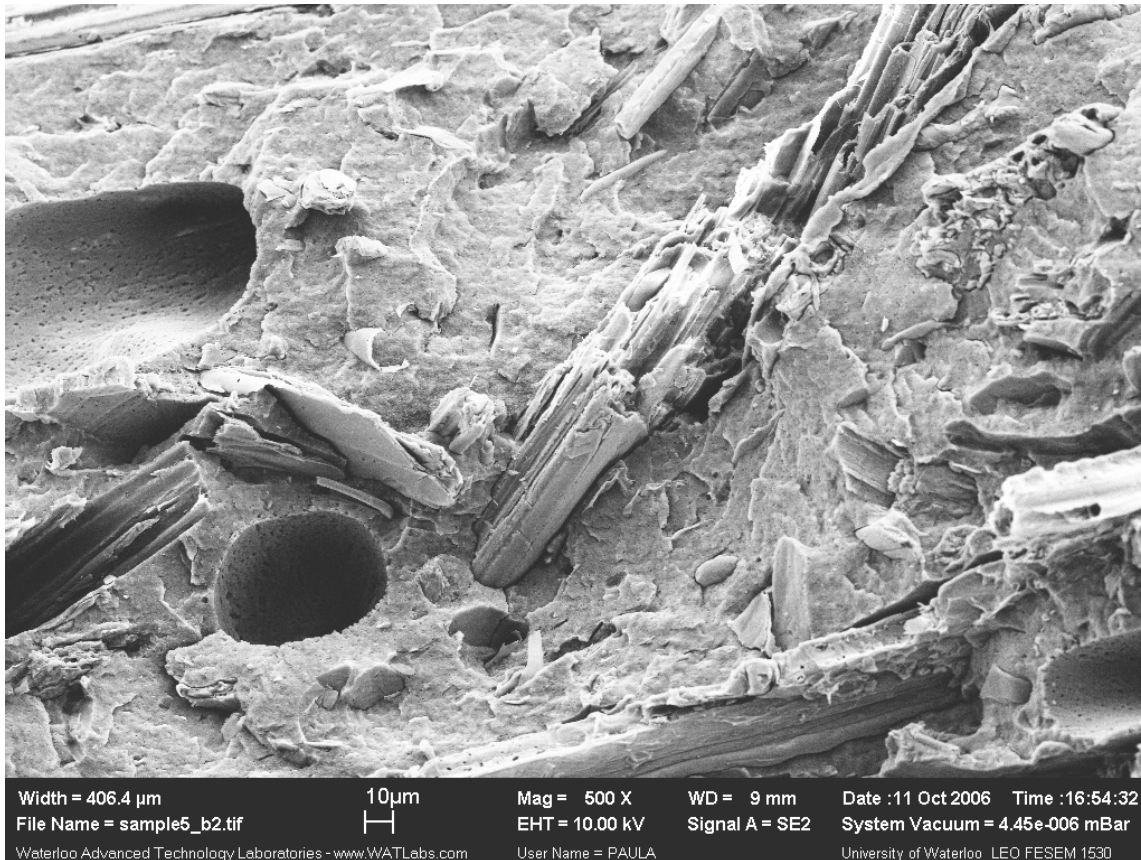
Figure 22: Electron micrograph of WS-polypropylene composite prepared at 160°C containing 30 wt-% of fibers. Mag (x 500)

Observations of the composites with the naked eye reveal a brown color on the samples. In addition, the higher the processing temperature resulted in a darker brown color of the samples. The coloration of the polymeric matrix is attributed to the degradation of wheat straw fiber components such as cellulose and lignin. Furthermore, as observed on the electron micrographs, the surface of the fibers was damaged; therefore, it is possible to affirm that very small fiber pieces, as well as microfibrils, were spread all over the matrix, increasing the dark coloration of the thermoplastic.

The dark brown tinge of the polymer matrix after compounding with kenaf fibers was reported by Sanadi et al. [Sanadi[2], 1999]. The matrix color was attributed to the material sheared off from the fibers' surface, which could have lignin, amorphous cellulose, oils and other surface extractives. In addition to the color observations in this study, a strong odour from the wheat

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straw particles was noticed in every sample; it was stronger in samples processed at higher temperature.

The analysis techniques employed here did not reveal differences in filler distribution in the matrix among all compositions prepared; therefore the filler distribution in this specific work is considered to be independent on the processing temperature, presence of additives or filler loading. This statement disagrees with previous findings, which suggest a better filler distribution in composites containing MAPP [Chen, 1998]. Further investigation not included in the scope of this project is necessary in order to evaluate filler distribution issues.

4.5 Properties

4.5.1 Thermal Properties and Crystallinity

From the DSC experiments, temperature of crystallization, T_c, (from run II) and melting point, T_m, (from run III) were obtained according to the maxima of the peaks in each curve. From the second heating run (run III), ΔH of fusion of each sample was calculated by the integration of the area under the melting peak. The first heating (run I) was ignored for collecting experimental data due to the previous heterogeneous thermal history of the samples. The thermograms for all composites, the polypropylene and the additives are shown in Appendix B.

The relative percentage of crystallinity (or the mass fraction of crystalline phase in the polypropylene matrix) was calculated based on the polymer content of the composites, with the following relation (Equation 3):

$$Xc = \frac{\Delta H}{\Delta H^o} \times 100 \qquad (3)$$

where $\Delta H°$ is the specific heat of fusion of 100% crystalline isotatic polypropylene and ΔH is the heat of fusion of the polypropylene content in the sample, calculated according to the mass

fraction of polymer in each formulation. ΔH° was considered 209 Jg^{-1}, according to the reference [Branrup, 1975].

Temperatures of crystallization, melting point and percentage of crystallinity of the composites prepared are summarized in Table 6 (regarding processing temperature), Table 7 (regarding filler loading) and Table 8 (regarding additives).

Table 6: Crystallization temperature, melting temperature and percentage of crystallinity of polypropylene and WS-polypropylene composites prepared for comparison of processing temperature.

Sample #	% Fiber	Temperature (°C)	Crystallization Temperature (°C)	Melting Temperature (°C)	Xc (%)
11	0	190	113.9	160.9	39.4
1	30	230	116.6	160.6	37.5
2	50	230	117.0	159.8	43.7
3	30	190	117.2	160.5	44.8
4	50	190	116.8	160.6	44.8
5	30	160	118.4	161.3	43.5
6	50	160	116.3	160.3	40.8

Table 7: Crystallization temperature, melting temperature and percentage of crystallinity of polypropylene and WS-polypropylene composites prepared at 190°C for comparison of wheat straw content.

Sample #	% Fiber	Crystallization Temperature (°C)	Melting Temperature (°C)	Xc (%)
11	0	113.9	160.9	39.4
7	10	117.2	160.3	45.4
8	20	117.1	160.6	43.2
3	30	117.2	160.5	44.8
9	40	117.1	160.1	32.6
4	50	116.8	160.6	44.8
10	60	115.4	159.6	39.8

Table 8: Crystallization temperature, melting temperature and percentage of crystallinity of polypropylene and WS-polypropylene composites prepared at 190°C for comparison of effects of additives.

Sample #	Additive	Crystallization Temperature (°C)	Melting Temperature (°C)	Xc (%)
11*	No additive	113.9	160.9	39.4
3	No additive	117.2	160.5	44.8
17	3% Lubricant	115.1	160.8	44.4
18	2% MAPP	116.1	160.4	40.2
19	2% MAET	116.9	160.4	39.4

* Pure polypropylene

As observed in Table 6, there was no significant change in the crystallization temperature with respect to the processing temperature of the composites. However, all composites presented higher crystallization temperatures compared to pure polypropylene. A small difference between samples containing 30 wt-% and 50 wt-% of filler was also observed in all temperatures tested.

It is important to mention that DSC replicate tests were not made; therefore, discussion presented in this work did not consider the reproducibility or uncertainty levels of DSC results obtained for the WS-polypropylene composites.

Figure 23 shows DSC scanning curves of samples containing 30 wt-% of wheat straw, prepared at different temperatures (160, 190 and 230°C). No significant changes in the melting temperature of composites containing the same amount of filler were observed with changes in the processing temperature. Moreover, the melting and crystallization curves were not significantly different; that is, no shoulders were observed in any of the curves.

For the sample containing 30 wt-% of fibers, processing at 230°C (Table 5) presented the lowest percentage of crystallinity among all specimens. Although antioxidant was added to the compounded mixture, at 230°C both polypropylene and wheat straw are likely to degrade. It is speculated that thermal degradation could have affected the thermal properties. Measurement of chemical composition or molecular weight distribution could provide evidence of polymer degradation, but those measurements were not considered in the scope of this work. Changes on the morphology of the WS with temperature or chemical reactions between the polymer chains and the WS can also be considered as a plausible hypothesis capable of affecting the thermal properties.
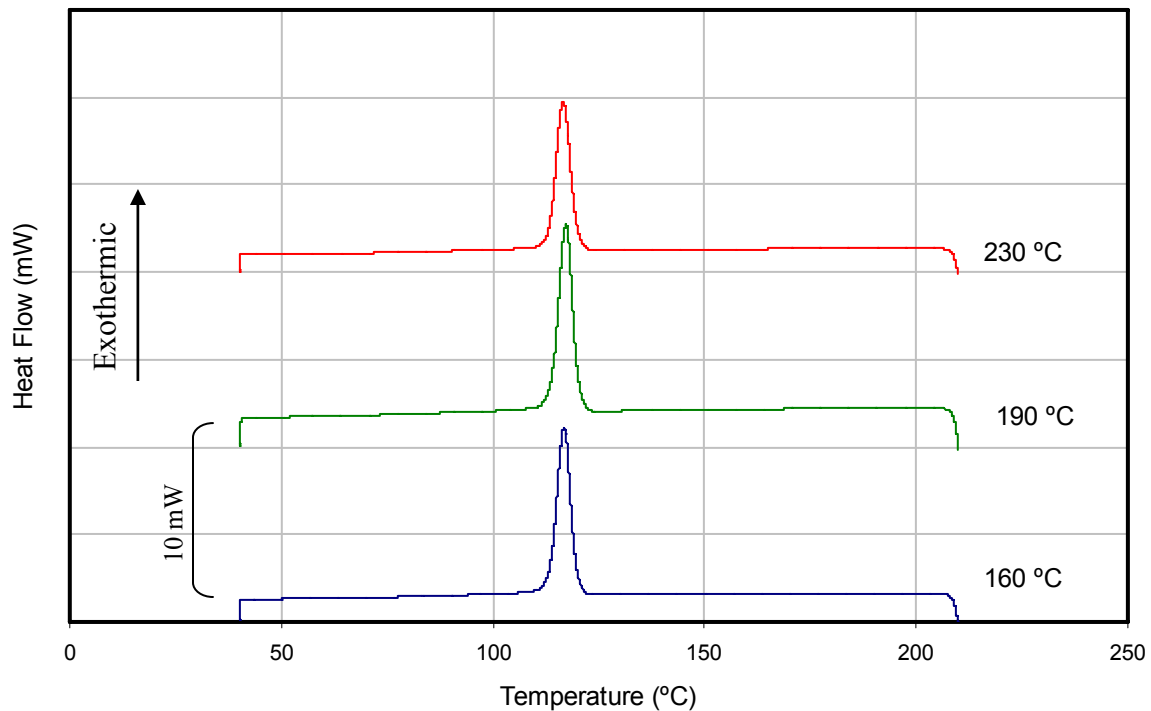
Figure 23: DSC cooling curves (run II) for samples containing 30 wt-% of wheat straw processed at 160, 190 and 230°C.

The effect of fiber loading in the melting point, crystallization temperature and percentage of crystallinity is presented in Table 7. From the data obtained, it is possible to observe that the addition of fibers increased the crystallization temperature of polypropylene; the increase is not proportional to the amount of filler in the composite though.

Wheat straw-polypropylene composites presented an increment on crystallization temperature with respect to the pure matrix. Similar observations were reported by Ganán and Mondragon [Ganán and Mondragon, 2003] in their research about thermal and degradation behaviour of fique fibers and thermoplastic matrix composites. In their work, composites presented higher crystallization temperatures than the neat PP. The normalized degree of crystallization for PP composites was also increased by the addition of fique fibers, according to those authors.

Regarding crystallization and melting temperature, it is interesting to notice that despite of the amount of fiber, the crystallization temperature is almost the same for most of the wheat straw composites. A unique crystallization temperature was also observed by Ichazo et al. [Ichazo, 2000] for composites made out of sisal fibers and polypropylene. On the other hand, this is opposite to reports from Mi et al. [Mi, 1997] mentioning the presence of a second melting peak at lower temperature for composites containing bamboo fibers as filler.

In the study reported here only one melting point was observed for each wheat straw composite and this point was located at a temperature slightly lower than the melting temperature of pure polypropylene. A marginal effect, of no clear tendency, was observed on the T_m of polypropylene for wheat straw composites, in agreement to the results reported by Amash and Zugenmaier in their work about fiber-reinforced polypropylene composites [Amash and Zugenmaier, 1997].

Melting curves for pure PP and composites containing from 10 to 60 wt-% of WS are shown in Figure 24. The integration of melting peaks reveals a small increase in the degree of crystallinity of the polymeric phase with addition of WS fibers. The significance of this small increase would be better evaluated with information about the reproducibility and uncertainty of the measurements. Sanadi et al. [Sanadi[2], 1999] reported no significant change in the degree of crystallinity of PP-kenaf fiber. Studies realized on henequem cellulosic fibers in low-density polyethylene matrix also showed that addition of natural fibers to thermoplastic matrices does not change the crystallinity of the polymer phase [Herrera-Franco, 1997].

For composites containing from 10 to 60 wt-% of wheat straw fibers, increases detected in the percentage of crystallinity range from 0.4 to 6.0%. However, no clear relationship between the increase in the percentage of crystallinity and the weight percentage of fiber in the composite was found. From these results, it can be affirmed that wheat straw fibers do not present extensive nucleating ability for polypropylene, in agreement with Avella et al. [Avella, 1995]. The composite sample containing 40 wt-% of fibers was the only exception, it presented lower percentage of crystallinity than the pure resin. This fact was attributed to possible experimental errors during the compounding process of this specific sample.
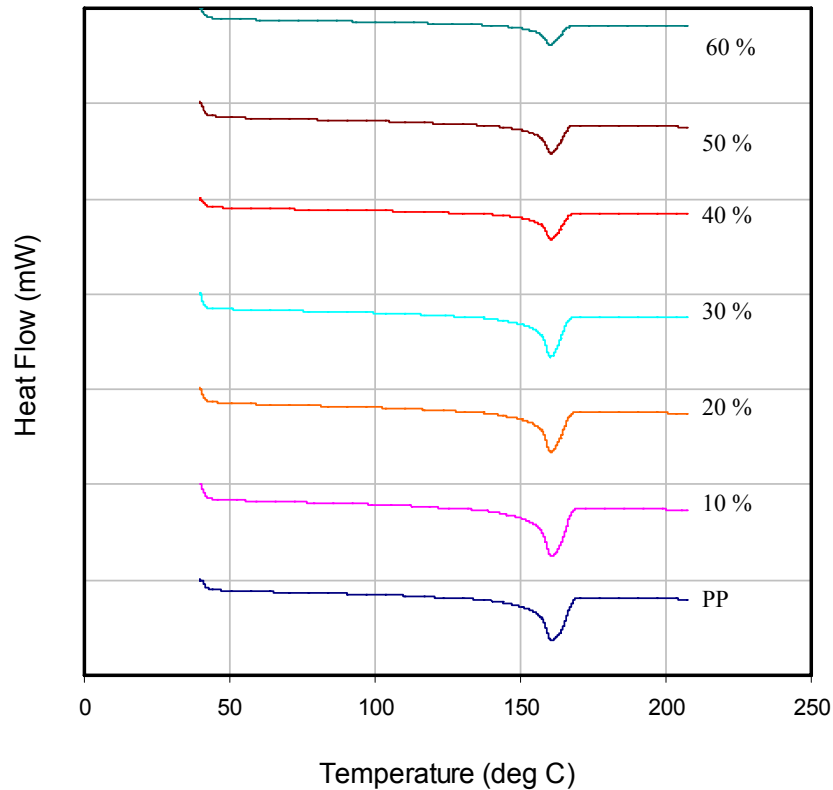
Figure 24: DSC heating curves (run III) for samples containing 0, 10, 20, 30, 40, 50 and 60 wt-% of wheat straw fibers. Composites were processed at 190°C.

From Table 8 it is possible to see that none of the additives investigated caused significant changes in the crystallization or melting point of the composites. The crystallization temperatures of composites containing the same amount of fibers, obtained from the peaks observed during the cooling run, are very much comparable between blends with and without coupling agent. The percentage of crystallinity observed in the composite containing MAET was slightly lower compared to the other samples; this might be attributed to the lower crystallinity of ethylene in comparison to polypropylene or the immiscibility of polyethylene and polypropylene.

For the sample containing lubricant (sample 17), a small peak with a higher temperature than the crystallization temperature was observed in the cooling curve obtained from DSC analysis. Figure 25 shows the cooling curve of this sample, where the small peak mentioned is located at 133.3°C. This peak is attributed to the presence of lubricant in the sample as the additive

presents a crystallization point at 142.5°C. Besides this small peak, the main crystallization point of the sample 17 is located at 115.1°C. This temperature is lower than the temperature registered for the sample that does not contain the additive. According to Harper and Wolcott [Harper and Wolcott, 2004], lubricants decrease the nucleation advantage of the fiber while increasing the nucleation ability of the bulk. Thus, it can be inferred that the small crystallization peak is related to the crystallization of the bulk while the higher crystallization temperature can be attributed to the crystallization on the fibers' surface, even if this is relatively small.
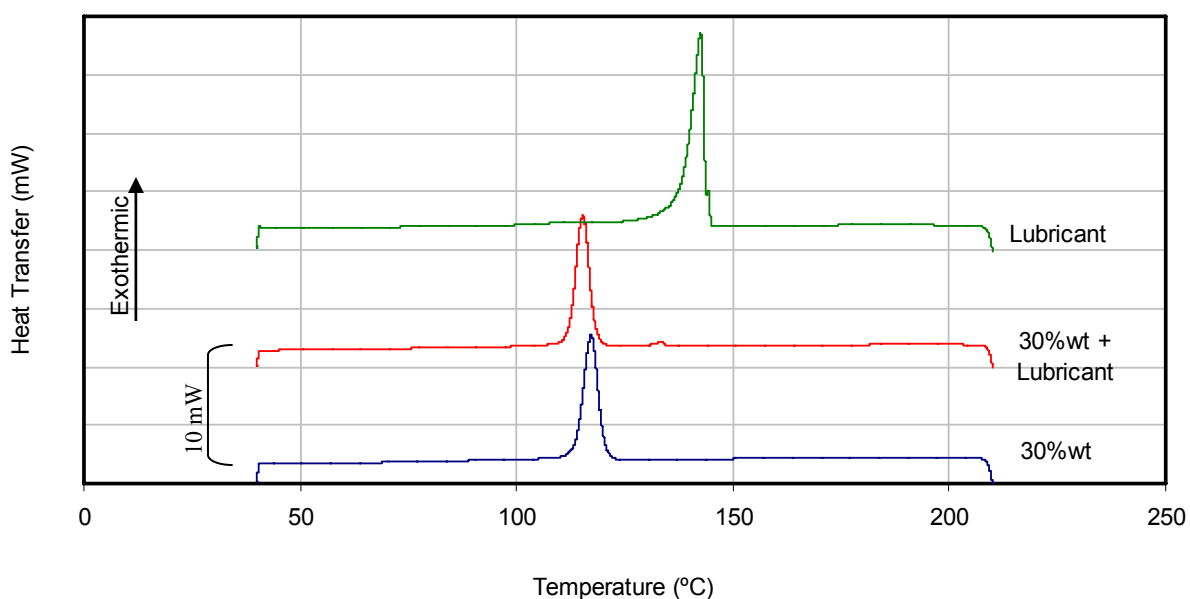

Figure 25: DSC cooling curves (run II) for the lubricant and composites with and without lubricant, both containing 30 wt-% of wheat straw. Blends were processed at 190°C.
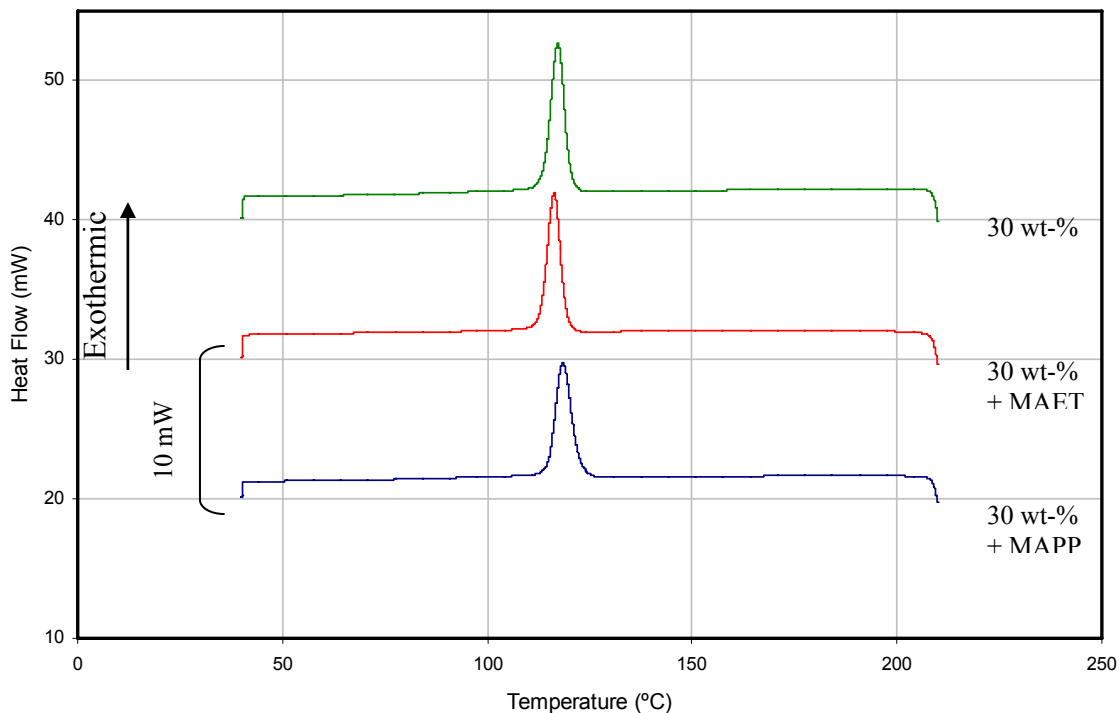
Figure 26: DSC cooling curves (run II) for composites processed at 190°C containing 30 wt-% of WS with MAPP, MAET and without coupling agent.

