POLYMER BLENDS FOR MULTI-EXTRUDED

WOOD-THERMOPLASTIC COMPOSITES

By

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of VIVIANE LOUISE VILLECHEVROLLE find it satisfactory and recommend that it be accepted.

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Chair

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ACKNOWLEDGMENT

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WOOD-THERMOPLASTIC COMPOSITES

Abstract

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 Wood-plastic composites (WPC's) are usually composed of wood blended with a single polymer. To address the issue of WPC's recycling and appraise the potential offered by using polymer blends in the making of WPC's, composites made of wood flour and several blends of isotactic polypropylene (PP), high density polyethylene (HDPE) and polyvinyl-chloride (PVC) were extruded. Both polymer blends and WPC's require intensive mixing to sufficiently homogenize the composite, therefore the influence of additional mixing was evaluated by re-extruding the composites another three times. Torque rheometry, bending tests and water sorption tests were performed to determine the influence of the repeated extrusions and the use of polymer blends on the composites' performances. The results indicated that the subsequent re-extrusions increased the water resistance and the brittleness of the composites. The use of polymer blends did not interfere with the processability and the strength. Within the tests performed, no disadvantage related to the use of polymer blends was discovered. Composites containing PVC were found easier to process and stiffer but more brittle and less water resistant than the composites made of PP or HDPE. PP-based composites were the most difficult to process, primarily due to extruder temperatures, but had the best water resistance. The performances of the composites depended on the nature of their components, not on the eventual presence of a polymer blend. Thermal properties were also investigated. The transition temperatures and the crystallinity of the samples

were determined through differential scanning calorimeters (DSC). Tests for oxidation induction times (OIT) were conducted utilizing DSC techniques as well. Wood increased the melting point of most blends and reduced the crystallization temperature of HDPE-based composites. On the contrary, PVC diminished the melting point of PP-based blends. The different components were deemed immiscible and seemed to melt and crystallize separately. Repeated extrusions on the WPC's apparently increased the crystallinity degree as well as the rate and temperature of crystallization, but decreased the melting temperature, indicating a potential structural degradation of the composites. PVC blends showed the best resistance to oxidation while the OIT of PP and HDPE blends were particularly short. The number of extrusions did not change the oxidation times of the composites tested.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Dedication

This thesis is dedicated to my parents, for their constant love and support.

CHAPTER I – INTRODUCTION

I. Background

The wood-plastic composites (WPC's) industry has been experiencing an important growth over the last decade and is thought to take a place more and more important in the construction materials market during the coming years [1][2]. A wood-plastic product is constituted of wood, in form of flour or short fibers, blended with a thermoplastic, the most common being high density polyethylene (HDPE)), polyvinyl chloride (PVC), and isotactic polypropylene (PP).

Usually, WPC's contain only one kind of polymer where polymer blends have been rarely considered in the making of such products. Knowledge in such a wide domain as that of polymers and polymer blends is still building up, limiting the range of products and the variety of polymers used and studied in the purpose of creating WPC's. Polymer blends can be especially complex to process, manipulate and study. Most polymers are immiscible, sometimes making blending difficult. The components dipersion in an immiscible blend is an issue that defines a blend's morphology, which has direct impacts on the thermal and physical behavior of the blend. The objective of creating polymer blends is the same as creating composites: two elements are mixed or associated in order to create a new product that could possess some properties of each of its components. Even if making these sort of product is challenging, the resulting performance can be extremely interesting. In the case of the WPC's, for example, the idea is to manufacture a

product having some of the wood's natural tensile strength to the water resistance and easy maintenance of plastic.

WPC's can be made of recycled materials, but recycling is sometimes difficult and expensive, especially because of the necessity of cleaning the waste and separating the different kinds of polymers. HDPE, PP and PVC figure among the most frequent plastic waste. If their separation was feasible, it would reduce the price of recycling, which is another reason to consider the possibility to use polymer blends and evaluate the feasability of using non-separated recycled polymers to produce WPC's.

The other aspect of recycling would be the re-use of old WPC's. Many manufacturers regularly reprocess their out-of-use WPC's to produce new ones. Multiple processing can be harmful by degrading the structure and eventually weakening the product. On the other hand, several extrusions can help achieve a homogeneous mix of the materials and thus improve the blends miscibility, adhesion and resistance. A blend well mixed offers less voids for the moisture to penetrate and more surface to enable stress transfer because of the increased dispersion of the fiber within the matrix. That said, mixing must be done carefully because heat and shear might deteriorate the materials.

The stresses are transferred in the composites by friction between the wood flour and the surrounding plastic. The wood gives its strength to the WPC's and to do that, contact must exist between the wood and the polymers. Having a good stress transfer means that all the components will contribute with the maximum of their capacity to the strength of the composite. Having a good stress transfer implies that the constituents of a composites will share the load applied on that composite, making it stronger [21].

Blending the composites is extremely important and influences the structure and the mechanical behavior of the products. Several authors state that the structure and morphology of a blend or a composite is directly linked to its mechanical properties and macroscopic behavior [6-9].

II. Problem statement

Today, the WPC's industry manufactures and sells mostly single polymer-based composites. This project focuses on the use of polymer blends in the making of composites of wood and the performances of those composites. The impact of multi-processing and re-mixing will also be adressed. HDPE, PP and PVC are the most common plastic on the market, the most recycled ones and the most often used by WPC's companies. Using these products separately limits the opportunities of facilitating recycling and restrains the potential for WPC technology to offer manufacturing flexibility. With oil prices steadily increasing, plastic is getting more and more expensive. Using recycled plastic materials with minimum additional processing steps, or a wider range of them would be quite economical in these critical times.

Blending several polymers can be challenging but extensive research has been accomplished by researchers from chemistry and polymer science. Blends of PP and HDPE, for example, have been studied for a long time and exhibit good mechanical performances [9-18]. In the case of WPC's, using coupling agents and compatibilizers usually helps the adhesion of the materials and strengthens the composite [19-20]. With this knowledge, one can assume that utilizing polymer blends to prepare WPC's should be possible and even constructive, since both WPC's and neat polymer blends have already

3

been investigated for a while. Moreover, the strength of a blend directly relates to its morphology and this morphology greatly depends on the phase dispersion, at least in the case of immiscible blends. Thus, improving the dispersion of the components in the blend should impact the mechanical performance, especially in terms of tensile strength and moisture resistance of the composites. Re-mixing is a way to insure better blending and will be assessed here.

III. Objectives of the project

The goal of the following project is to investigate and determine the performances of polymer blends-based WPC's in comparison with single polymer based composites. Utilizing polymer blends to create WPC's should not be an issue since polymers are already used and polymer blends, even if immiscible, can show good properties. The impact of the polymer blends on the mechanical performance should not be significant, although the processing effort might increase and the strength be intermediate, depending on the nature of the blended polymers. Problems at the interface between polymers might also arise and diminish water resistance and stress transfer.

Mixing is decisive for the components dispersion and to guarantee good performances of the WPC's. Re-processing should increase the degree of blending and homogenize the blends, improving the resistance of the composites. Yet, degradation might occur as well. the real impact of multiple processing will be investigated.

The impact of the presence of polymer blends within WPC's will be looked at, as well as the repercussions of re-mixing on the physical and thermal properties of the composites.

To attain these goals, the following objectives were undertaken:

- Utilize torque rheometry to evaluate the mixing and processing characteristics of WPC's containing polymer blends,

- Compute the strength characteristics and the water resistance of polymer-blend WPC's,

- Determine the crystallization mechanism, the melting point and the oxidative resistance of composites made of polymer blends,

- Use multiple extrusions to determine the influence of extensive mixing on the thermal characteristics and mechanical properties of the polymer-blend WPC's,

- Compare the evaluated performances of the polymer-blend WPC's with the single-polymer WPC's.

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CHAPTER II – STRENGTH, STIFFNESS, CAPACITY OF DEFORMATION AND WATER RESISTANCE OF WPC'S CONTAINING POLYMER BLENDS

Abstract

Composites made of wood flour and blends of isotactic polypropylene (PP), high density polyethylene (HDPE) and polyvinyl-chloride (PVC) were extruded, granulated and re-extruded three more times. The wood-plastic composites (WPC's) were extruded several times to monitor the influence of melt-blending on the behavior and product performance of WPC's made with polymer blends. To determine the implication of re-extruding and introducing polymers blends on the composites' performances, torque rheometry, bending tests and water sorption tests were performed. The results suggested that re-mixing increased the water resistance and the brittleness of the WPC's. Polymer blends did not impact the results obtained during torque rheometry tests, nor the results found during flexural testing. In fact, these results were due to the nature of the polymers used. Composites of PVC were particularly stiff, brittle and easy to process, but lacked of water resistance in comparison with WPC's made of PP or HDPE. PP-based composites were the most difficult to process because of the extruder temperatures, but had the best water resistance.

I. Introduction

Polymer blends

Usually, WPC's contain a single polymer species and polymer blends have been rarely considered in the making of such composites. Polymer blends can be especially complex to process, manipulate and study. Most polymers are immiscible with each other, adding to their complexity. The creation of a polymer blend generally results in a new product that will exhibit some of the properties of each of its components. Even if making such a product is challenging, its new performance can be very interesting. In the case of the wood-plastic products, for example, the idea is to manufacture a product having some of the wood's natural tensile strength to the water resistance and easy maintenance of plastic. Blends of PP and HDPE have been studied for a long time [1][20-26]. These blends can display good mechanical performances. Using coupling agents and compatibilizers usually helps the adhesion of the materials and strengthens the blend.