Figure 26 shows the cooling curves for WS-PP blends where the effect of maleic-anhydride based coupling agents on the thermal properties can be evaluated. Composites containing coupling agent (MAPP or MAET) presented slightly lower crystallization points and lower percentages of crystallinity compared to the WS-PP composite without coupling agents (as indicated in Table 8). In agreement with Yin et al. [Yin, 1999], addition of small amounts of MAPP to polypropylene slightly reduces the extent of crystallization of the material. The low degree of crystallinity observed in samples containing coupling agents can be attributed to the lower crystalline content of the maleated component (PP or PE) with respect to the pure iPP [Chen, 1998] or to the MAPP/MAET nucleating action, which produces a smaller size of spherulites and consequently a more pronounced presence of amorphous phase in the system [Avella, 1995].

Differences observed for the melting point among composites containing different additives and pure resin are not significant (Table 8). Results obtained here are in agreement with those

reported by Sanadi et al. [Sanadi[2], 1999] for natural composites containing kenaf fibers, where the softening temperatures for composites containing coupling agent were slightly higher than for the uncoupled systems.

4.5.2 Water Absorption

Water sensitivity is an important selection criterion for many practical applications of composites. Water absorption in lignocellulosic filled composites can be significant; the migration of water through the material can lead to a disturbance of the filler/polymer interface, thus changing the characteristics of the system.

It is well known that in natural fiber composites the main factor that is responsible (if not the only one responsible) for the composite moisture absorption is the fiber; sorption by thermoplastic matrices can be neglected (if polymeric matrices are hydrophobic like in the case of polypropylene). Filler content, filler size, use of coupling agent and processing method are the main groups of influencing factors on moisture uptake; filler content was by far the largest influence on all responses in previous experiments [Steckel, 2007]. Generally it is accepted that to avoid water absorption, natural fibers must be well wetted by the matrix, so that the polymer will encapsulate the fibers, keeping them away from moisture present in the environment. The wetting of the fiber by the thermoplastic matrix depends on the surface energy compatibility of the two components.

In order to verify the water absorption behaviour of WS-polypropylene composites, immersion experiments were performed. Figure 27 shows the increase in weight of polypropylene and PP based composites with 30 wt-% of WS fibers, prepared at different temperatures and containing different additives. The experiment recorded the absorption of water for all selected specimens during 90 consecutive days.
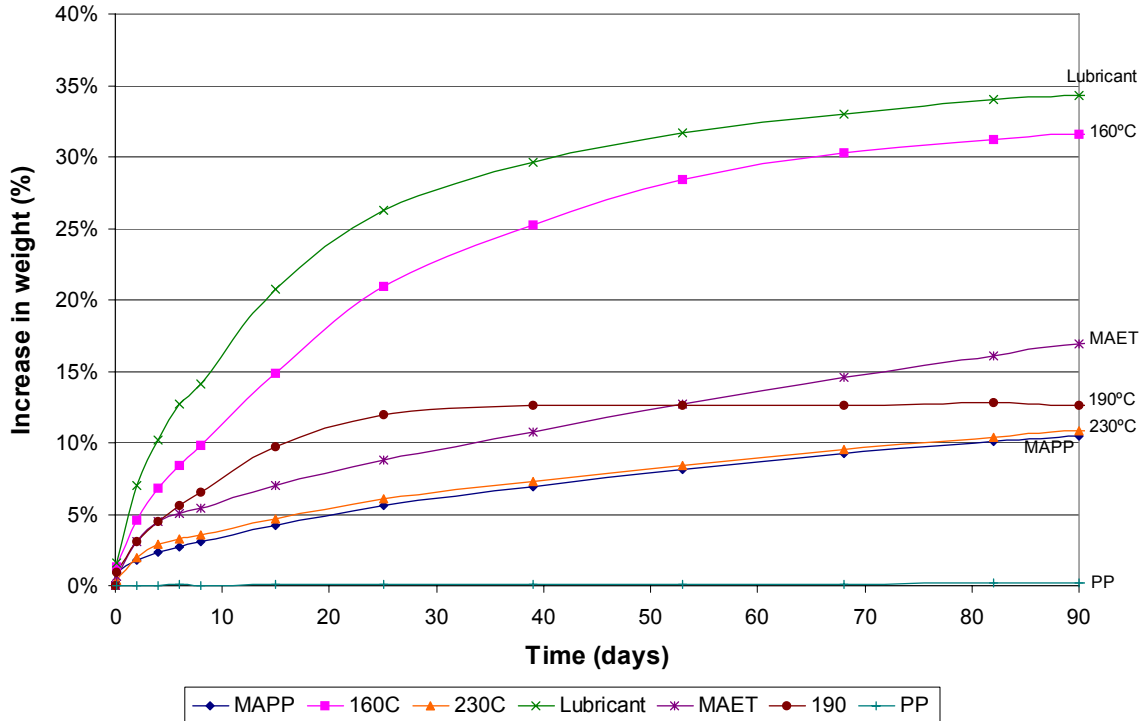
Figure 27: Amount of water absorbed with time of PP and composites containing 30 wt-% of WS fibers processed at 160°C, 190°C and 230°C. Composites processed at 190°C contain coupling agent (MAPP or MAET), lubricant or no additives.

After 90 consecutive days, the gain in weight recorded for some samples achieved a plateau while for others it was still increasing in relation to the previously measured point. At 30 wt-% WS fiber content, some composites tested were significantly different regarding their water uptake behaviour while others presented minor differences among themselves.

It can be clearly seen that the sample containing lubricant exhibits the highest increase in weight (around 34.3%) over the immersion time studied in this project; while the smallest amount of water absorbed was observed for the sample containing coupling MAPP. Composites processed at 160ºC also presented high increases in weight (about 31.6%); the amount of water absorbed decreased as the processing temperature of the composites increased.

In agreement with these findings, Steckel et al. [Steckel, 2007] detected reduced hygroscopicity of wood particles in thermoplastic matrix when exposed to elevated temperatures during processing. At high processing temperatures organic components such as cellulose, hemicellulose and lignocellulose are likely to decompose, therefore diminishing their ability to "capture" water molecules. Thus, it can be concluded that at 190ºC and 230ºC, natural fibers were partially chemically changed due to thermal degradation, decreasing the capacity of some components to form hydrogen bonds with water molecules.

Regarding the effect of coupling agents over water uptake behaviour of WS-PP composites, after 53 days the system containing MAET exhibited larger weight increase than the composite containing 30 wt-% of WS fibers without additives (both processed at the same temperature). It can be inferred that the efficiency of the ethylene based coupling (MAET) agent is lower than the efficiency of the PP based one (MAPP). Indeed, the presence of a second polymer in the composite introduces a new factor to the system: the interaction between the two types of polyolefin. It is possible that the interaction between molecules of polypropylene and molecules of polyethylene, due to structural reasons, were not able to entangle or mix, creating irregularities in the matrix. The interference caused by the polyethylene could also affect the interaction between the filler and the PP matrix, decreasing the wetting ability of the matrix. In other words, the system containing only one type of polymer (PP) was able to better encapsulate the filler, avoiding the contact between WS fibers and water.

In previous findings [Van de Velde and Kiekens, 2001], among polymers such as LDPE, HDPE, PC, PET and PEEK, polypropylene was the resin that provided to flax fibers the best possible protection against water; which verifies that weight gain characteristics also depend on the matrix polymers [Chow, 2007].

The increase in fiber-matrix adhesion attributed to the presence of coupling agent was noticed in previous works [Hornsby, 1997; Mishra and Verma, 2006], which reported lower water absorption for system with coupling agents in comparison to non-coupled systems. Mishra and Verma [Mishra and Verma, 2006] reported hydrophobic characteristics of wood flour/PP composites modified with maleic anhydride as identified through FTIR measurements. In some

cases, the lower water absorption in compatibilized systems was attributed to some of the hydrophilic –OH groups reacting with acid anhydride to form ester linkages [Rana, 1998]. In addition, according to Sanadi et al. [Sanadi[2], 1999], the amount of coupling agent also affecs the water absorption in natural fiber composites, thus an optimum point is expected on the relationship between amount of coupling agent and weight gain.

In the presence of certain fibers, preferential crystallization can occur if the fiber surface acts as a good nucleating agent, thus creating a layer of crystalline material around the fiber. The presence of a crystalline layer formed by the polymer matrix on the fiber surface (also called transcrystallinity) is expected to help against moisture uptake of the composites, working as a barrier; however, as of yet the phenomenon of transcrystallinity is not completely understood.

Sanadi et al. [Sanadi[2], 1999] suggested the existence of enhanced transcrystallinity around the fibers in coupled systems as responsible for decreasing the rate of water absorption of the composite material. Yin et al. [Yin, 1999] reported the increase in the nucleation capacity of woodfibers for polypropylene when a small portion of MAPP was added. Furthermore, the surface crystallization for that system dominated over bulk crystallization and a transcrystalline layer was formed around the fibers. The transcrystalline layer was not observed in uncoupled systems, and so the results were in agreement with the ones reported by Mi et al. [Mi, 1997].

According to Ton-That and Jungnickel [Ton-That and Jungnickel, 1999], water diffusion is only possible through the amorphous phase of semicrystalline materials. The crystalline layer around the fibers would act by protecting the fibers against water. It is known that polymer segments on the amorphous phase of semicrystalline thermoplastics have much more mobility than polymer segments arranged in crystalline structures. The higher mobility of the polymeric chains is likely to facilitate sorption of water molecules by helping them to move into the polymeric phase. Thus, it is acceptable to conclude that transcrystallinity for WS-polypropylene systems reported here (Figure 27) containing MAPP is likely to happen.

After 90 days exposed to water, some of the WS-polypropylene composites presented significant change in color while others presented almost no change. In general both fiber and

matrix faded, losing the dark tinge obtained from the melt mixing process. Figure 28a-b shows a comparison of the specimen containing 30 wt-% of WS fibers and lubricant (sample 17) before and after the immersion in water procedure (90 days), respectively. It is clear from this image that the specimen faded after immersion in water presenting the same behaviour as agroplastics tested by Johnson et al. [Johnson, 1999]. According to Falk et al. [Falk, 2000], natural fiber-thermoplastic composites are likely to fade when exposed to weathering, having in mind that one of the most expressive weathering agents is moisture; the effect of weathering depends on the type of thermoplastic as well as on the filler content.

Since the matrix dark color is attributed to natural fiber components sheared off during processing [Caulfield, 1999], it could be possible that those components were washed out from the matrix by water. However, the water bath (about 400 ml) used in this experiment was changed weekly and such water remained transparent throughout the entire experiment time. The degree of fading was also different from sample to sample, depending on the formulation and processing conditions. The specimen containing lubricant presented more intense color changes and at the same time the highest increase in weight due to water uptake; nevertheless, no direct relationship was found between the amount of water absorbed and the color fading among the samples.
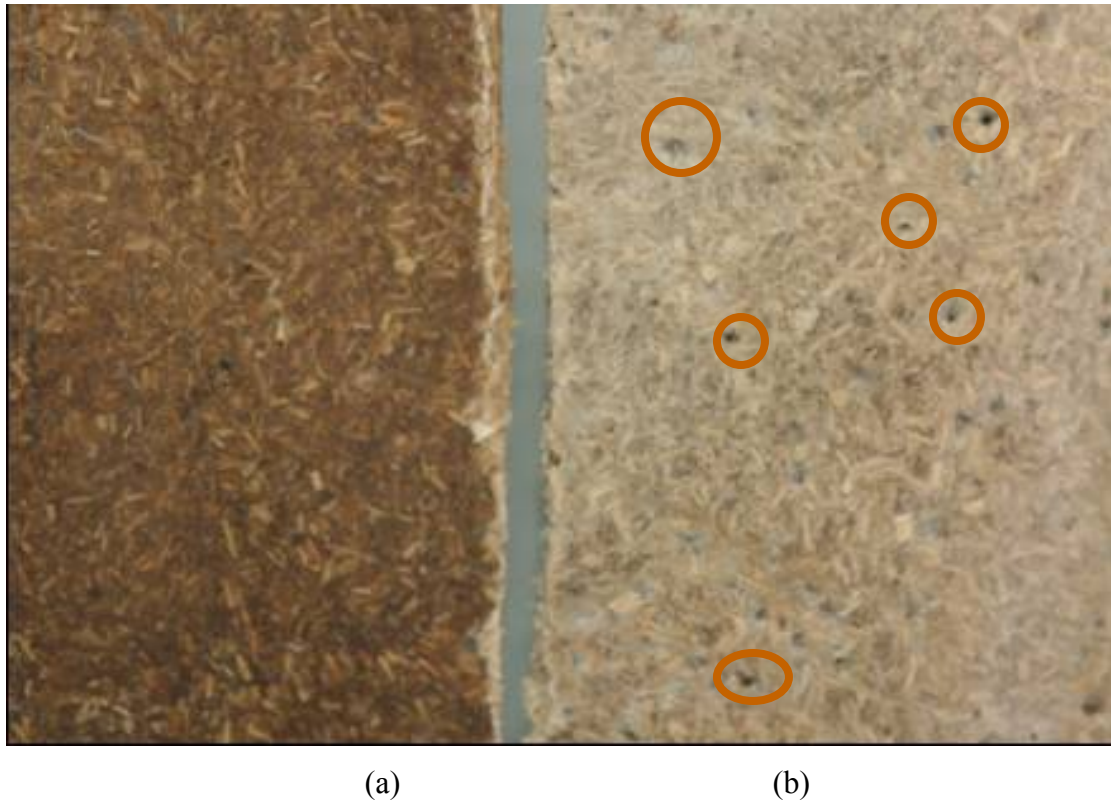
(a)	(b)

Figure 28: PP- 30 wt-% wheat straw fibers composite containing lubricant before immersion in water (a) and after immersion in water (b).

Besides the color change, after 90 days immersed in water all composites presented more visible fibers at the surface than previous to the test. The wheat straw fibers seem to be swollen, appearing bigger at the end of the experiment time. Swelling of the composite due to moisture absorption can lead to dimensional stability problems in lignocellulosic fiber composites [Rowell, 1999]. Dimensional changes were markedly observed in composite samples prepared at 160°C, containing lubricant and containing MAET (samples 5, 17 and 19, respectively). In those three samples, the average thickness was around 3.80mm after immersion in water, representing 15% of increase in this dimension. Changes in the other dimensions were negligible. The composite specimen containing MAET (sample 19) presented some sort of waves (elevations) on the surface after immersion in water. Although noticeable, the elevations on the surface were relatively small; however, it clearly denoted the dimensional stability problems.

In addition to fiber swelling phenomena, small holes or voids were identified in the surface of some composite specimens (identified in Fig. 28 b). Not only in the surface of the composites, but also in the surface of the fibers even smaller holes were identified (in the order of 1µm of diameter or less), as indicated in Figure 29. Round openings on the wheat straw surface are attributed to the contact of the wheat straw with water for a prolonged time; yet, the formation mechanism for the openings is not completely understood. It is plausible to speculate that that water could have dissolved some of the chemical components of the natural fiber, thus weakening its structure and leading to the formation of those small holes; this hypothesis could have been further investigated with chemical analysis of the water bath used for immersion of the composite samples.

Voids on the composite surface can be recognized as cracks caused by the size expansion of the fibers by absorption of moisture or as heterogeneity within the composite, which can have regions with different amounts of water [Rowell, 2001]. In addition to that, the matrix structure can also be affected by processes such as chain reorientation and shrinkage after water absorption [Espert, 2004].

Imperfections on the fibers and matrix interface work as paths for the water to get inside the sample allowing the contact between water and filler particles that are placed in the interior of the composite. In those voids, water molecules can also be trapped, hence increasing the weight of the tested specimen. Indeed, water was found trapped inside the composites investigated here after they were removed from the water bath. The internal structure of the specimens presented cavities where little drops were allocated.
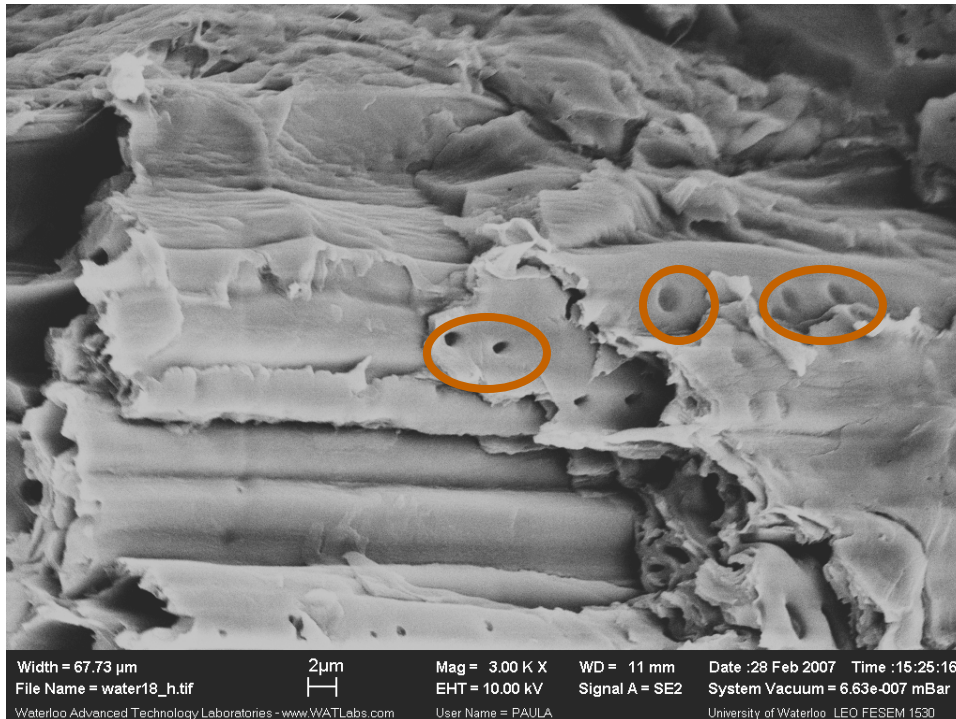
Figure 29: Wheat straw particle after exposition to water during 90 consecutive days. Mag (x 3000)

Overall, typical consequences of water absorption in natural fiber composites reported in the literature were: matrix swelling, fiber-resin debonding, oxidation and microcracks [Johnson[2], 1999]. Among those consequences of water absorption, oxidation on the surface of the composites was the only one that was not observed in the WS-polypropylene composites studied here.

All samples tested for water absorption contained 30 wt-% of wheat straw fibers (except the pure resin sample). It can be expected that at higher fiber contents the water absorption would be more pronounced; however, it could be that the effect of fiber content would appear only at high soaking times, as observed by Tajvidi et al. [Tajvidi, 2006]. Immersion times are also related to the level of degradation of composites and filler.

Serious debonding between fibers and matrix has been reported to occur in sisal/PP composites [Chow, 2007] after 72h of water immersion; however, the sisal fiber was still relatively intact, the only damage was observed at the fiber/matrix interface. After 216h, the interface between

PP and fibers has been totally removed, in addition, a significant portion of the lignin and hemicellulose have been leached out in the water immersion treatment.

Depending upon the environmental conditions and the condition of the material, natural fiber composites can either absorb or lose moisture. Some authors have reported that after it has reached a maximum value, the weight gain of the composite decreases gradually with the increase in water immersion time [Chow, 2007]. This fact was attributed to the dissolution of lignaceous material and waxy substances on the sisal fiber suface. This phenomenon was not observed in the experiments conducted in the present work; yet, after they were removed from water all specimens presented some decrease in weight when left exposed to the laboratory environment at 23 ± 1ºC and 50 ± 5% of relative humidity. After 21 days, all composite formulations presented a decrease in weight, meaning that water was desorbed from the samples. The amount of water desorbed in this period of time is shown in Table 9, which is expressed in terms of percentage of the total amount of water absorbed by each specimen previously. From those results, it is possible to see that WS-PP composites are able to release water to the ambient when left exposed to regular atmospheric conditions. Moreover, natural fiber composites can lose up to 97% of the moisture content, which is almost the total water uptake during immersion time. It is important to mention that physical characteristics such as color and dimensions of all samples did not change after water desorption.