Most polymers are immiscible even if they apparently blend. In thermodynamic terms, miscibility refers to a single-phase system at the molecular level, but in practice, a seemingly homogenous blend will be considered miscible or more exactly compatible [21-22][31]. The necessary condition for two polymers to mix is that the Gibbs free energy of their blend is smaller than the sum of the Gibbs free energies of the separate polymers, meaning that ΔG, the change in free energy on mixing, should be negative. The change in Gibbs free energy is expressed as $\Delta G = \Delta H - T.\Delta S$, where ΔG is the change in free energy, ΔH is the change in enthalpy, T is the temperature of mixing and ΔS is the

change in entropy. If ΔG<0, blending is favored, also implying that an increase in the entropy will help polymer mixing [31]. Entropy can be defined as the amount of energy which is not available to do work, or as a measure of the disorder of a system [32].

Some pairs of polymers will be more or less miscible, depending on temperature and composition. Even if polymers often are immiscible, some techniques are still available to the scientist to make stable and reproducible blends of immiscible materials, like using copolymers or crosslinking. A mixture of immiscible polymers will give a phase-separated solution called an immiscible blend. The miscibility and morphology of a blend directly influences its mechanical properties [21-22][27-30].

Mechanical properties of WPC's

As the market steadily grew, the mechanical and physical properties of WPC's have been widely investigated. In their review of the general assets and properties of the WPC's, Wolcott and Englund [4] explained how the performances of the composites varied in function of their components. In general, the wood increased the mechanical properties and the thermal stability of the thermoplastic matrix, while the moisture barriers of plastic increased the water resistance of the wood.

In a WPC, the water sorption is due to voids or wood particles located at the surface of the composite. Any filler that is at the surface and therefore, susceptible to moisture exposure will undergo water sorption until the composite reaches an equilibrium moisture content (EMC). Klason et al. [5] exposed molded PP-wood flour composites to a 50% relative humidity (RH) at 23°C for a hundred and fifty days and observed an EMC of 1.6% at a filler loading of 60%. The EMC decreased with the flour percentage. Then,

10

they subjected the same samples to a water immersion test in a 90°C water bath during seven days and found that wood flour percentages between 20% and 60% resulted in an 8% to 10% moisture content.

A very interesting aspect of the WPC's is that they can be created with all recycled materials. These environment-friendly materials can be made of recycled wood as well as recycled thermoplastics. Not only HDPE, PP and PVC are the most common plastics on the market and therefore, the most recycled ones, but they are also the main constituents of most WPC's [3][10-11]. Plastic wastes are one of the major volumes of global municipal solid waste. Today, a city in a developing country with a population of three million inhabitants daily produces around 400 tons of plastic waste. This generation of plastic is said to increase of 25% every year [20]. If recycling efforts have been done over time, finding new ways of using these recycled materials is still crucial and the WPC's seem to offer good opportunities in that prospect.

Objectives

Most of the knowledge supported today in the domain of WPC's concerns products made of a single polymer, but nothing indicates that polymers blends cannot be used to manufacture wood-plastic materials that would still show correct performances. This project explored and determined the performances of polymer blends based WPC's in comparison with single-polymer-based composites and proved that they are viable products for the industry. The other important issue of the project was to determine the effect of extensive melt-blending through multi-extrusions on the properties of the composites.

11

Composites made of wood floor with different concentrations of PP, HDPE and PVC were extruded several times and their processability, strength and water resistance investigated.

The objectives were to:

- Identify the processability of mixed polymer systems for WPC's utilizing torque rheometry.

- Utilize repeated extrusions to determine the influence of melt-blending on the composite properties,

- Test the composite blends for mechanical and physical performance

II. Materials and testing methods

1. Materials

HDPE, PP and PVC are common polymers often used for WPC's. Petrothene® LB010000 from Equistar was chosen for HDPE, Innovene H04F (HB9200) from BP Amoco Chemical Company was selected for PP and PVC came from Georgia Gulf Compound. HDPE's melt index was 0.5 and PP's melt index was 4.0 g/10 min.

The wood floor was a commercial 60-mesh eastern white pine (Pinus strobus) from American Wood Fibers. Lubricants, ethylene bis stearamide (EBS) wax and zinc stearate, were added to the blends for improved processability of the composites. The general formulation of the blends was to use 58% of wood floor and 39% of thermoplastics (see Table 2-1). The amount of lubricants was constant at 3%. The individual components were weighed and mixed in a drum blender before being extruded into a solid profile of 38x10 mm (1.5×0.4 inches). 10 kg batches were used so that there would be enough material to prepare several extrusions of the materials.

Table 2-1 Composition of the wood-plastic blends studied in this project.

	Blend 1	Blend 2	Blend 3	Blend 4	Blend 5	Blend 6
Wood	58%	58%	58%	58%	58%	58%
HDPE	39%			19.5%	19.5%	
PP		39%		19.5%		19.5%
PVC			39%		19.5%	19.5%
Zinc Stearate	2%	2%	2%	2%	2%	2%
EBS wax	1%	1%	1%	1%	1%	1%

2. Torque rheometry: processability

The torque rheometer used was a Haake Rheomix 600p. No lubricants were used for this test since the goal is to evaluate the natural processability of the materials. Blends following the compositions of Table 2-1 without lubricants (60% of wood flour and 40% of thermoplastics) were mixed for 10 minutes at screw speed of 20 rpm and a temperature of 180ºC with a roller rotor. Virgin polymers, polymer blends and WPC's were tested and for each material, three samples were run into the rheometer. As these tests were made before any extrusion, only one set of tests was carried out.

3. Extrusion

The products were extruded four times through a 35 mm twin-screw extruder. The approximate melting point (T_m) of HDPE and PP are respectively 130 ºC and 160 ºC and wood usually begins degrading around 210 ºC. Moreover, the required processing zone of PVC is 162ºC to 168ºC. To ensure that PP would melt without making the wood burn, the extrusion was carried out at a die and an extruder temperature of 180ºC. The velocity of the screws was set on 20 rpm for the first extrusion but was changed to 10 rpm for following three extrusions due to the higher feeding capacity of the pelleted material.

The composites were extruded into the 38x10 mm (1.5×0.4 inches) solid profile and were cut and ground through a 40 mesh screen in a knife mill after each extrusion so they could be re-extruded. A sufficient amount of material was reserved to perform the flexural and water resistance tests. Extrusion processing parameters are located in Appendix E.

4. Flexural testing: strength and deformation

Flexure tests were conducted in accordance with ASTM D 790 [17] requirements. Six samples of 203×38×10 mm (8×1.5×0.4 inches) were cut and stored 24 hours in a 20ºC and 60% relative humidity conditioning room. The test span was 152 mm (6 inches). A universal testing apparatus was utilized for the test, while load and deflection were collected in real-time and used to calculate the MOE, the MOR and ε_{break} .

5. Water sorption: moisture resistance

The composites obtained from the four extrusions were planned to a thickness of approximately 6 mm (0.25 inches) to remove the polymer-rich surface of the boards and cut into specimens of 127×25 mm (5×1 inches). The samples were then immersed in distilled water at ambient temperature (20ºC) for 16 weeks. The thickness and weight of the samples were measured at several moments in time to determine their water sorption (mass change) and thickness swelling (thickness change). They were measured everyday during the first three days and then every week for a month. After that first month, the measurements were taken every two weeks until the end of the test at sixteen weeks or about 2660 hours of immersion. Before any measurement, the surface water was wiped away to avoid any additional mass.

III. Mechanical properties of the tested WPC's

1. Torque rheometry

This test measures the torque and the energy needed to mix a blend of polymers, reflects the resistance of the material to shear deformation during the mixing process and gives an idea of the viscosity and processability of the components. As noted by Yang et al. [14], the most interesting similarities are that the thermal stress and oxygen will influence the structure of the melt and change its apparent viscosity. This apparent viscosity is related to the shear stress, and thus the torque. Here, only the torques and energies will be looked at since they can express the same general behavior of the blends.

As the maximum torque corresponds to the time when the plunger pushed the material and closed the chamber, the value of this maximum torque is not accurate and will not examined. Instead, a closer look at the equilibrium or stabilized torques (T_e) should give a sufficient insight on the processability and viscosity of the materials. Here, the time "0" corresponds to the time when the chamber is completely closed. After four minutes of blending, the torque T usually converged to a constant value corresponding to T_e [15]. T_e can also be an indicator of a complete melt or softening or with filled polymers a fully mixed system. The trends provided in the following torque rheometry figures are representative curves taken from a sample of three runs.

Tests on neat polymers

During the unfilled polymers' tests, the highest T_e and the highest energy were that of the HDPE, even if PP developed a greater energy for the five first minutes of blending. PVC was the polymer that required the least energy and shear stress. On Figure 2-1, the slopes of the curves of the energy for PP and HDPE look very steep at the beginning, in the linear part of the curve, and then diminishes greatly. On the contrary, the energy curve of PVC is almost linear all along after the fusion. The observed behavior of the can be due to the processing temperature of the tested polymers.