Table 9: Weight percentage of water desorbed from the wheat straw composites containing 30 wt-% of fibers after 21 days exposed to 23 ± 1ºC and 50 ± 5% of relative humidity.

Sample #	Temperature (°C)	Additives	Weight of water desorbed after 21 days out of water (%)
1	230	No additives	61.8
3	190	No additives	91.7
5	160	No additives	91.6
17	190	3% Lubricant	97.1
18	190	2% MAPP	46.6
19	190	2% MAET	63.0

Knowledge of moisture uptake and transport properties is essential for predicting the moisture content of natural fiber composites and thus for estimating their life-time when exposed to high humidity environments. According to Espert et al. [Espert, 2004], moisture penetration into composite materials is likely to be conducted by three different mechanisms. Diffusion of water molecules inside the microgaps between polymer chains is considered the main process, followed by capillary transport into the gaps and flaws at the interfaces between fibers and polymer (because of incomplete wettability and impregnation). Transport by microcracks in the matrix, formed during the compounding process is also a significant mechanism.

The diffusion coefficient or diffusivity measures the "speed" by which the moisture concentration changes inside the material. It is of great significance for composites because it tells how much of a liquid diffuses into a composite, how rapidly and to what extent. From the curves of water absorption as a function of time the water diffusion coefficients were calculated for each specimen. Among several authors, Fick's second law is generally considered the starting point of the mathematical description of diffusion, although it may not be obeyed by polymers or polymer composites. The Boltzmann's form of Fick's general diffusion equation used in this work is given in Equation (4). The last term in the equation is a geometrical correction. Since the one-dimensional Fickian diffusion equation for thick samples can bring in errors, the correction introduced in the equation minimizes possible errors based on the geometry of the sample used for testing.

$$D = \pi \cdot \left(\frac{h}{4M_\infty} \right)^2 \cdot \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \cdot \left(1 + \frac{h}{w} + \frac{h}{l} \right)^{-2} \qquad (4)$$

where:

D = diffusivity, mm^2s^{-1};

M_∞ = mass uptake value at equilibrium time, gr;

t_1 and t_2 are absorption times, s;

M_1 and M_2 are two mass uptake values corresponding with t_1 and t_2, gr;

h= sample thickness, mm;

w= sample width, mm;

l= sample length, mm.

Based on Fick's second law and considering diffusion of water in only one dimension, water diffusion coefficients were calculated for each composite formulation; the results are presented in Table 10, as well as the value considered as water uptake at equilibrium time for the calculations.

Table 10: Water diffusion coefficients calculated for pure polypropylene and different formulations of WS- polypropylene composites.

Sample #	Temperature (°C)	Additives	D (mm^{2}s^{-1})	M_∞ (%)
11*	190	No additives	8.9029E-09	0.15
1	230	No additives	3.1064E-07	10.80
3	190	No additives	4.0531E-07	12.61
5	160	No additives	1.9758E-07	31.61
17	190	3% Lubricant	2.7666E-07	34.34
18	190	2% MAPP	1.4613E-07	10.50
19	190	2% MAET	2.2534E-07	16.91

* Pure polypropylene

Diffusion coefficients of water in natural fiber composites have been previously reported. Steckel et al. [Steckel, 2007] have calculated the diffusion coefficient for systems containing wood flour and polypropylene. In their experiments, different methods (exposition to air with high moisture level and immersion in water) were observed to yield different values for diffusion coefficients. According to Shen and Springer [Shen and Springer, 1976] experiments that evidence the maximum moisture content depend on the moisture content of the environment. This is in agreement with the results observed by Steckel et al. since the maximum moisture uptake value is considered in the diffusivity calculations. Diffusivity was also calculated for polypropylene containing different natural fibers such as kenaf and rice hulls; the results demonstrated the dependence of water diffusion on the type of fiber and formulation of the composite [Tajvidi, 2006].

The diffusivity calculated for wheat straw-polypropylene composites (Table 10) is about 2 orders of magnitude higher than pure polypropylene, which differs in one order from results reported for natural fiber composites and polypropylene in a previous work [Tajvidi, 2006]. All composite samples in Table 10 presented diffusivity values in the same order of magnitude. Comparison among them reveals that addition of coupling agent decreased the diffusivity; those results agree with the fact that samples containing MAPP or MAET absorbed lower amount of water than samples without additives during the same period of time. Similarly, slightly reduced equilibrium water uptake and remarkable reduction in water uptake rate were denoted for MAPP-modified samples of short flax fiber-PP composites [Arbelaiz, 2005].

Since diffusivity is a measurement of how fast water can get into the material for a fixed period of time, higher diffusivities will lead to higher amounts of water inside the materials. In addition, recalling the fact that composites containing coupling agent are likely to present transcrystallinity in their structure, previous investigations on transcrystalline layers of PP revealed that the diffusion coefficient of a low crystallinity PP is smaller than that of amorphous material [Ton-That and Jungnickel, 1999], thus suggesting that the diffusivity in the crystal phase is lower than that in the amorphous phase of a polymer.

The specimen containing lubricant, which presented the highest increase in weight, did not present the highest diffusion coefficient. Considering that the diffusivity can provide a perspective on the amount of water absorbed by the specimen, that result was not expected. It could be that the lubricant interfered in the interaction between filler and matrix, allowing the formation of voids between the surfaces; however, further investigation on the effects of lubricants in natural fiber-polymer composites is needed to confirm this hypothesis.

As expected, the neat PP showed the lowest value of diffusivity among all the samples.

Among the composites, the lowest value of diffusivity was observed for the composition containing MAPP ($1.4613E-07$ mm^2s^{-1}). Furthermore, diffusivity values calculated for composites prepared at different temperatures did not show correspondence to the amount of water absorbed by samples at the end of the experiment (Table 10). The inconsistency between

diffusivity values and final weight increase in the composites can lead us to the conclusion that water diffusion into wheat straw-polypropylene composites does not completely follow the Fickian relationship with time, i.e., there is a deviation from Fick's law. Those results are in opposition to results from Mishra et al. [Mishra, 2006], where the kinetics of water absorption in polypropylene/wood flour foamed composites was found to obey the Fickian behaviour.

In general, there are three different categories of diffusion behaviour [Espert, 2004]: (a) Fickian diffusion, in which the rate of diffusion is much less than that of the polymer segment mobility and the equilibrium inside the polymer is maintained with independence of time; (b) the opposite, when the rate of diffusion (penetrant mobility) is much greater than other relaxation processes of the polymer chains; (c) non-Fickian or anomalous, when the penetrant mobility and the polymer segment relaxation are comparable.

Possible deviations from the classical Fickian behaviour are shown in Figure 30. Curve A represents pseudo-Fickian behaviour, with a short linear portion and anomalous dependence on the specimen thickness; curve B is a sigmoid; and curve C is a two-stage behaviour, where equilibrium appears to have been achieved but further sorption occurs later. In the case of fiber reinforced resins, it is suggested that one of the causes for deviation from Fick's law is the progressive formation of microvoids in the matrix through damage induced by chemical or physical processes [Hodgkinson, 2000]. Furthermore, sometimes a plot of mass uptake against time shows a second plateau, as shown in curve C; thus meaning that diffusion experiments, which do not allow sufficient time for the second plateau to effectively appear, can be misleading about the final equilibrium water uptake. The second plateau is attributed to additional space for incoming permeant created by swelling stresses [Hodgkinson, 2000].
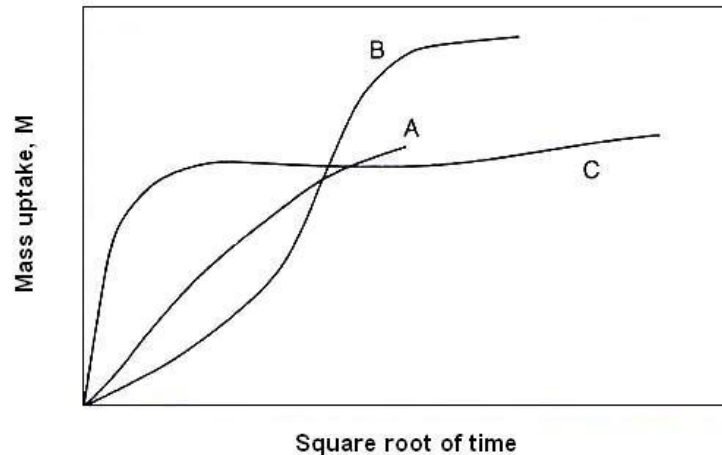
Figure 30: Water uptake curves- possible deviations from classical Fickian behaviour. (A) Pseudo-Fickian behaviour, (B) Sigmoid and (C) Two-stage curve [Hodgkinson, 2000].

In our studies, immersion experiments were stopped after 90 days; however, not all samples had reached a saturated moisture level within this time. There was a small difference (not significant) between the two last weight increase values for most of the samples.

 The difference between the true equilibrium point and the mass uptake used in the diffusivity calculations (value measured after 90 days of experiment) certainly introduces errors to the results. As indicated in Equation 4, the mass uptake value at equilibrium is inversly proportional to the diffusion coefficient; when higher values are introduced in the equation, the diffusivity obtained is lower. Besides, contributions of voids, holes, or similar distortions to the deviation of Fick's model must be considered when calculating diffusivity in WS-PP composites.

As already observed, high processing temperatures promoted voids in the composite matrix and long water exposure times promoted the creation of little holes on the surface of wheat straw particles. Additionally, the sample containing lubricant presented openings in its surface, as shown in Figure 28.

For Fickian behaviour, the curves of sorption and desorption with time should be superimposable. Nevertheless, the water content 21 days after the samples were removed from

the immersion bath did not agree with values obtained during sorption, i.e., sorption and desorption curves of WS-polypropylene composites are not superimposable.

4.5.3 Mechanical Properties

Flexural properties of polypropylene and polypropylene-wheat straw composites were measured in the three point loading mode. The bending moment in a three-point bend test increases linearly from zero at the supports to a maximum located at the central loading point, whereas the shear force is uniform along the length of the beam [Hodgkinson, 2000].

From stress-strain curves, flexural modulus (defined as the ratio, within the elastic limit, of the applied stress to the corresponding strain) and yield strength (defined as the stress at which the stress-strain curve deviates by a given offset – in this case 0.2% from the tangent to the initial straight line portion of the stress-strain curve) [ASTM D-790-03, 2003] were recorded. Typical curves of every composite formulation tested are presented in Appendix C. Because of experimental limitations (the miniature materials tester has a small travelling zone), all tests were stopped at the point where the data collected was enough to calculate the properties of interest. The tests were not performed on the samples up to their breaking point (necessary to calculate the flexural strength). Furthermore, due to lack of yield strength data in the literature, results obtained in this work will be compared to flexural strength values in the references in terms of trends. Flexural strength is understood as the maximum flexural stress sustained by the test specimen during a bending test (or stress necessary to break the specimen).

Average flexural moduli of virgin polypropylene and polypropylene/wheat straw composites at different fiber loadings, all prepared at 190°C, are shown in Figure 31. Error bars show plus and minus one standard deviation.
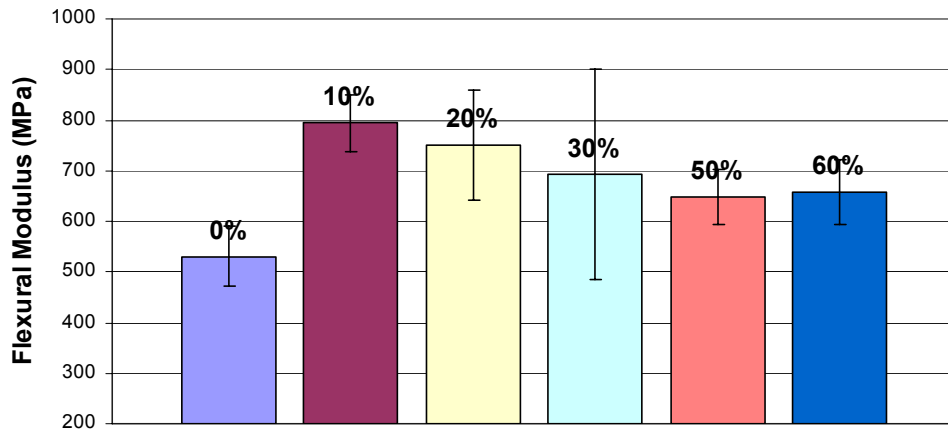
Figure 31: Flexural modulus of composites processed at 190°C containing 0, 10, 20, 30, 50 and 60 wt-% of WS fibers.

Addition of wheat straw fibers enhanced the flexural modulus of the virgin polymer, in agreement to the results observed by Panthapulakkal et al. [Panthapulakkal, 2006] for a 30 wt-% WS- polypropylene composite. In another work, flexural modulus of 30 wt-% natural fiber composites were on average 2.5 times greater than virgin polypropylene [Johnson, 1998]. Improvement in the resin flexural modulus with addition of wood and kenaf fibers was also observed by other groups [Coutinho, 1998; Sanadi[2], 1999].

A loading of 10 wt-% of WS fibers raised the flexural modulus by 50% compared to the pure resin, however, the increase in flexural modulus became less accentuated with further loading of filler. Samples containing 50 and 60 wt-% of filler presented roughly the same results, suggesting that the 10% increase in filler, in that case, would provide a material with lower density and cost without changing significantly that specific mechanical property. Opposite results were observed in mechanical tests performed on sisal-phenol-formaldehyde composites, where flexural modulus increased with addition of fibers and a maximum was obtained at 0.5 fiber volume fraction (approximately 22 wt-%) [Zárate, 2003]. It has to be considered that the standard deviation observed for each fiber loading was very high; the highest standard deviation was observed for the sample containing 30 wt-% of WS fibers. Therefore, from the results in the present work it is possible to conclude that addition of natural fibers increased the

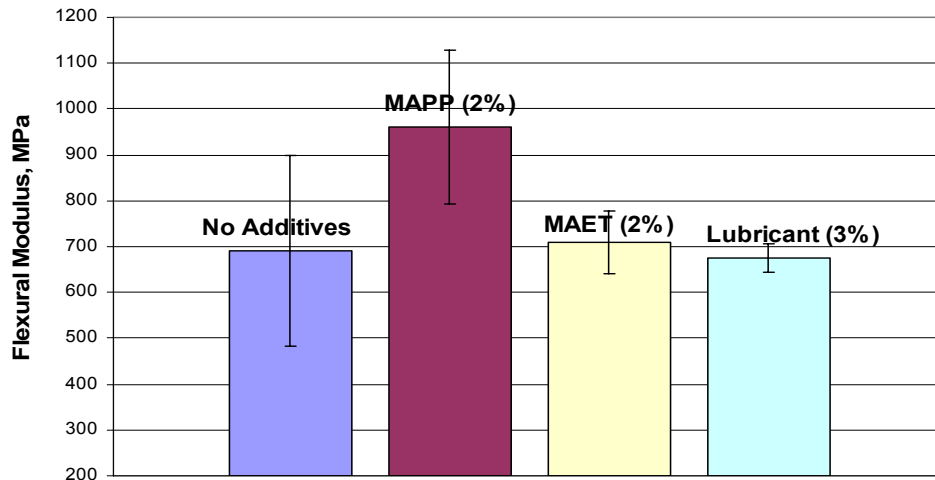flexural modulus of the polypropylene, however, the optimum fiber loading was not precisely determined.

Figure 32: Flexural modulus of composites containing 30 wt-% of WS fibers processed at 190°C with MAPP, MAET, lubricant and without additives.

The effect of additives in the flexural modulus of the composites was investigated here. Figure 32 shows a comparison of flexural modulus for composites prepared under the same processing conditions, with 30 wt-% of WS fibers. Introduction of coupling agent based on PP increases the flexural modulus of the system while the introduction of coupling agent based on ethylene or addition of lubricant did not change significantly flexural modulus values in relation to the formulation without additives. In agreement with this Arbelaiz et al. [Arbelaiz, 2005] detected modulus values of natural fiber composites slightly increasing with addition of maleic anhydride based coupling agent. In contrast to these results, Hornsby et al. [Hornsby[2], 1997] reported no significant alteration on flexural modulus values with addition of maleic anhydride modified polypropylene in 25 wt-% filled composites. Flax straw-polypropylene composites studied by the same group presented equivalent flexural modulus results between grafted and ungrafted samples as well. On the same track, uncoupled PP/kenaf systems presented higher flexural moduli than coupled systems [Sanadi[1], 1999].

Apart from finding some results opposite to the ones cited in the literature, the small increase in flexural modulus observed here in the MAPP coupled system can be attributed to the better interaction between filler and matrix promoted by an additive. Furthermore, maleic anhydride grafting is able to enhance the dispersion of fibers inside the PP matrix; this phenomenon was observed by Fung et al. [Fung, 2003] during compounding experiments of sisal fibers and PP. Even if the dispersion of wheat straw fibers in PP matrix was not observed to be enhanced by MAPP, it is possible that the coupling agent had improved the interaction between matrix and filler. Moreover, it has been reported in the literature that the amount of coupling agent used also has influence in the mechanical properties; for example, the optimum dose for 2 different coupling agents tested by Arbelaiz et al. [Arbelaiz, 2005] was 5 or 10%, depending on the structure of the compound.

The flexural modulus of composites prepared at different processing temperatures was also investigated. Higher temperatures did not change significantly this mechanical property. Based on the results presented in Figure 33 higher flexural modulus was achieved when WS-PP composite was prepared at 190ºC. Yet, standard deviations are quite high for these results, so no solid conclusion is possible regarding the temperature effect on flexural modulus of WS-PP composites. The very large uncertainty for the flexural moduli suggests that the samples tested were not homogeneous or some problems were faced during the tests. The hypothesis of tests errors was discarded since all tests were performed under same conditions and results recorded on the tester machine did not present any issues. Further investigation of the samples would be necessary to verify their homogeneity.
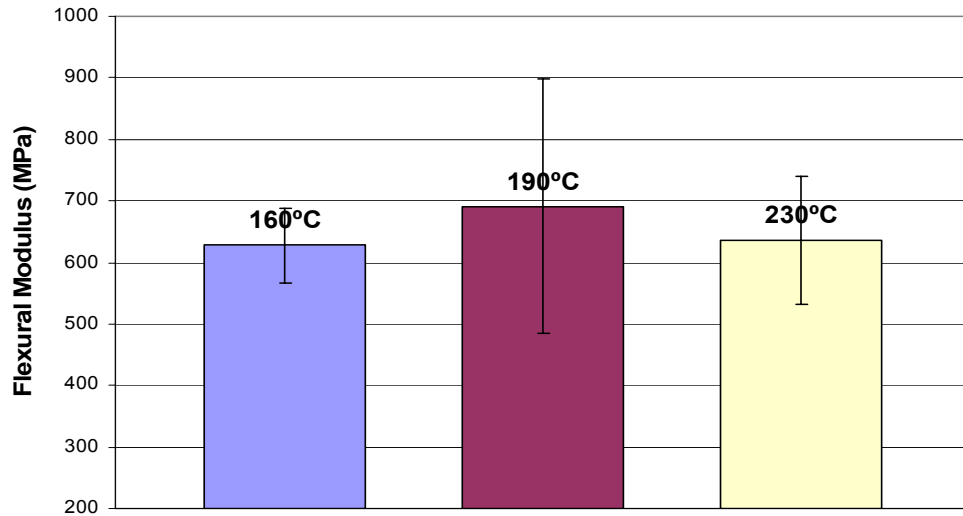
Figure 33: Flexural modulus of composites containing 30 wt-% of WS fibers processed at 160, 190 and 230°C.

The effect of WS loading on yield strength is shown in Figure 34. As the filler loading was increased, the total interfacial area between matrix and filler was enlarged. In such case, the poor interfacial bonding between filler and matrix became more significant and lead to a decreasing in the yield strength of the composites.

The opposite behaviour was observed for kenaf fibers-polypropylene composites; flexural strength increased as the filler content was raised [Karnani, 1997]. According to Yang et al. [Yang, 2004], for irregularly shaped fillers, the strength of the composites decreased due to the inability of the filler to support stresses transferred from the matrix. In addition to that poor interfacial bonding caused microspaces between filler and matrix that could obstruct stress propagation and induce brittleness. Furthermore, the elevated amount of fibers allows the contact among themselves to reduce the composite adhesion and ability of the matrix to transfer stresses.
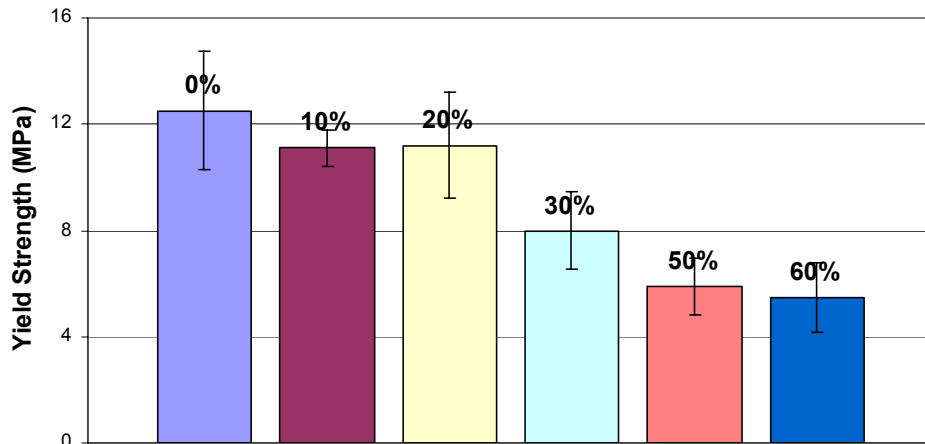
Figure 34: Yield strength of composites processed at 190°C containing 0, 10, 20, 30, 50 and 60 wt-% of WS fibers.

According to Joseph [Joseph, 1996], plastics that do not have high ductility, when filled with 40-50% of fibers, become brittle and lose strength considerably. Once smaller scale, it can happen with polyolefins such as polypropylene, which generally have high ductility. As suggested by Rowell et al. [Rowell, 1999], fiber surface is likely to act as a boundary restricting the mobility of polymer molecules. On the other hand, in a previous work, flexural strength of virgin polypropylene was found to be enhanced by the presence of natural fibers; increases ranging from 13 to 48 percent were observed depending on the fiber processing technique and the final fiber size [Johnson, 1998].

The influence of fiber loading in some mechanical properties is clearly still a point of discussion. The presence of fillers in polymer matrices creates further complexities in the morphology of the polymeric systems broadening the possibilities of response of the systems to mechanical testing. Several errors during mechanical testing, responsible for misleading results, arise from imperfections in the composites that originate during processing. Possible defects include imperfect alignment or dispersion of the fibers, broken and kinked fibers, incompletely wetted fibers, voids and general mismatches between the components [Hodgkinson, 2000].

Besides fiber loading effects, fiber length and processing technique play important roles in the final mechanical properties of composites. Strengths of the composites are supposed to be

limited by the fibers' lengths whereas the processing technique is mainly responsible for fiber dispersion in the matrix phase. For example, the stress transfer can be maximized using maximized lengths of the fibers in the final composite [Rowell, 1997].

The yield strength of samples containing different additives was investigated; the results are shown in Figure 35. The only additive that promoted significant changes in a 30 wt-% WS-PP composite was maleic anhydride modified polypropylene (MAPP), the increase was about 67%. A similar trend was observed in flexural strength results reported in the literature, where increases were about 40-60% with the addition of coupling agent [Arbelaiz, 2005]. When higher bonding forces act between matrix and filler, the transfer of the load applied to the composite material is well transferred between the phases, thus allowing the material to perform elastic deformation. In this case, the elastic deformation observed under higher stress loads can be attributed to the interfacial bonding promoted by the coupling agent. Interfacial bonding increments were also denoted by Rana et al. during flexural strength measurements of compatibilized systems [Rana, 1998].

Although the discussion of molecular characteristics of the coupling agents employed in wheat straw-PP composites are not in the scope of this thesis, it is valid to mention that the efficiency of coupling agents and their effect on mechanical properties also depend on the grafting rate and on the average molar mass of the graft copolymer coupling agent. Lower amounts of maleic groups per chain length do not produce optimum coupling efficiency while lower molecular weights reduce the chances of entanglements with the matrix. [Arbelaiz, 2005].

Figure 36 shows yield strength results for 30 wt-% wheat straw composites prepared at different temperatures. Among the different samples, yield strength did not vary considerably. Temperature has direct influence in fibers characteristics due to thermal degradation that can be promoted during processing. As it seems, the transformations occurred in the fibers due to exposure to higher temperatures were not sufficient to manipulate yield strength results. On the other hand, reinforcing efficiency for low temperature processed sisal fibers/PP was found to be slightly higher than high temperature processed samples [Fung, 2003]. The pre-impregnation of the sisal fibers with MAPP could be the responsible for such results.
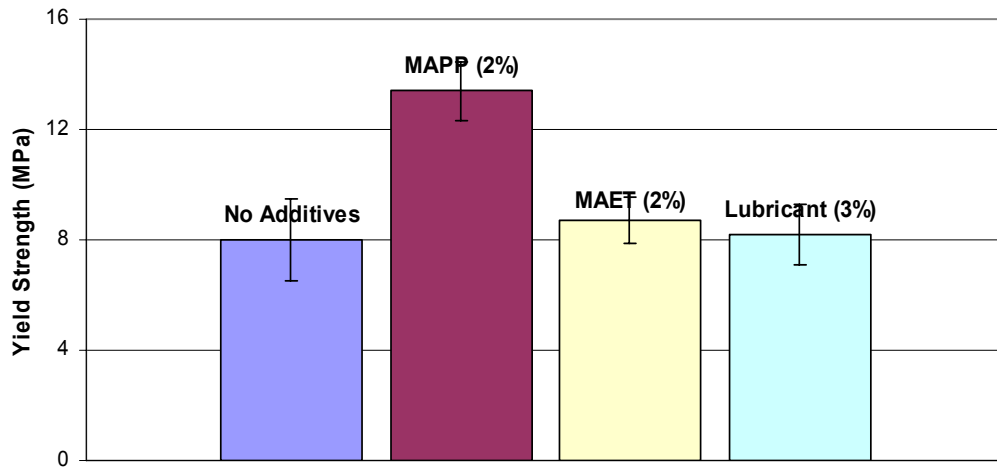
Figure 35: Yield strength of composites containing 30 wt-% of WS fibers, processed at 190°C with MAPP, MAET, lubricant and without additives.
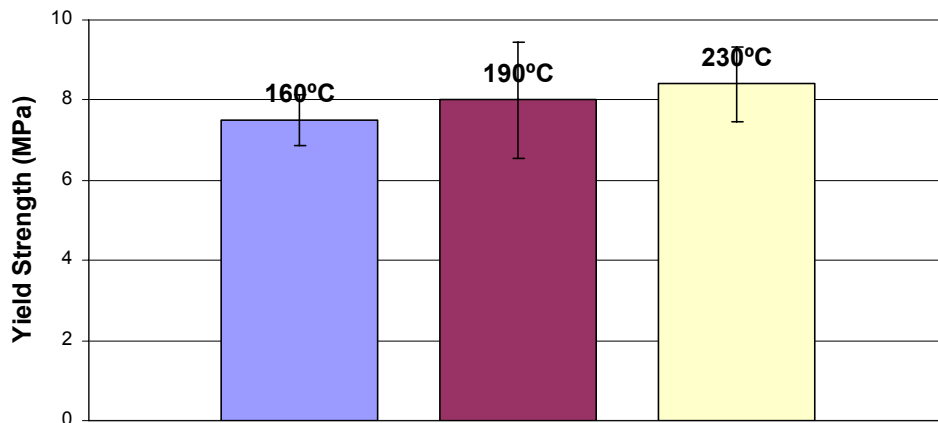

Figure 36: Yield strength of composites containing 30 wt-% of WS fibers processed at 160, 190 and 230°C.

4.5.4 Summary

4.5.4.1 Processing Temperature Effect

In order to evaluate the effect of temperature on the properties of the final composite, wheat straw-polypropylene composites containing 30 wt-% of fibers were processed at three different temperatures: 160, 190 and 230ºC.

From torque curves it can be seen that the lower the temperature the higher the torque required to promote mixing between filler and matrix; which infers that composites processed at 160ºC would present the lowest quality of filler dispersion among the samples. The filler dispersion quality was not subject of this work; therefore, the poor dispersion of filler is just speculation. Composites processed at 160ºC also presented high increase in weight due to moisture sorption (31.6 wt-%); the amount of water absorbed decreased as the processing temperature of the composites increased.

It can be inferred that at high processing temperatures (190ºC and above) partial degradation of fibers took place and this changed their capacity to absorb water, which could be a beneficial characteristic. An increase in the processing temperatures produced damage in the wheat straw fibers and led to the lowest percentage of crystallinity among the compounds with 30 wt-% of fibers. Recalling the statement that water diffusion occurs mainly in amorphous phase, one could expect to find higher amounts of water uptake in samples prepared at 230ºC; however, among the three temperatures tested, that was the composition that presented the lowest increase in weight. The poor water absorption in this case is attributed to the chemical modifications caused by severe thermal treatment.

The effect of temperature on mechanical properties was also investigated. Both flexural modulus and yield strength did not vary significantly; a slightly higher flexural moduli was achieved when wheat straw-PP composites were prepared at 190ºC. The supposed poor dispersion of filler particles in the polymeric matrix of samples prepared at lower temperature (160ºC) is in accordance with the average of mechanical test results for those samples, which are lower than composites prepared at 190ºC or 230ºC; however, taking into consideration the

large amplitude of deviation found in each case, mechanical properties measured in the present work are still considered not significantly different regarding the effect of processing temperature.

4.5.4.2 Effect of filler content

The amount of filler added to a polymeric matrix can drastically change its properties. Filler loading in the range from 10 to 60 wt-% were inspected and behaviour tendency caused by the increase in weight percentage of wheat straw fibers in polypropylene are discussed in the following paragraphs.

Different fiber content did not cause a significant influence on the equilibrium torque, which can lead to the conclusion that the viscosity of all samples containing from 10 to 60 wt-% of WS fibers is similar. The torque is only an indication of flow behaviour of the samples. Viscosity measurements were not part of the scope of the present work.

Addition of wheat straw fibers slightly increased the crystallization temperature of polypropylene. Dispersed on the polymeric phase, natural fibers can act as nucleating agents, facilitating the initiation of crystallization phenomenon. The integration of the area under the melting peaks reveals a small increase in the percentage of crystallinity of the polymeric phase with addition of WS fibers; however, final percentage of crystallinity cannot be directly related to the rate of nucleation.

Since a high percentage of crystallinity in materials usually results in improved mechanical properties, the promotion of crystallization due to addition of natural fibers is observed as a beneficial change in the flexural modulus. Despite that, the enhancement of flexural modulus is not proportional to the fiber loading. Therefore, it can be inferred that higher fiber loadings increased the interfacial area between matrix and filler and the poor interfacial bonding between those two phases caused the decrease of yield strength.

4.5.4.3 Effect of additives

Three additives tested on wheat straw-polypropylene composites containing 30 wt-% of fibers, all processed at 190ºC: two coupling agents, MAPP and MAET, and one lubricant. Pertinent findings regarding the effects of these additives on the properties of the composite are listed below.

Torque measurements confirmed the poor interaction between filler and matrix obtained when lubricant is added to the system. The lack of adhesion between the components of the composite was mainly observed in the water absorption experiment, where large amounts of weight were gained by composites that presented weaker interfacial adhesion between filler and matrix; the highest water uptake was from the sample containing lubricant.

Freeze fracture surface images evidenced the good interaction between wheat straw fibers and polypropylene in composites containing MAET or MAPP. Taking into consideration that torque measurements presented higher values for the sample containing MAPP, plus this was the sample with the smallest water uptake, it is possible to infer that the coupling agent based on polypropylene promotes better interaction of the system.

The transcrystallization phenomenon is suggested for the sample containing MAPP. The suggested phenomenon is in accordance to the amount of water absorbed by the sample, taking into account that the transcrystalline layer would protect the fibers from the contact with water, thus avoiding high weight gains. Still, no further investigation for evidence of transcrystallinity was pursued in this project, so that this phenomenon could not be confirmed. Slightly lower percentages of crystallinity were observed in all samples containing coupling agent; this can be attributed to the low percentage of crystallinity of the maleated component used.

Flexural tests are in agreement with results obtained by other techniques, where the most pronounced enhancement of properties was detected in the sample grafted with MAPP, thus proving the good adhesion between filler and matrix obtained in this system.

Chapter 5 - Conclusions and Recommendations

5.1 Conclusions

Literature survey was made on the lignocellulosic filled thermoplastics. Polypropylene – wheat straw fibers composites were prepared by melt mixing process. Fiber loading, additives and processing temperatures were investigated. Physical properties of filler and composites were studied with suitable analysis tools. Prior to compounding, wheat straw fibers were characterized with respect to their size and morphology. The compounded materials were analyzed with respect to their morphology, thermal and mechanical properties, as well as water uptake behaviour.

From the work mentioned above, the following conclusions can be drawn:

* Abundant availability of inexpensive agro-residues such as wheat straw makes the production of high value fiber composites very attractive for both agricultural economy and composites industry;

* Fiber loading, processing temperature and presence of additives are important criteria for the selection of a suitable composite for specific applications;

* The amount of water absorbed by wheat straw-PP composites decreased as the processing temperature of the composites increased;

* Both flexural modulus and yield strength did not vary significantly with processing temperature, with addition of WS fibers to polypropylene flexural modulus increased while yield strength decreased;

* There is a small increase in the degree of crystallinity of the polymeric phase with addition of WS fibers;

* Poor interaction between filler and matrix was obtained when lubricant was added to the system, the highest water uptake was the one from the sample containing lubricant;

* The most pronounced enhancement of mechanical properties was detected in the sample grafted with MAPP.

5.2 Recommendations for future work

There is a significant expectation for natural fiber composites to develop their own niche in the composites market in the future. The success of those products is dependent on the understanding of the system components on the final properties. Optimization and establishment of the best compromise between properties of the final product are required for each particular application. The following recommendations for future work intend to expand the knowledge in natural fiber thermoplastics both in academy and industry.

In this study wheat straw was used as received, no previous treatment other than drying and grinding was performed. As mentioned in the literature review, there are several treatments and fiber preparation techniques available that could modify the crop material in a positive way, improving desired characteristics for filling purposes. Therefore, it would be of interest to try some of the modification methods and evaluate their effectiveness on wheat straw.

The present work was limited in the number of final properties of the natural fiber composites tested. Future work including mechanical tests such as tensile and impact could give extra information on the mechanical behaviour of wheat straw-polypropylene composites. Furthermore, degradation agents other than water (e.g. ultra violet light and fungal attack) could also be included in a forthcoming work.

There is definitively room for improvement on the study of the effects of filler loading, additives and thermal processing conditions on the percentage of crystallinity of wheat straw-PP composites; either determining the percentage of crystallinity by using other techniques

(such as X-ray diffraction) to obtain in depth information or investigating the effects of lignocellulosic fibers on the crystalline morphology of the thermoplastic. Suitable observation techniques could also be extended to the determination of transcrystallinity on the fibers surface.

In addition, in this work a number of factors (fiber loading, processing temperature and presence of some additives) affecting the composites properties was looked into; however, each factor was investigated isolated. It would be of interest to obtain information regarding the interactions between them and the effects of these interactions on the final product.

Continuation of this project would consider other processing techniques such as extrusion or injection molding. Those techniques would take the production of wheat straw-polypropylene composites to the next level, closer to those used in industry and therefore to the commercialization of the composites. Production of wheat straw composites could also be further extended to the use of other thermoplastic resins, bringing up completely new systems to be studied and evaluated.

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Appendix A: Scanning Electron Micrographs
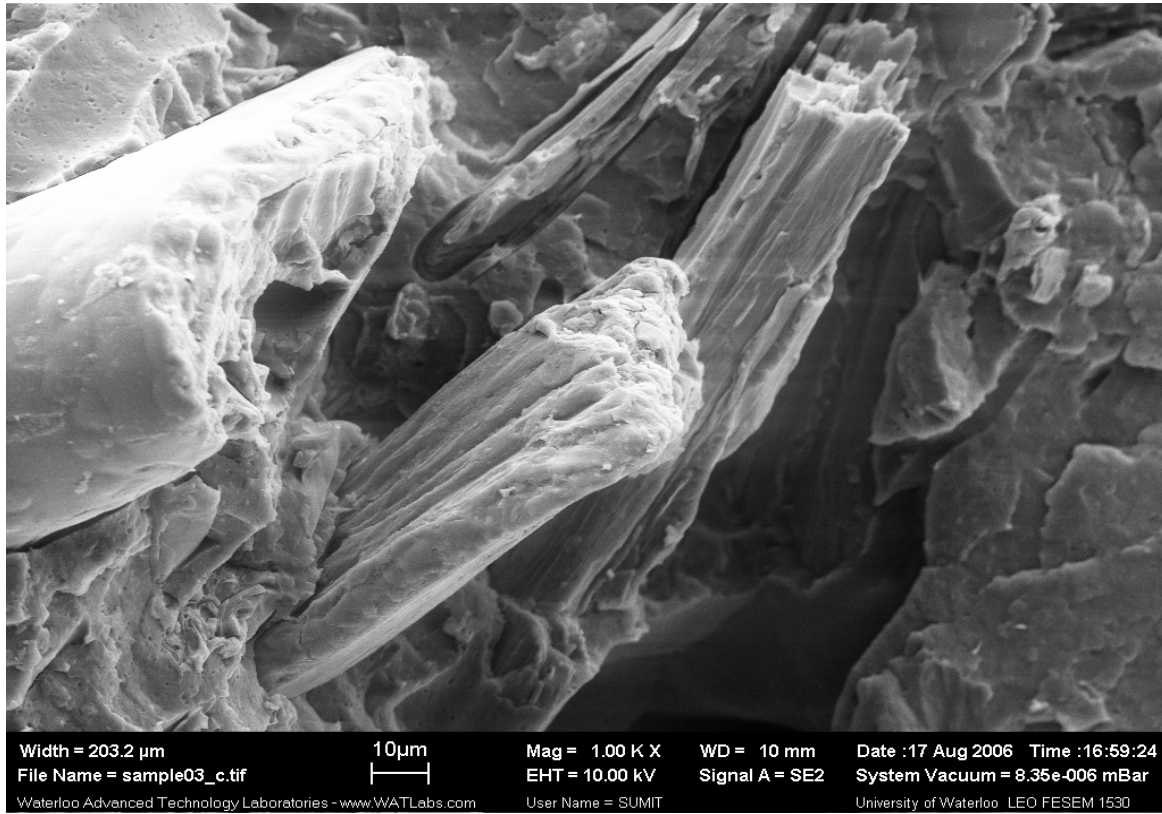
Figure A1.1: Electron micrograph of WS-PP composite prepared at 190°C, containing 30 wt-% of fibers. Mag. (x 1000)