The results from torque analysis gave a different insight. On Figure 2-2, the T_e of HDPE was still the highest but PVC required a higher T_e than PP. These observations could mean that HDPE has a higher apparent viscosity than PP and PVC, PVC having the least apparent viscosity. Nevertheless, the curve of the PVC on figure 2-2 exhibited a bump between one and two minutes after the onset of the test. This is due to the fusion of PVC, as explained through similar work with WPC's by Matuana and Kim[2]. The fusion is the thermal reduction of PVC's particles (grains) boundary surface. The grains are destroyed and the resulting microparticles are compacted when the heat increases. The fusion of PVC might have increased T_e and could explain why the torque is high and the energy gets linear.
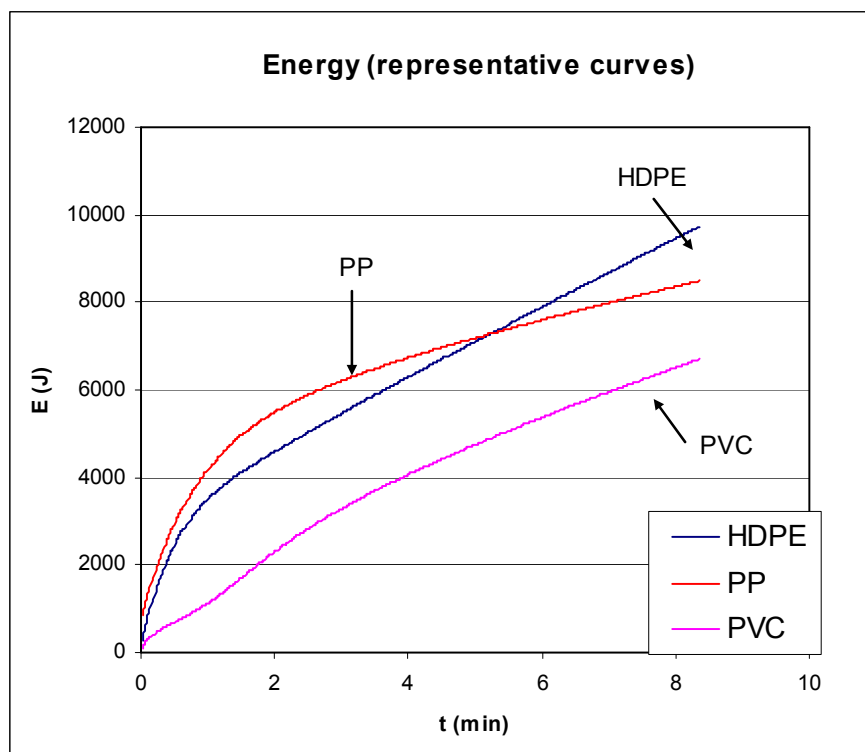
Figure 2-1 Curve of energy vs. time for each polymer.
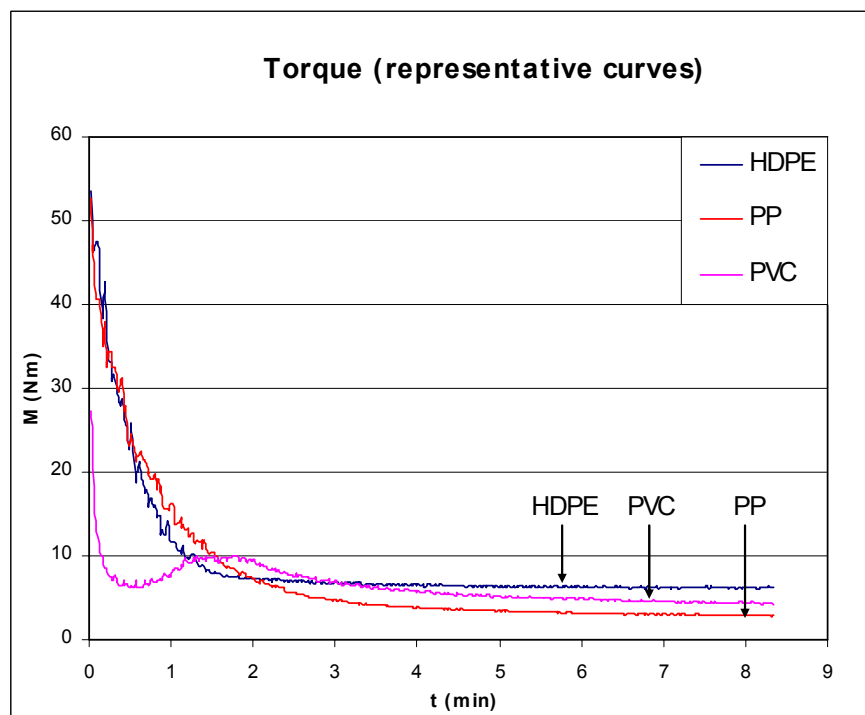
Figure 2-2 Curve of torque vs. time for each polymer.

18

Tests on polymer blends

The curves of the energies of HDPE/PP/PVC and HDPE/PP, Figure 2-3, almost superpose. They are joined by the curve corresponding to the HDPE/PVC blend at the end of the test. Only the PP/PVC curve stands out, with smaller values than the others.

Interestingly, the plot of the torques on figure 2-4 shows a different hierarchy, with HDPE/PVC developing the highest torque. The curves of HDPE/PP/PVC and HDPE/PP are very close again and the curve of the PP/PVC blend is still under the others. Apparently, HDPE/PP/PVC and HDPE/PP have the same processability, which means PVC did not influence the blend. The blends containing HDPE seem to need more energy and shear stress than the blends containing PP but the difference remains small.