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Waterloo Advanced Technology Laboratories - www.WATLabs.com User Name = SUMIT   University of Waterloo LEO FESEM 1530
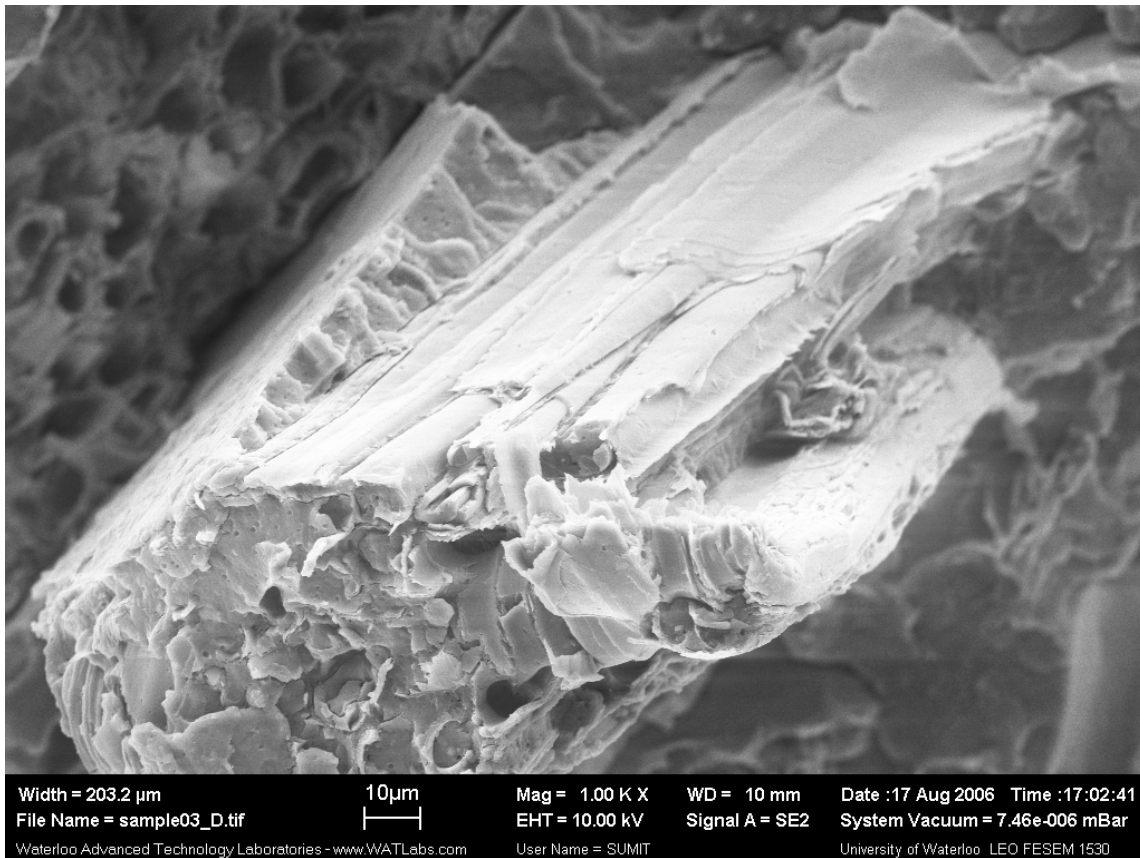
Figure A1.2: Electron micrograph of WS-PP composite prepared at 190°C, containing 30 wt-% of fibers. Mag. (x 1000)
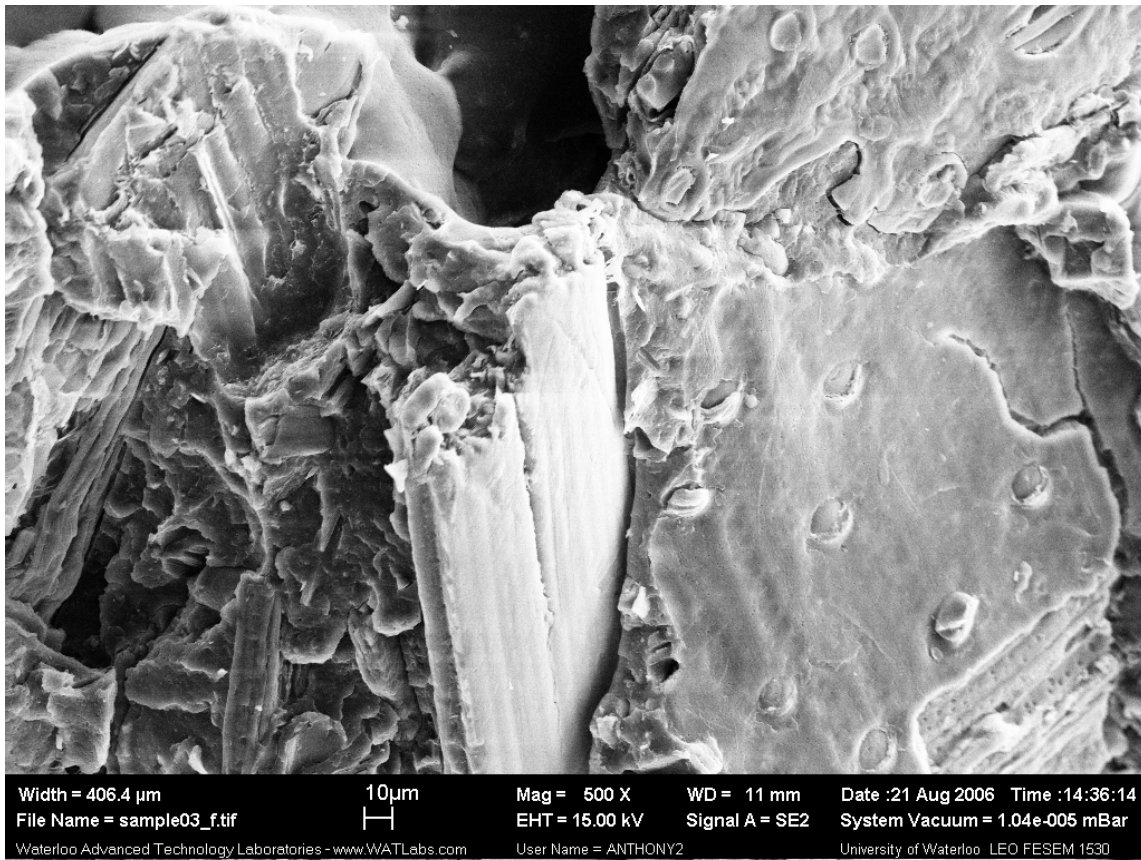
Figure A1.3: Electron micrograph of WS-PP composite prepared at 190°C, containing 30 wt-% of fibers. Mag. (x 500)
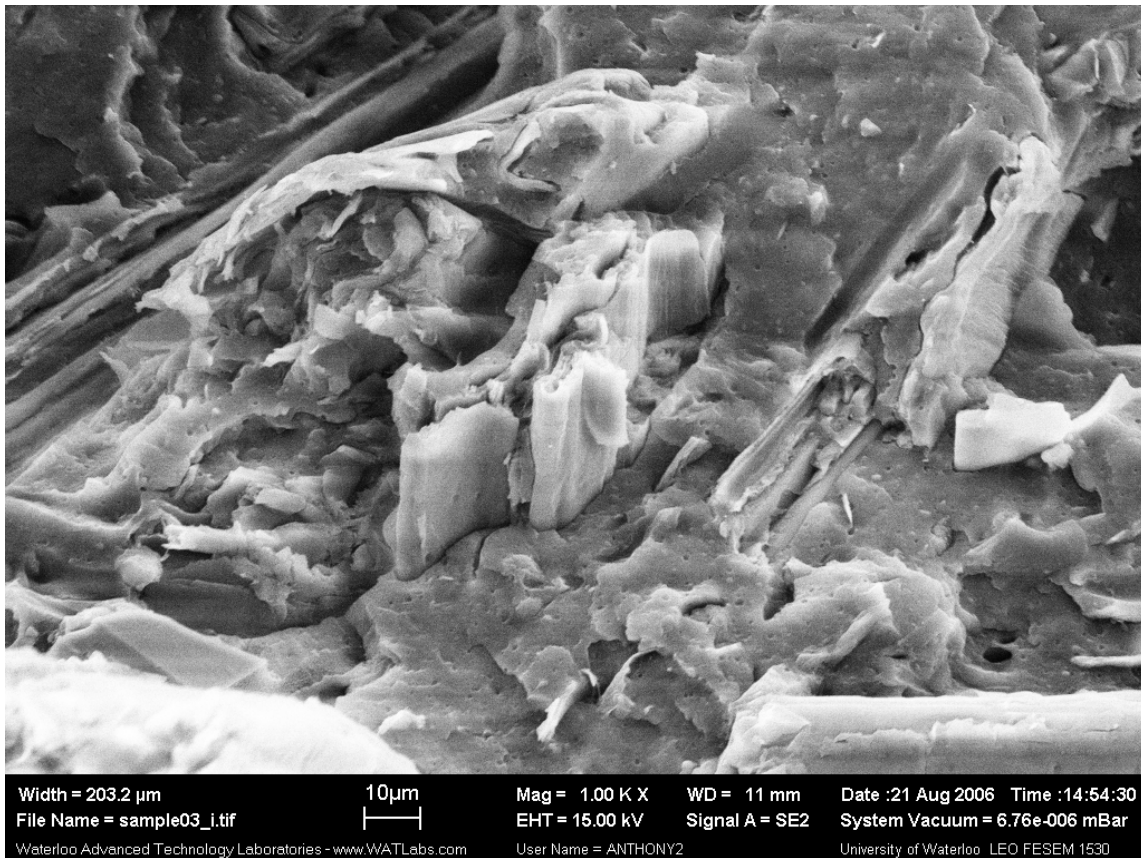
Figure A1.4: Electron micrograph of WS-PP composite prepared at 190°C, containing 30 wt-% of fibers. Mag. (x 1000)
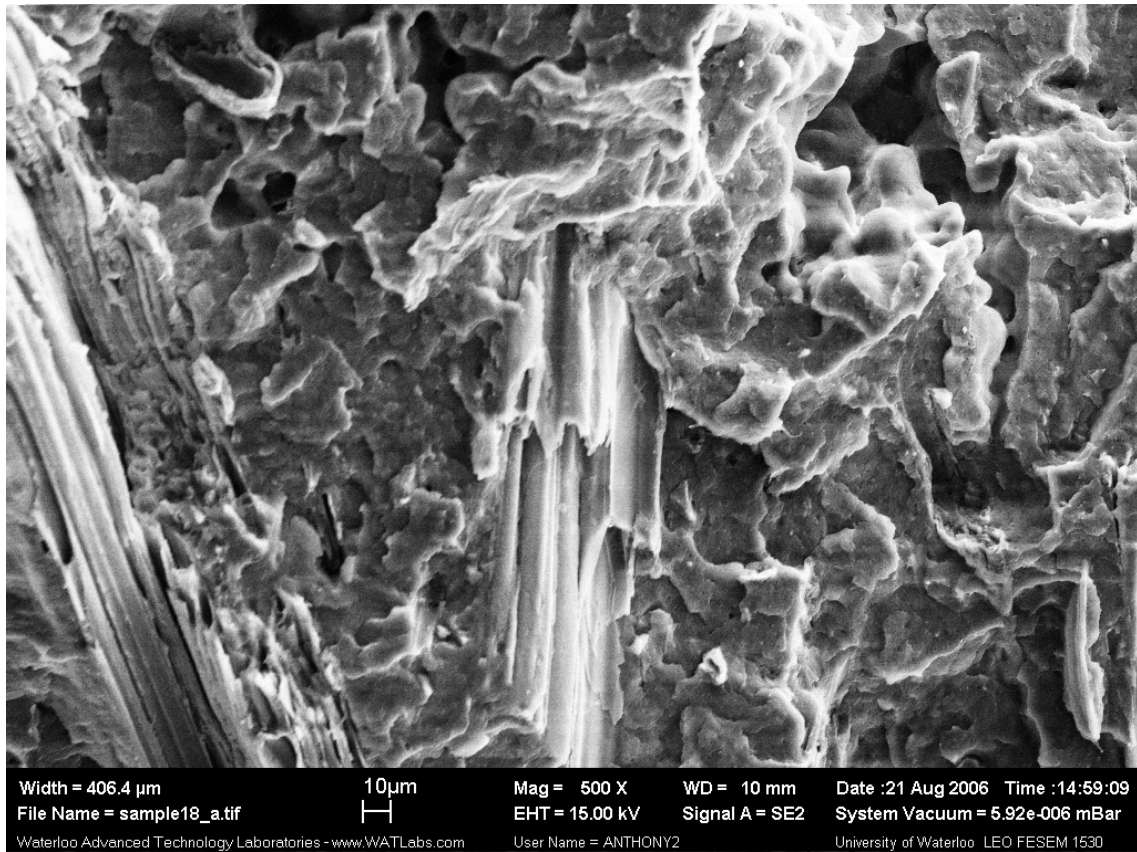
Figure A1.5: Electron micrograph of WS-PP composite prepared at 190°C, containing 30 wt-% of fibers and coupling agent MAPP. Mag. (x 500)
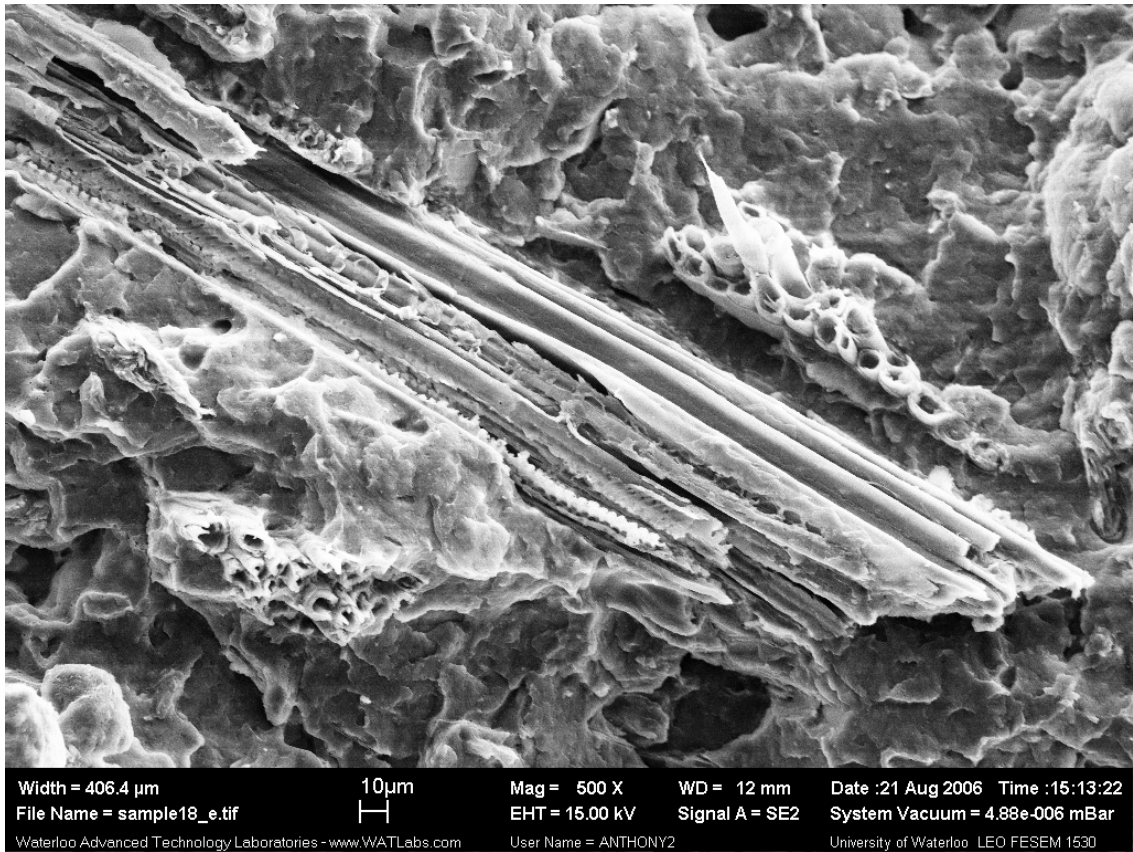
Figure A1.6: Electron micrograph of WS-PP composite prepared at 190°C, containing 30 wt-% of fibers and coupling agent MAPP. Mag. (x 500)
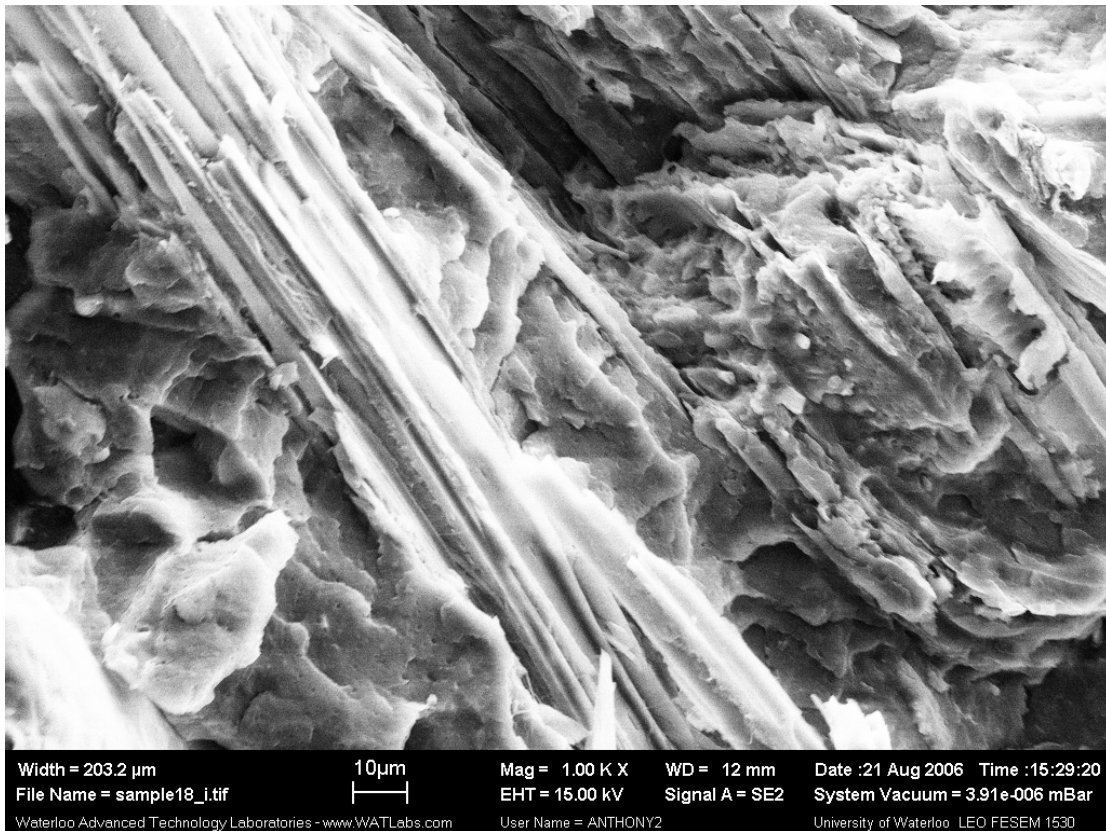
Figure A1.7: Electron micrograph of WS-PP composite prepared at 190°C, containing 30 wt-% of fibers and coupling agent MAPP. Mag. (x 1000)
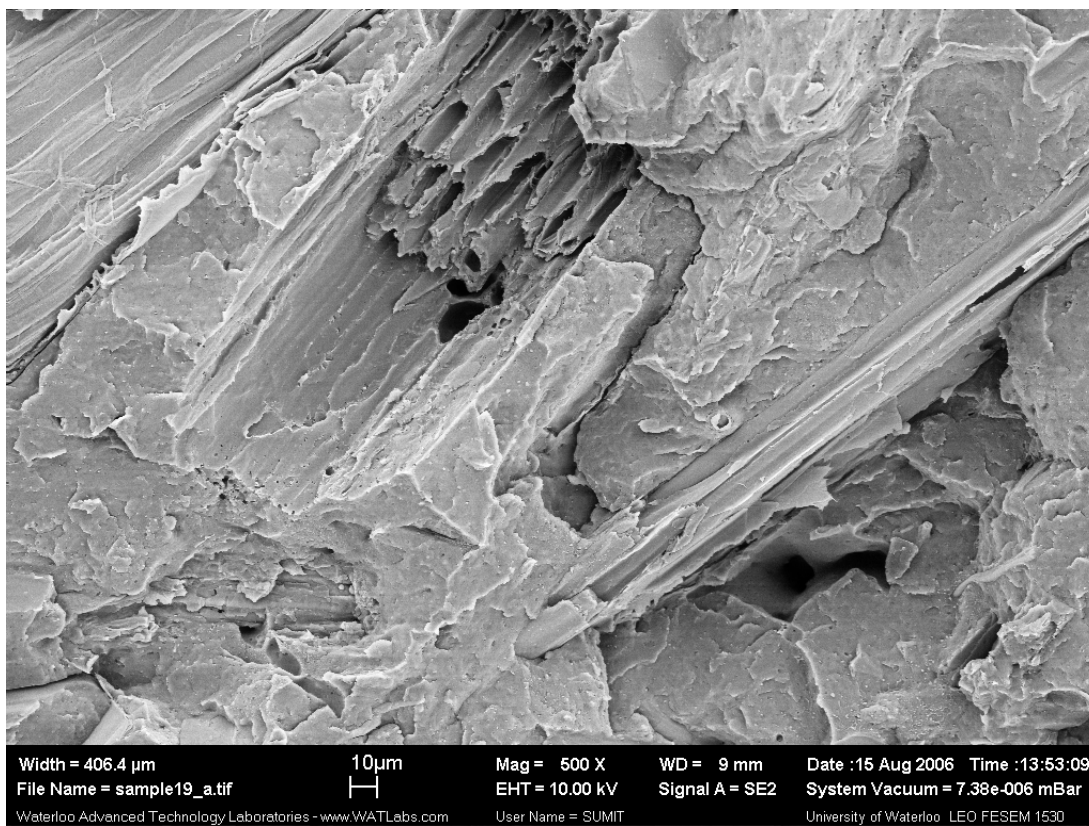
Figure A1.8: Electron micrograph of WS-PP composite prepared at 190°C, containing 30 wt-% of fibers and coupling agent MAET. Mag. (x 500)
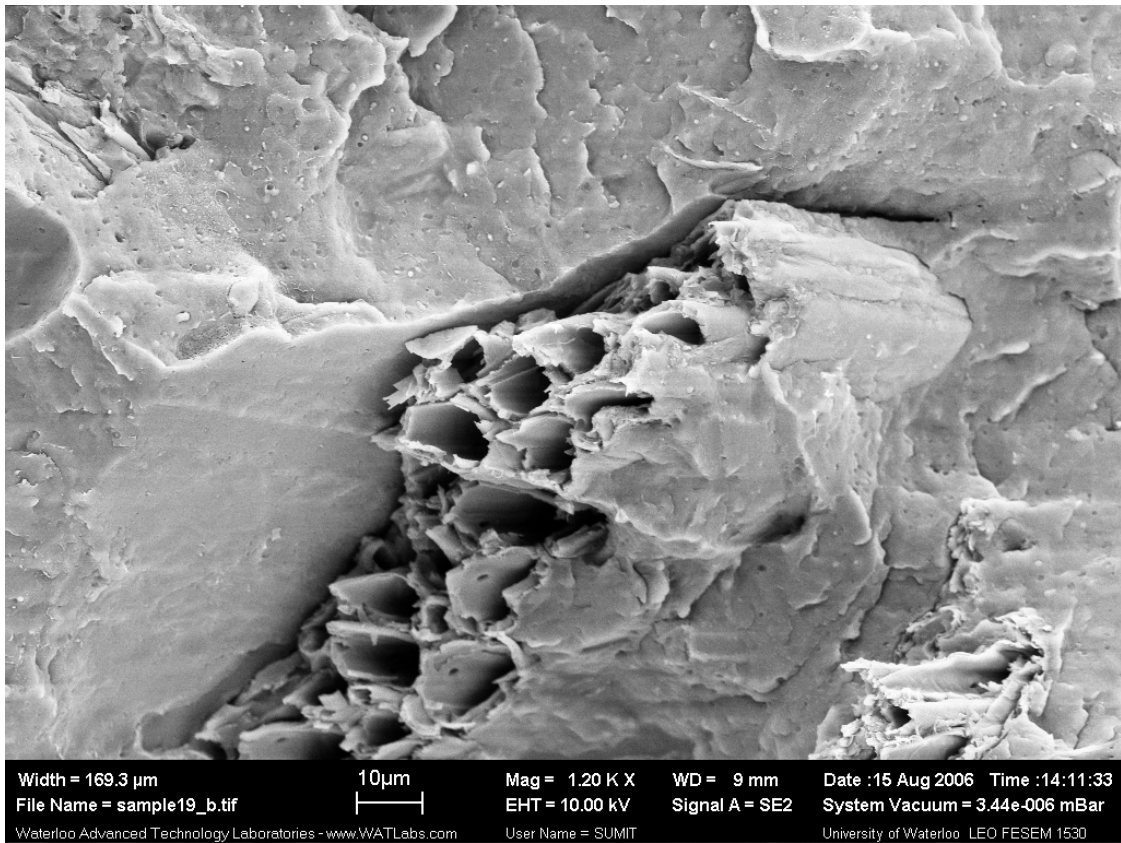
Figure A1.9: Electron micrograph of WS-PP composite prepared at 190°C, containing 30 wt-% of fibers and coupling agent MAET. Mag. (x 1200)
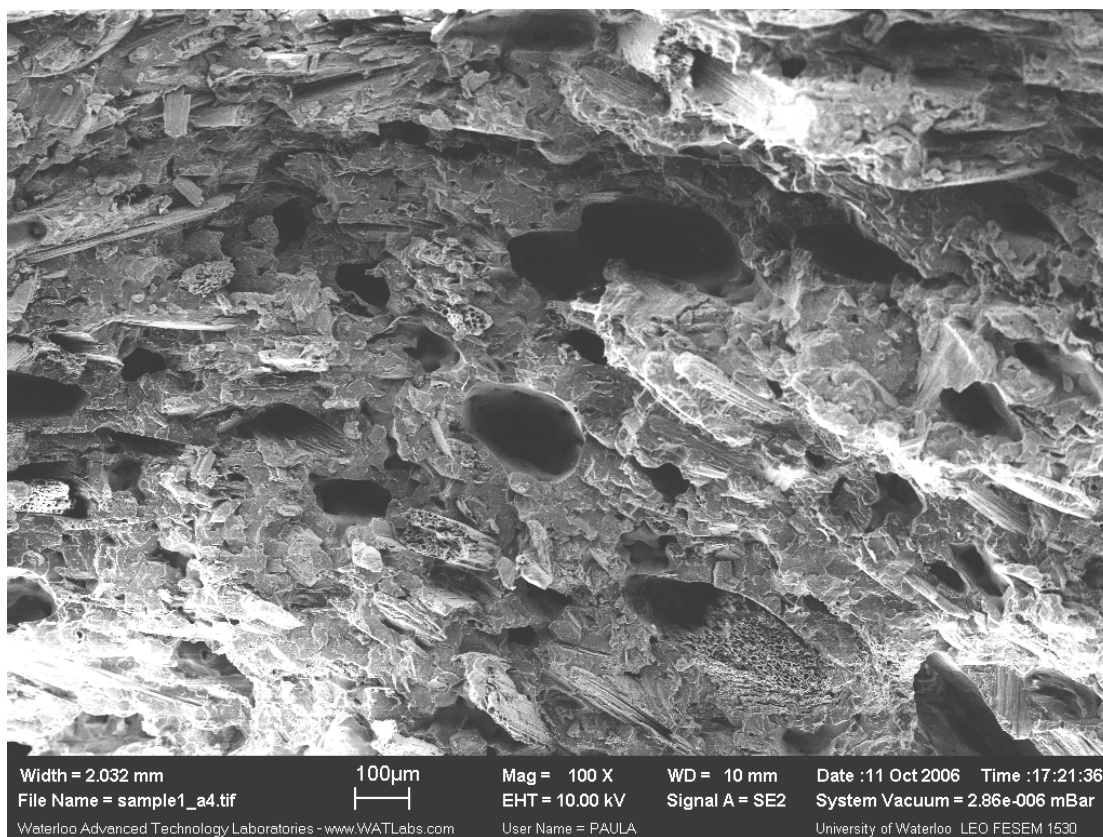
Figure A1.10: Electron micrograph of WS-PP composite prepared at 230°C, containing 30 wt-% of fibers. Mag. (x 100)
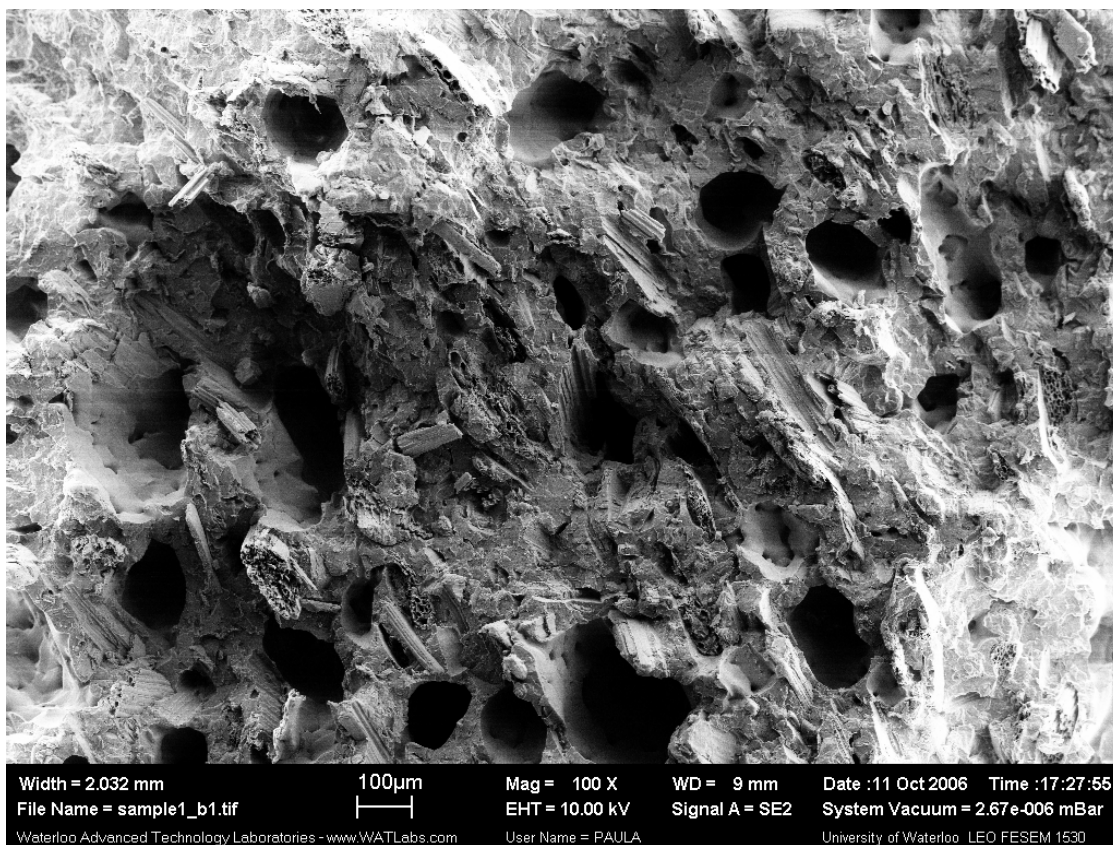
Figure A1.11: Electron micrograph of WS-PP composite prepared at 230°C, containing 30 wt-% of fibers. Mag. (x 100)
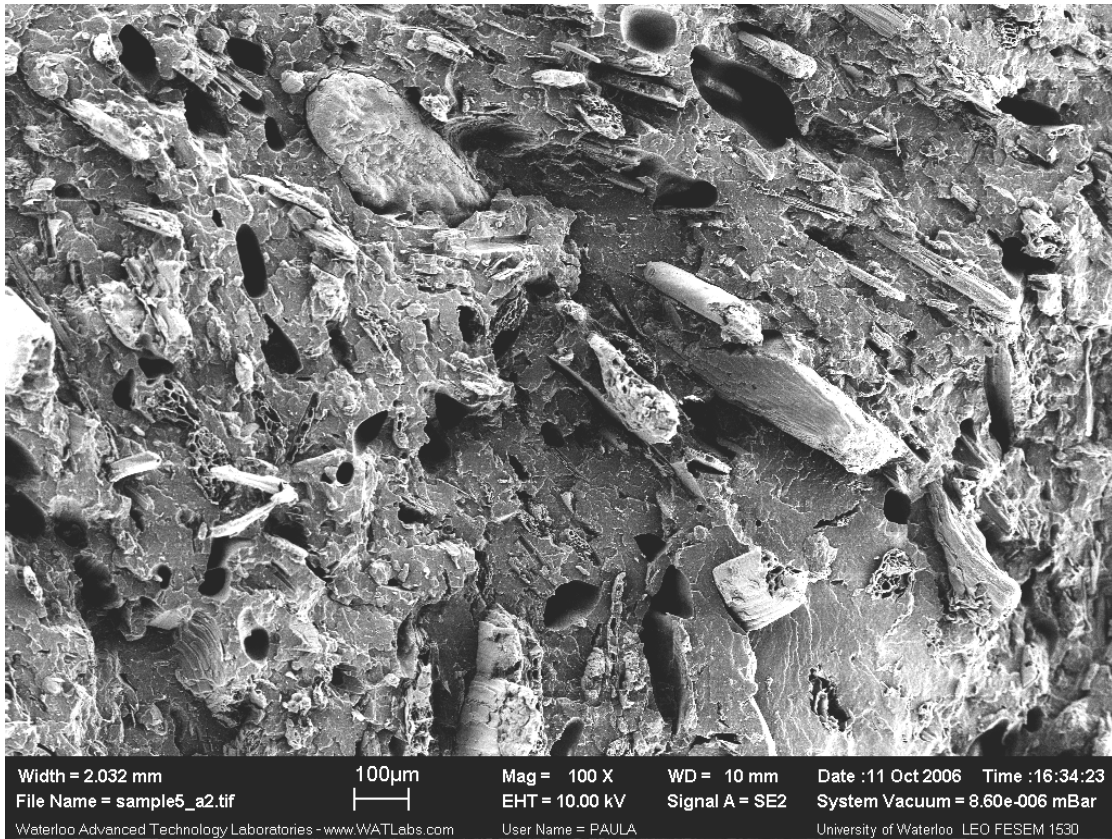
Figure A1.12: Electron micrograph of WS-PP composite prepared at 160°C, containing 30 wt-% of fibers. Mag. (x 100)
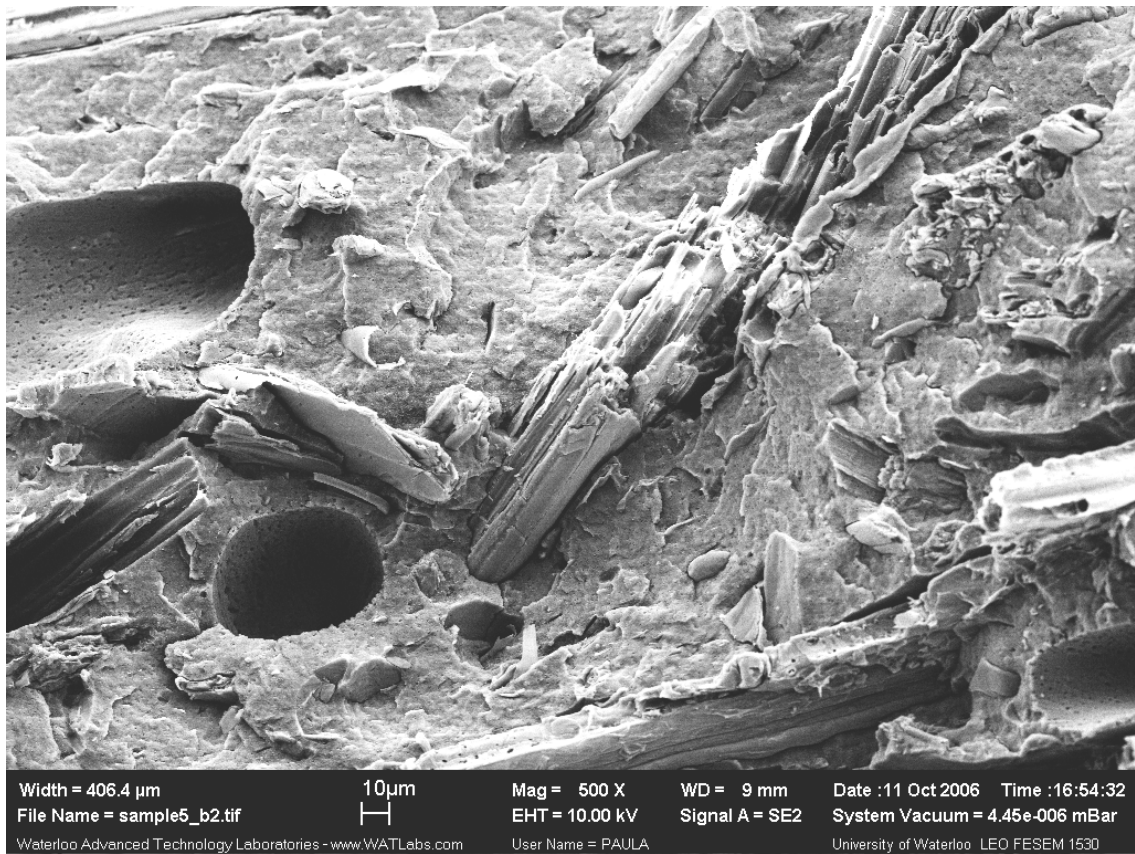
Figure A1.13: Electron micrograph of WS-PP composite prepared at 160°C, containing 30 wt-% of fibers. Mag. (x 500)

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Waterloo Advanced Technology Laboratories - www.WATLabs.com   User Name = PAULA   University of Waterloo LEO FESEM 1530
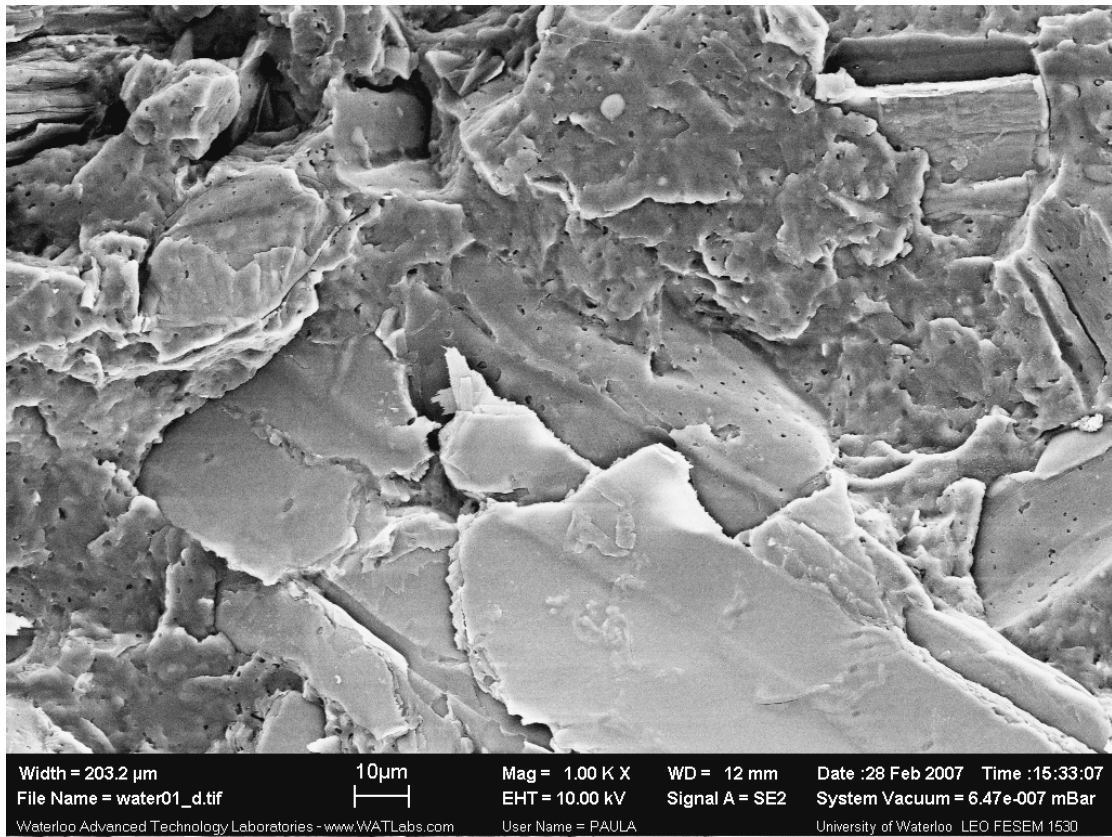
Figure A1.14: Wheat straw-PP composite prepared at 230°C and containing 30 wt-% of fibers after water absorption experiment. Mag. (x 1000)
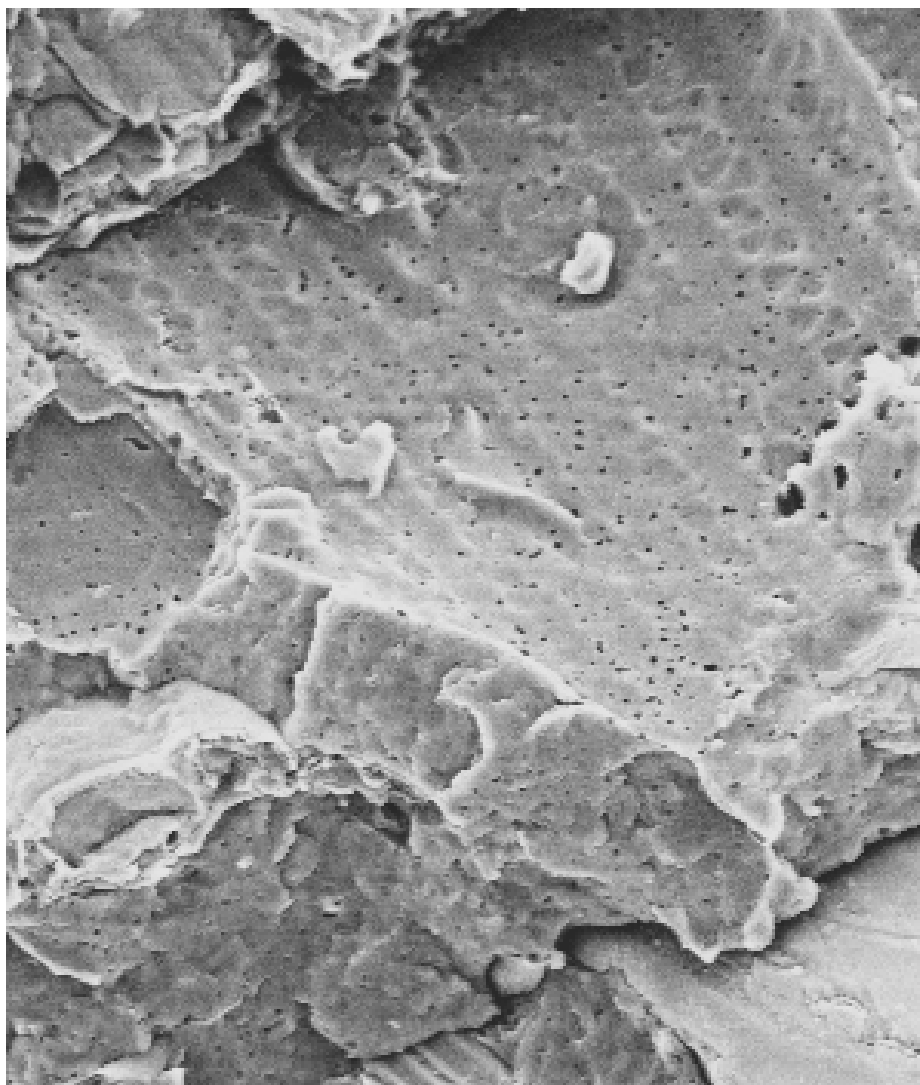
Figure A1.15: Polypropylene matrix of WS-PP composite prepared at 230°C after water absorption experiment. Mag. (x 1000)
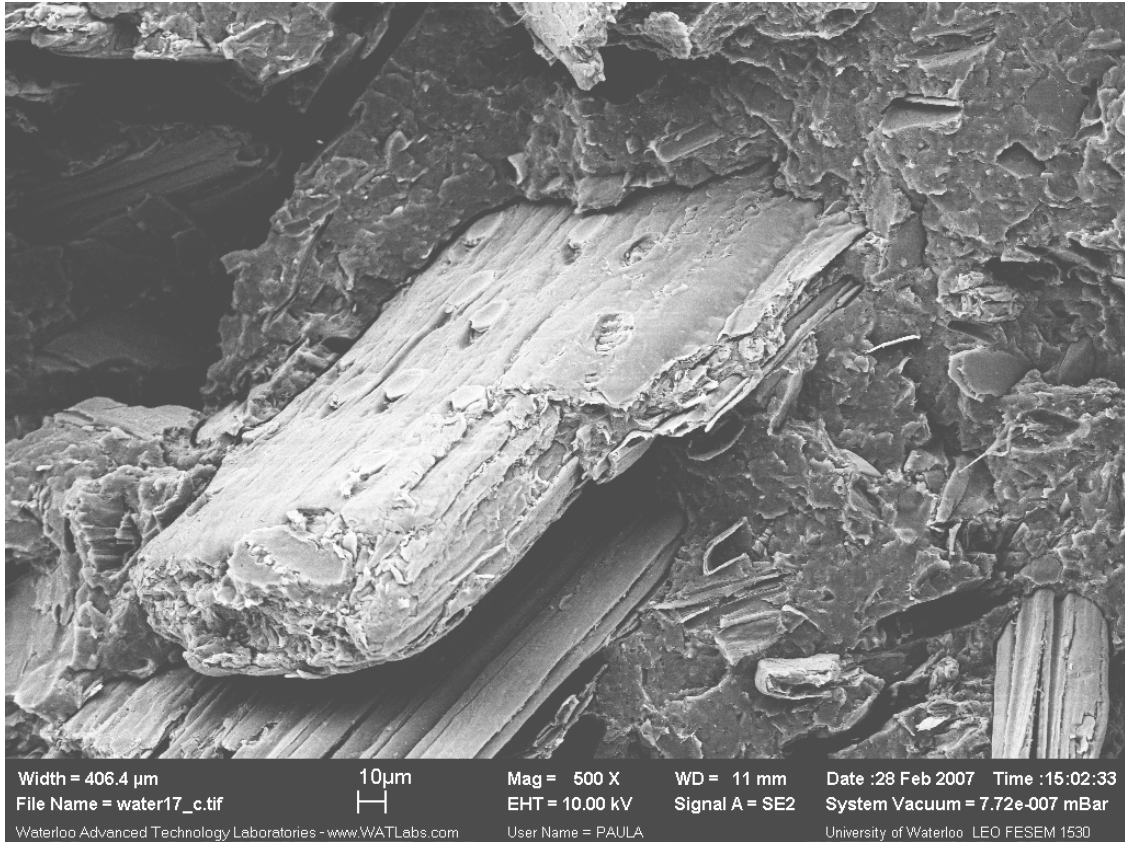
Figure A1.16: Wheat straw-PP composite prepared at 230°C, containing 30 wt-% of fibers and lubricant, after water absorption experiment. Mag. (x 500)
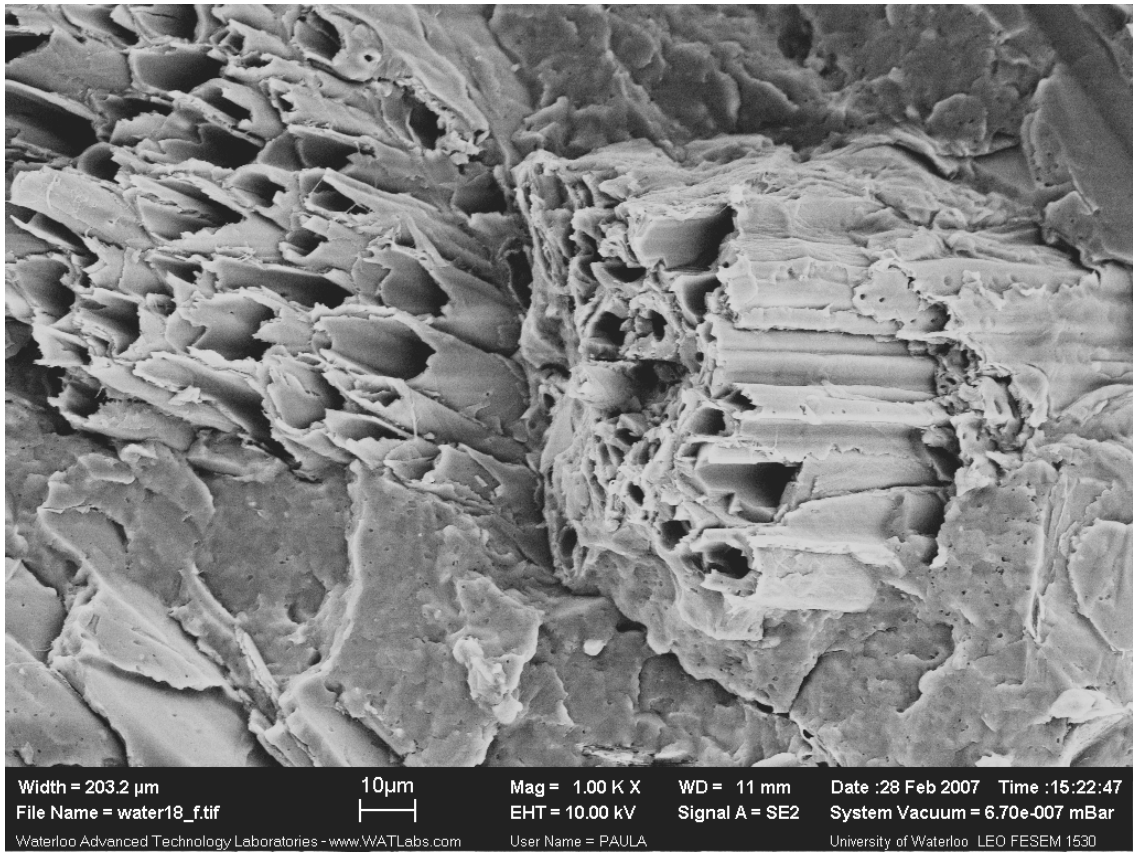
Figure A1.17: Wheat straw-PP composite prepared at 230°C, containing 30 wt-% of fibers and coupling agent MAPP, after water absorption experiment. Mag. (x 500)