The different processability noticed might be due to the higher melt index of PP over HDPE which means PP is less viscous than HDPE. The reasons why HDPE is more viscous than PP are that the molecular weight of HDPE (0.953 here) is higher than that of PP (0.900 here) and that HDPE has long linear chains favoring entanglement.
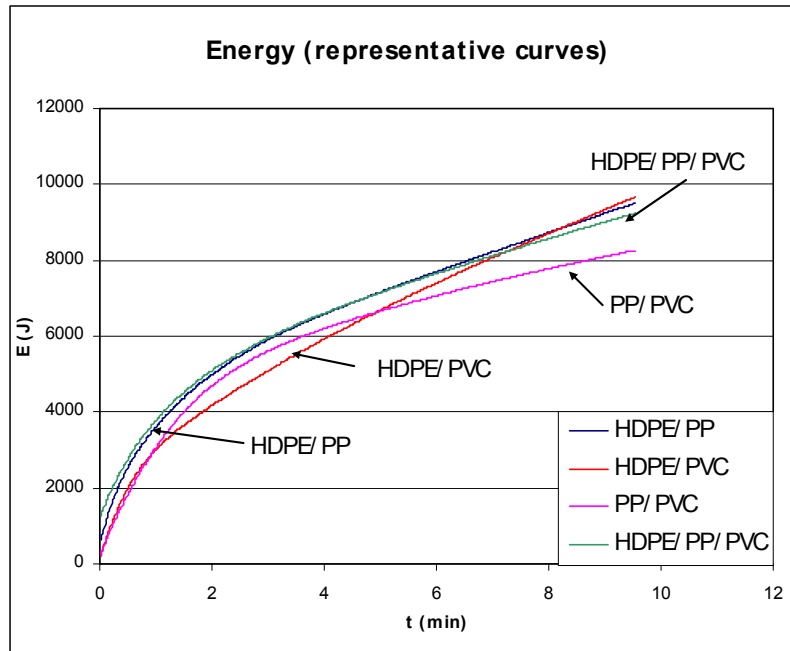
Figure 2-3 Curve of energy vs. time for each polymer blend.
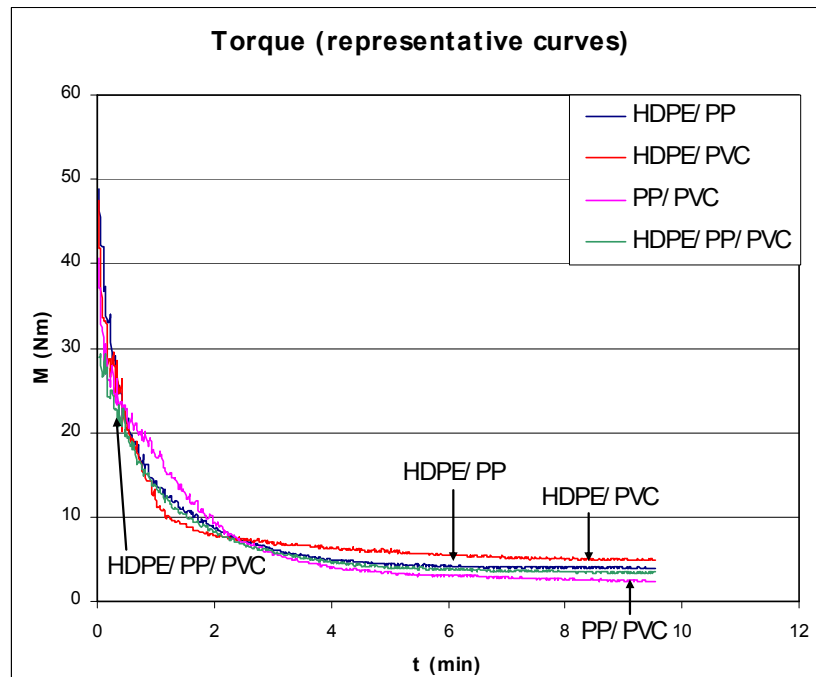
Figure 2-4 Curve of torque vs. time for each polymer blend.

Wood-plastic composites testing

After the experimentations conducted on the polymers, the six formulations of WPC's were run under the same torque rheometry conditions as with the polymers and their blends. On Figure 2-5, all the energy curves seem to grow steadily, their slopes at the beginning are smaller than those of polymer blends and their curves get more or less linear after the first three or four minutes of melting. From the results on the tests of the polymer blends, expecting to find the energy and the torque of the composites of HDPE higher than those of the composites containing PP would make sense but, surprisingly, WPC's made of PP are the ones requiring the highest energy and shear stress. Wood/PP has the highest curve, followed by wood/HDPE/PP and wood/PP/PVC. The torques, Figure 2-6, come on the same order, with wood/PP and wood/HDPE/PP curves almost superposing and greater than for the others blends. These observations show that composites of PP are being more difficult to process than composites of HDPE and PVC. HDPE has a lower melt index and is more viscous but the higher T_m of PP ($T_m = 160$ºC for HDPE and 160ºC for PP, see chapter 3, section 3.1.2.4) might be the cause of the high energy and torque required by PP-based blends.