# Appendix B: Differential Scanning Calorimetry Curves

30% WS, 230°C
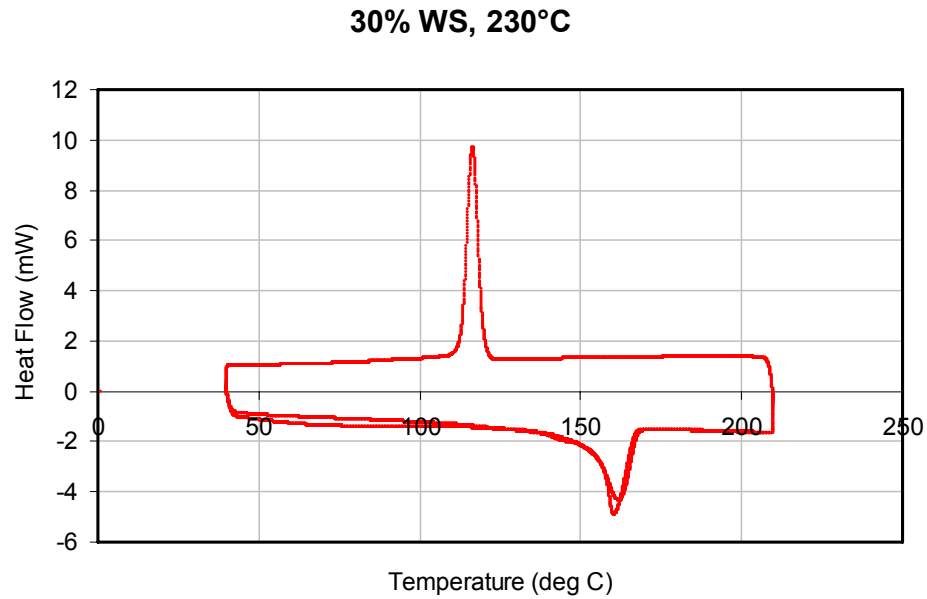
Figure A2.1: DSC curves for the three scans performed on wheat straw-PP composite prepared at 230°C, containing 30 wt-% of fibers.
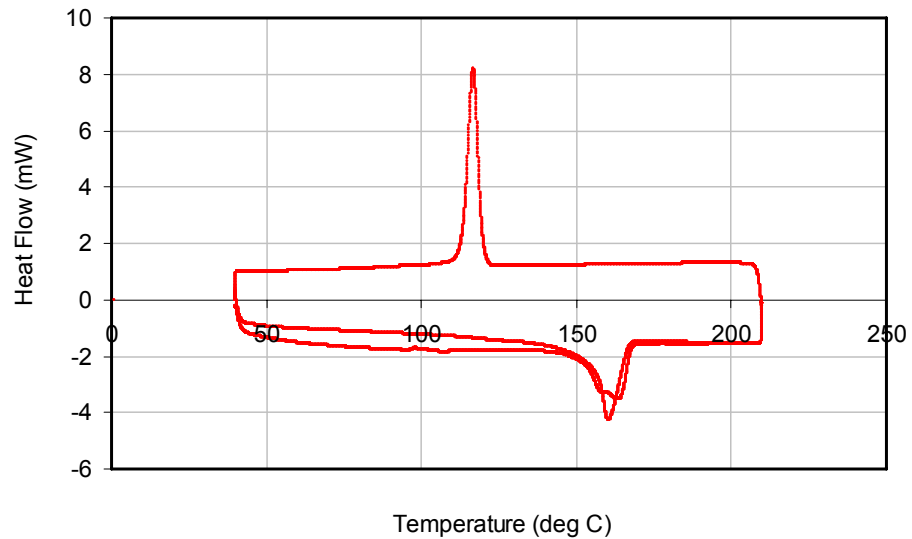
50% WS, 230°C
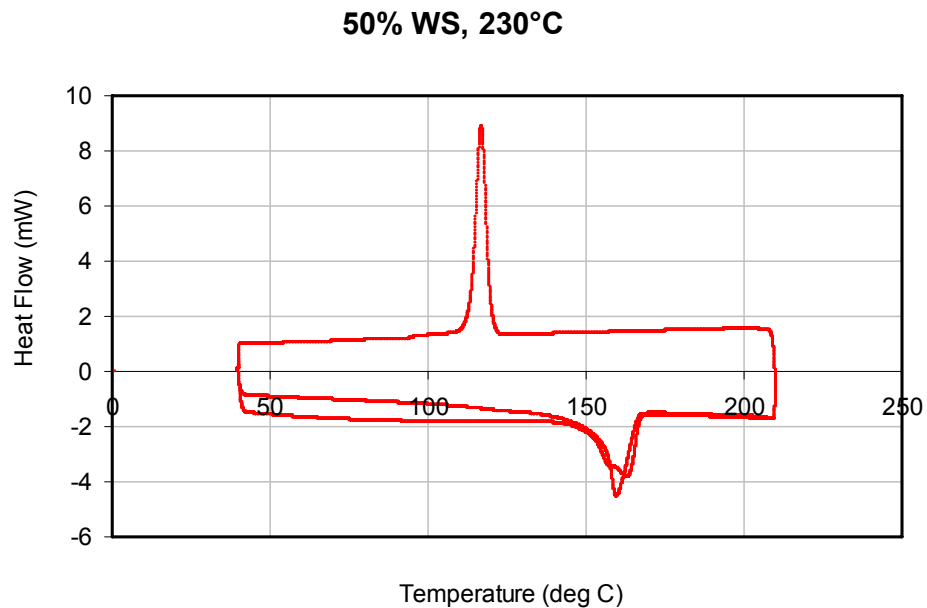
Figure A2.2: DSC curves for the three scans performed on wheat straw-PP composite prepared at 230°C, containing 50 wt-% of fibers.

30% WS, 190°C
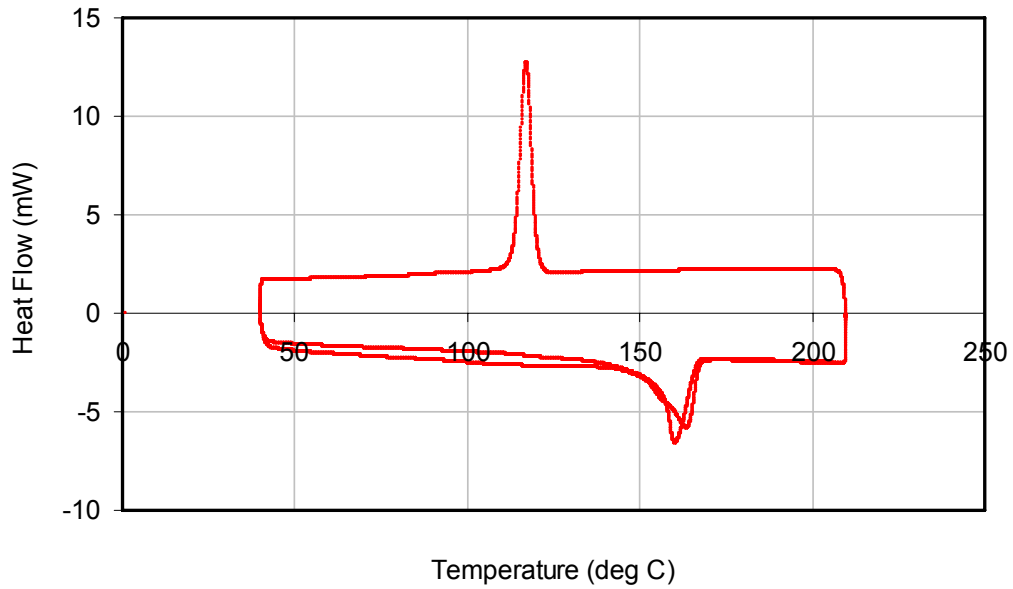
Figure A2.3: DSC curves for the three scans performed on wheat straw-PP composite prepared at 190°C, containing 30 wt-% of fibers.
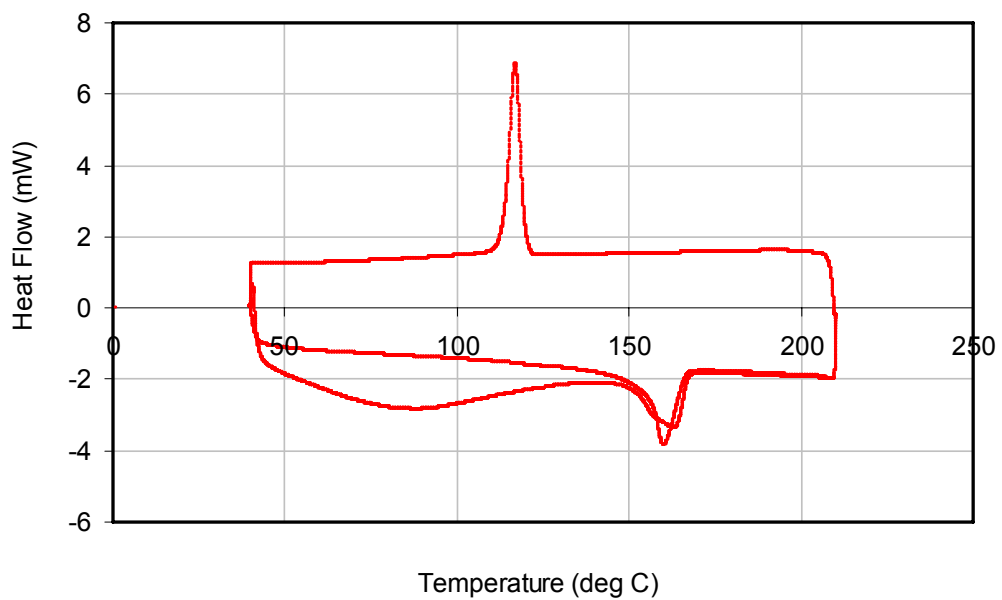
50% WS, 190°C
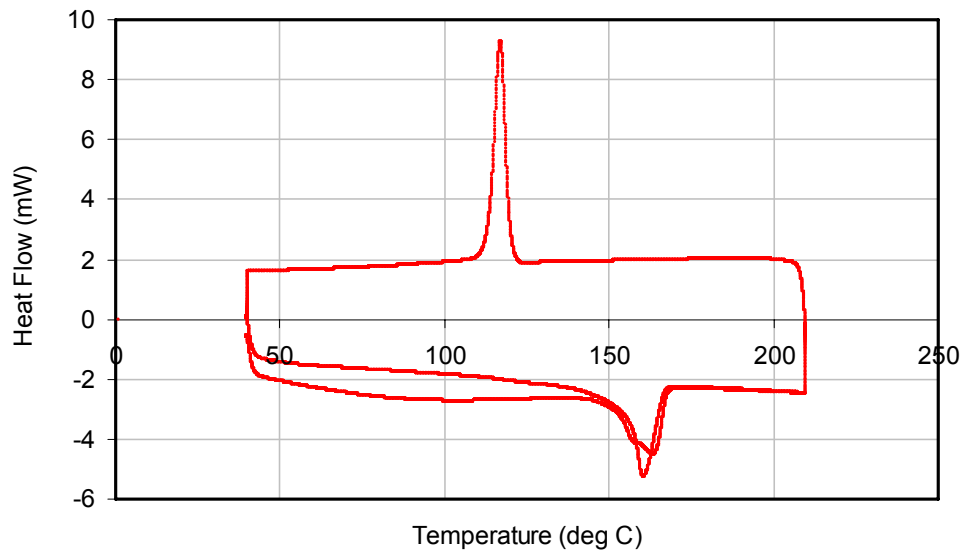
Figure A2.4: DSC curves for the three scans performed on wheat straw-PP composite prepared at 190°C, containing 50 wt-% of fibers.

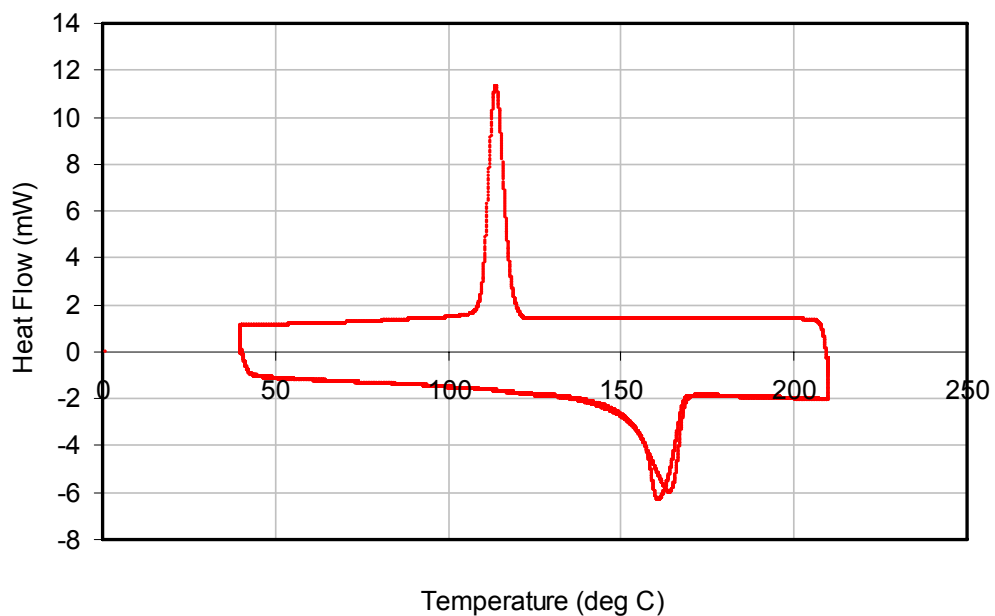**30% WS, 160°C**
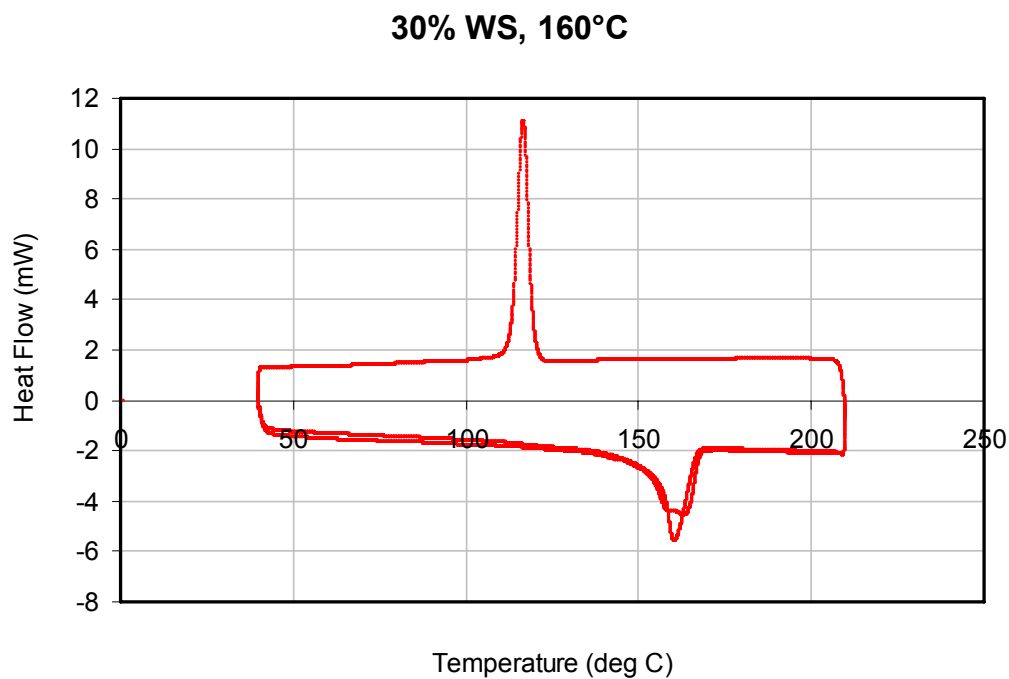
Figure A2.5: DSC curves for the three scans performed on wheat straw-PP composite prepared at 160°C, containing 30 wt-% of fibers.