Composites of wood and polymer blends

When compared to those resulting from the tests of polymer blends, the torque and energies required for WPC's were much higher because of the addition of wood, particularly for blends containing PP. Whereas T_e slightly increased for composites of HDPE and PVC, T_e doubled for these composites. The high T_m of PP can be an explanation to the difficult processing of the PP-based composites. Wood certainly

21

increased the overall viscosity of the blend and reinforced the effects of the high T_m that characterizes PP. The best processability was found for wood/HDPE/PVC, PVC seeming neutral on the viscosity on the blends. The WPC's containing several polymers did not seem to be more difficult to process than the other ones; they developed torques and energies depended on the nature of the polymers they were made of, not the fact that they contained several polymers.
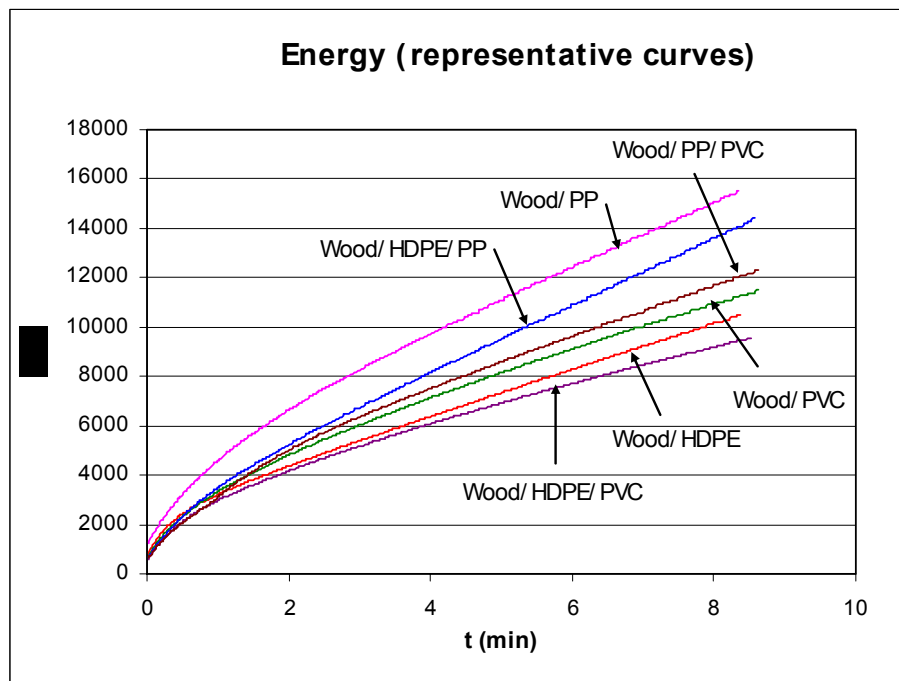
Figure 2-5 Curve of energy vs. time for each blend.
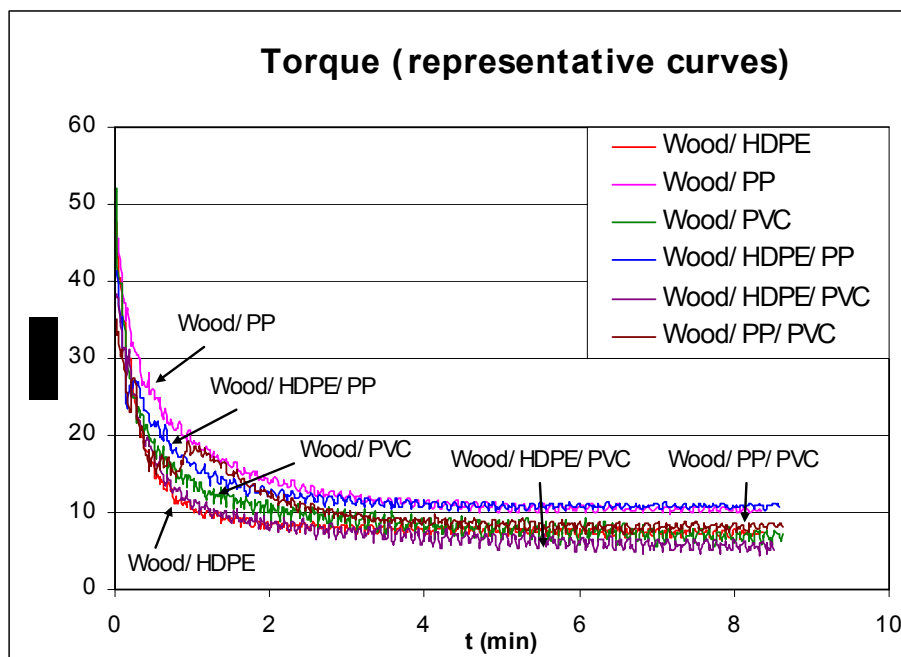
Figure 2-6 Curve of required torque vs. time for each blend.