50% WS, 160°C
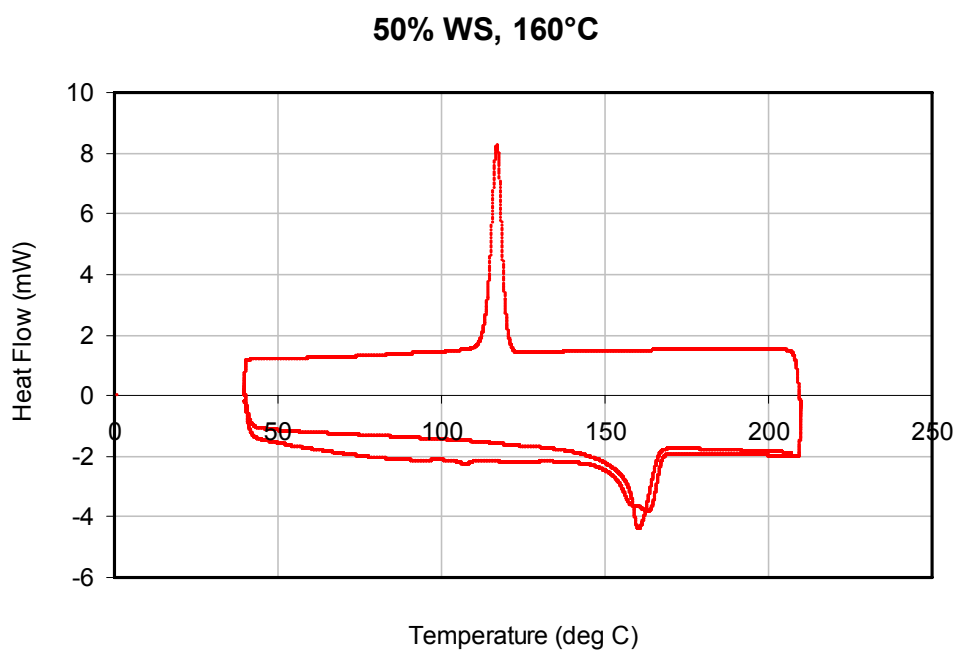
Figure A2.6: DSC curves for the three scans performed on wheat straw-PP composite prepared at 160°C, containing 50 wt-% of fibers.
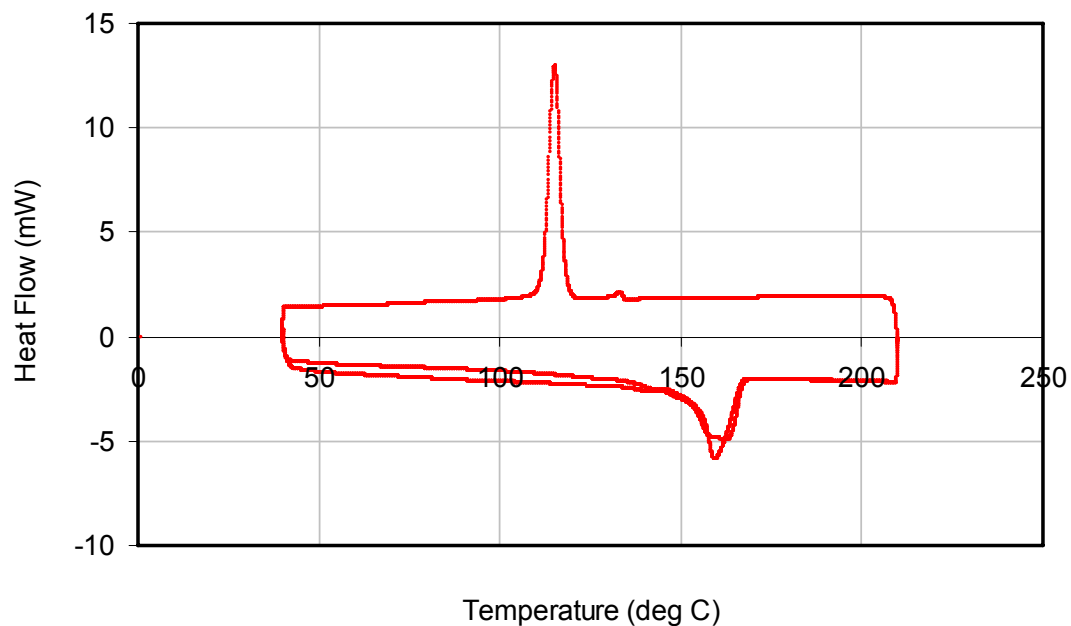
10% WS, 190°C
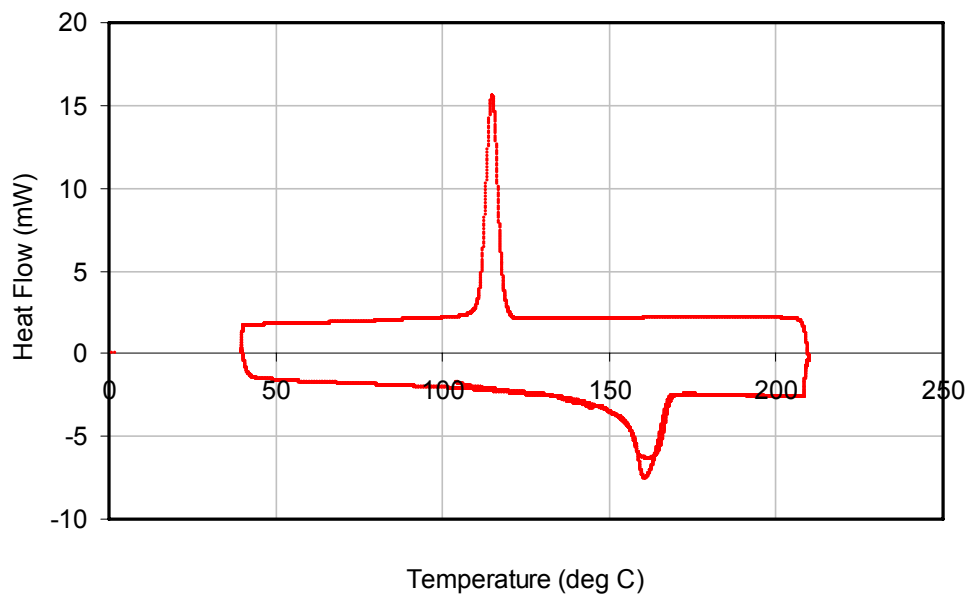
Figure A2.7: DSC curves for the three scans performed on wheat straw-PP composite prepared at 190°C, containing 10 wt-% of fibers.

20% WS, 190°C
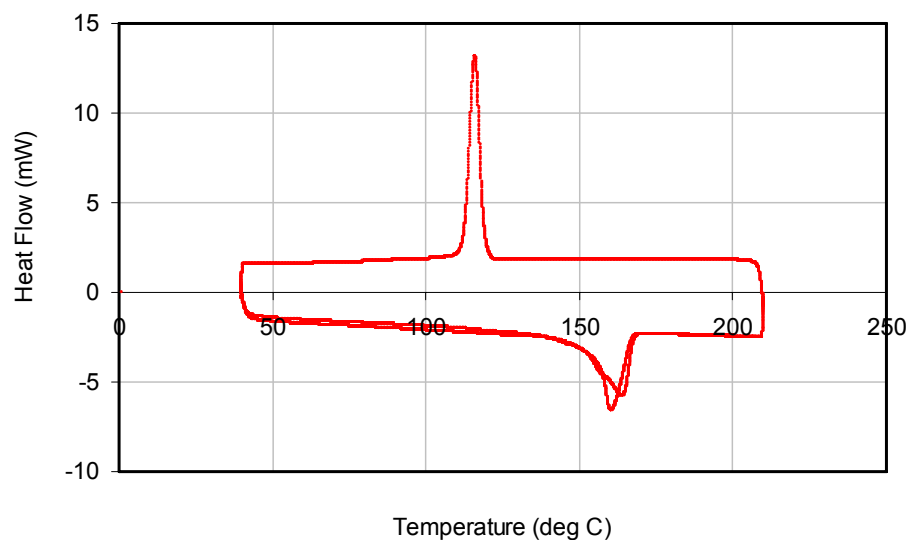
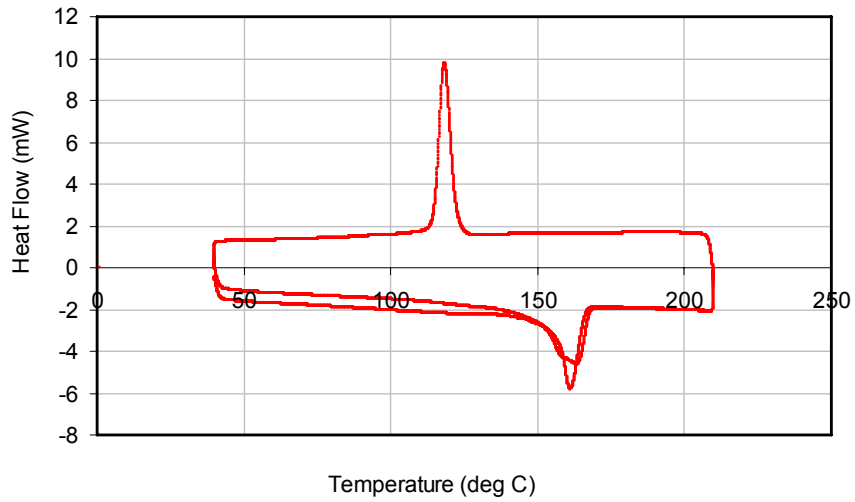**Figure A2.8:** DSC curves for the three scans performed on wheat straw-PP composite prepared at 190°C, containing 20 wt-% of fibers.

40% WS, 190°C

Figure A2.9: DSC curves for the three scans performed on wheat straw-PP composite prepared at 190°C, containing 40 wt-% of fibers.
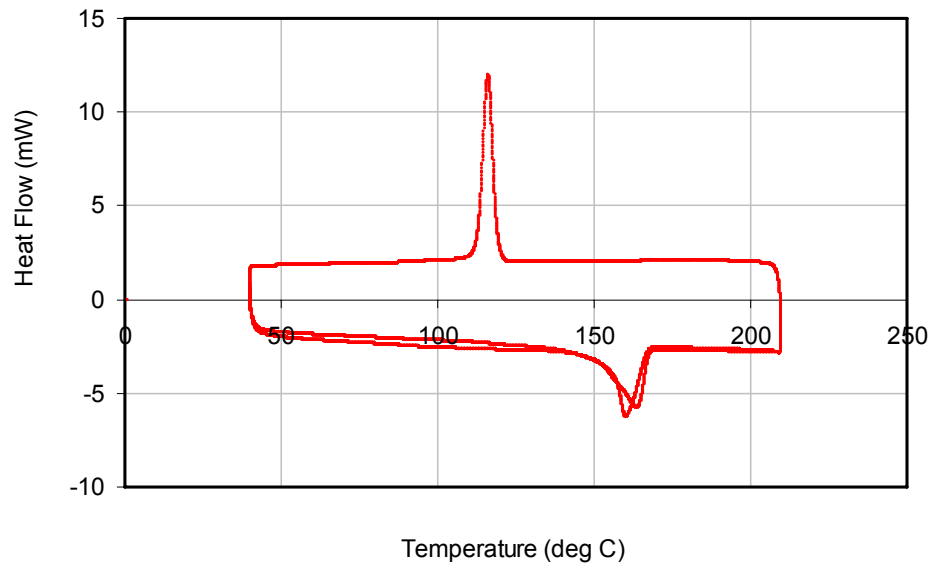
60% WS, 190°C

Figure A2.10: DSC curves for the three scans performed on wheat straw-PP composite prepared at 190°C, containing 60 wt-% of fibers.

Polypropylene

Figure A2.11: DSC curves for the three scans performed on virgin polypropylene.

30% WS, 190°C, Lubricant

Figure A2.12: DSC curves for the three scans performed on wheat straw-PP composite prepared at 190°C, containing 30 wt-% of fibers and lubricant.

30% WS, 190°C, MAPP

Figure A2.13: DSC curves for the three scans performed on wheat straw-PP composite prepared at 190°C, containing 30 wt-% of fibers and MAPP.

30% WS, 190°C, MAET

Figure A2.14: DSC curves for the three scans performed on wheat straw-PP composite prepared at 190°C, containing 30 wt-% of fibers and MAET.
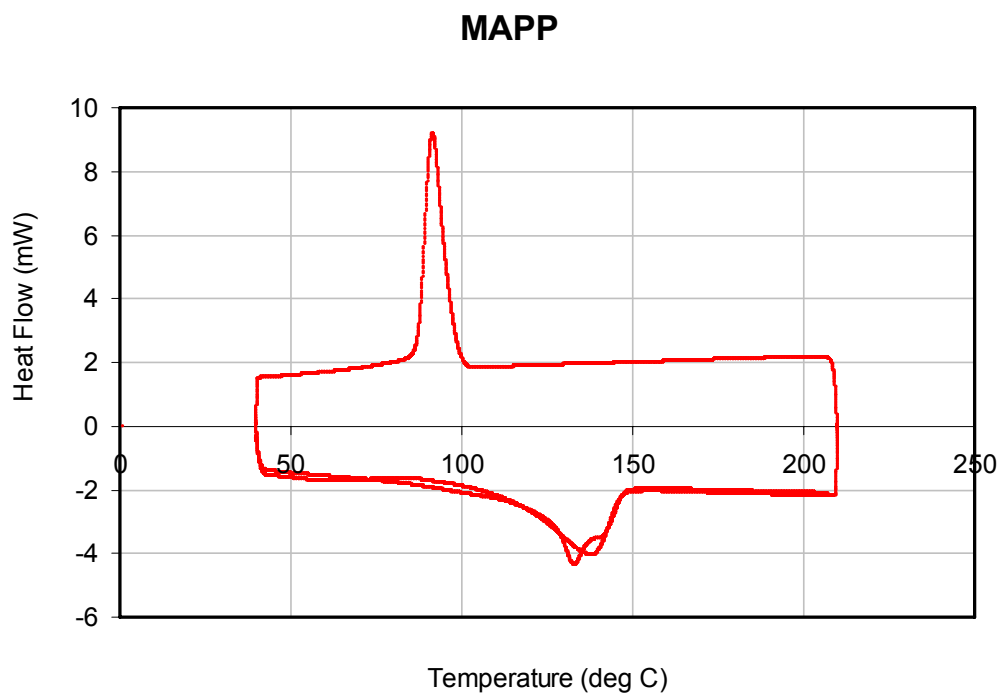
MAPP

Figure A2.15: DSC curves for the three scans performed on maleic anhydride polypropylene (MAPP).
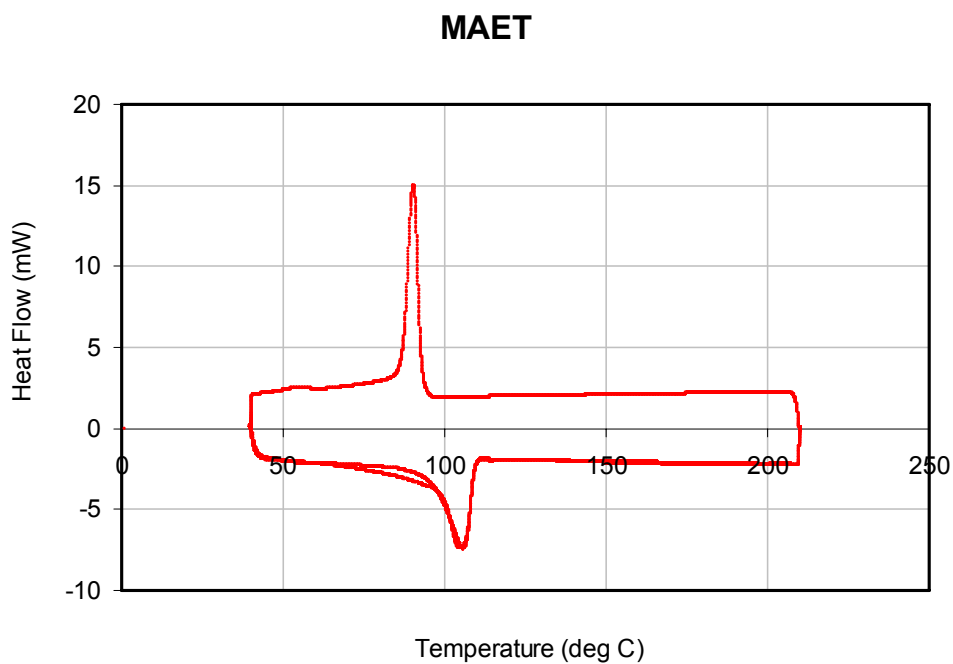
MAET

Figure A2.16: DSC curves for the three scans performed on maleic anhydride ethylene (MAET).
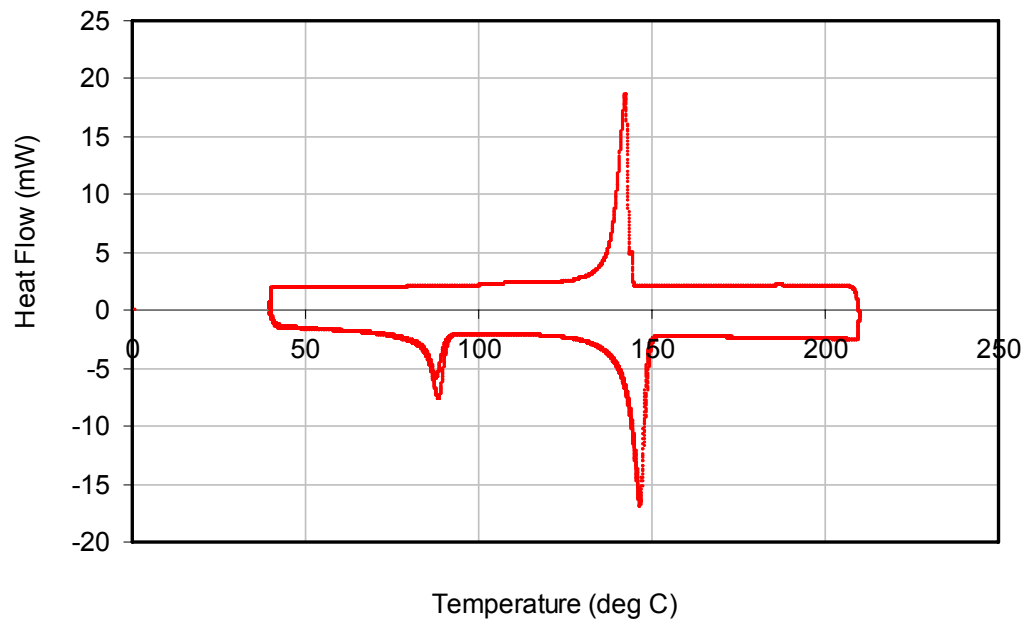
Lubricant

Figure A2.17: DSC curves for the three scans performed on lubricant (Glycolube WP 2200).

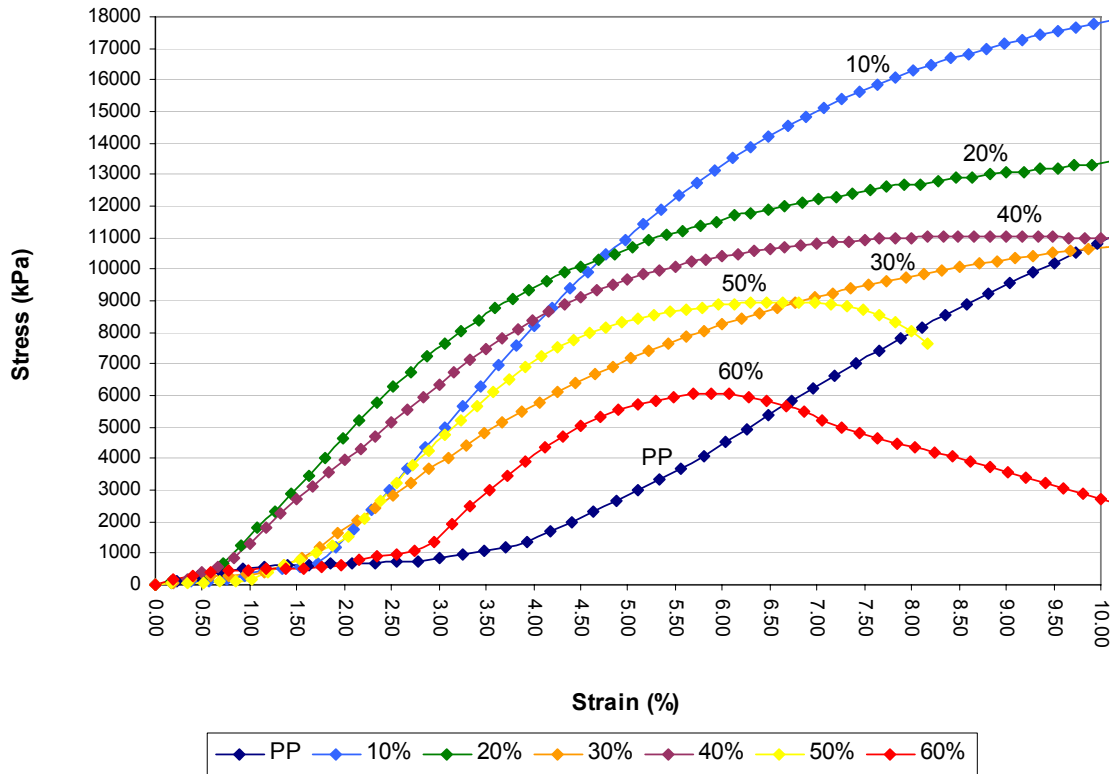# Appendix C: Flexural Test Curves

Figure A3.1: Typical stress-strain curves from flexural test performed in polypropylene and wheat straw-PP composites prepared at 190°C, with fiber loading in the range of 10 to 60 wt-%.