2. Strength and deformation capacity

The goal of the bending tests is to determine the mechanical capacities of each board. With the load and the related extension, the MOE as well as the MOR and the ε_{break} can be calculated, using the formulas provided by ASTM D 790 [17]. Tables displaying more results can be found in Appendix A.

The MOE is presented on Figure 2-7. As expected, the wood/PVC exhibited a much higher MOE than its counterparts. The other composites made of PVC followed, wood/PP/PVC first, then wood/HDPE/PVC. Obviously, the products made with PVC were not only more brittle but also stiffer. The three other WPC's exhibited values similar to one another.

Looking at ε_{break} on Figure 2-8 confirms the stiffness and brittleness of the PVC-based composites. PP increased the capacity of deformation of the blends. The composites made of both HDPE and PP showed intermediate capacity of deformation and strength, at mid-way between those of wood/HDPE and wood/PP.

The MOR corresponding to the maximum load applied on the samples is presented Figure 2-9. Here, the blend of wood/PVC stands out again with a very high MOR but the other blends made of PVC did not experience any particularly high MOR this time. Wood/PP/PVC and wood/HDPE/PVC had a high MOE but small ultimate strain and MOR. They were rather brittle but did not bear a high load before breaking, while wood/PVC and wood/PP were the strongest composites according to their MOR.

The polymers strongly influenced the composites: PVC enhanced their brittleness and stiffness while HDPE and PP favored their ductility and increased their capacity of deformation.

As mentioned earlier, the samples seemed to become more brittle after each extrusion. These visual observations are backed up by the data on Figure 2-7 to 2-8. When the number of extrusions increased, the MOE increased and the ε_{break} decreased. Repeated extrusions tended to stiffen the boards and increase their brittleness. Likewise, in 2004, Clemons wrote a review of WPC's and emphasized the importance of recycling these materials. He pointed out some recycling issues, among them multiple-processing, and explained how processing could lead to a thermal degradation of the components. He cited the example of HDPE that could result in cross-linking if exposed to a high heat during its processing, and thus increase the brittleness. The fiber could also degrade because of repeated heat cycle exposures and mechanical degradation (fiber attrition). In

the end, multi-processing helps mixing the composites and increases the strength but sacrifices some ductility along the way. An increase in the degree of crystallinity C might also explain the better strength and high brittleness of multi-extruded composites, but must be proven by further testing. However, in crystaline polymers, toughness is mainly dependent on C because the crystals create molecular inflexibility, resulting in moderate impact strength and ductility [27].

Wolcott and Englund [4] wrote a review on the industry of WPC's and presented some of the general mechanical behavior to be expected from these products. They explained how WPC's are more ductile but weaker than solid wood. The data presented here agrees with that notion, the maximum MOE being 6,200 MPa for wood/PVC whereas common MOE values for a 51 mm (2 inches) wide #3 southern pine would have been 9600 MPa (NDS 2005 edition [18]). In 2005, Kazemi-Najafi et al. [7] conducted several mechanical tests on pressed composites of wood flour and recycled and virgin PP and HDPE. They found PP composites stronger and stiffer than HDPE composites, but of lower unnotched impact strengths and attributed these results to the superior mechanical properties of PP in comparison with those of HDPE. They also discovered that the composites made of PP and HDPE blends showed tensile properties comparable to those of composites made of PP or HDPE and concluded that using both plastics in a composite was possible and did not threaten the mechanical properties of the composite. The same observations can be done here, with PP blends usually having a slightly higher MOE and MOR.
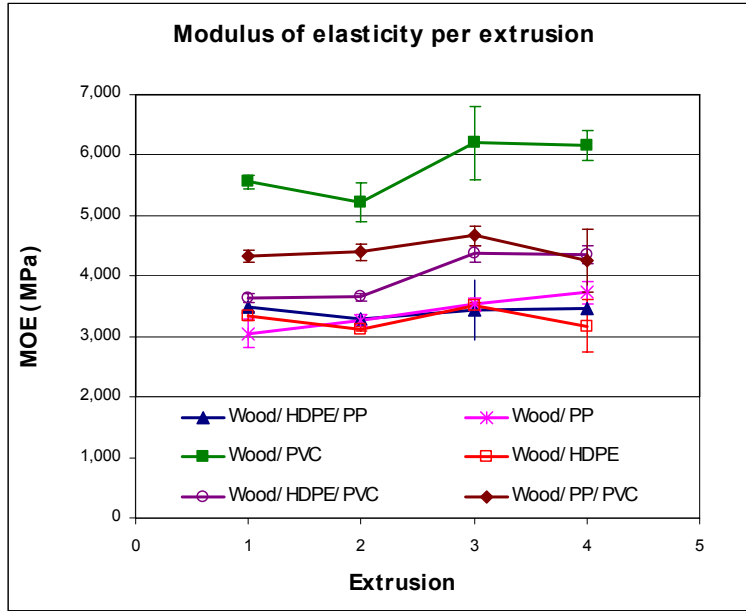
Figure 2-7 Modulus of elasticity of the blends, using representative curves.
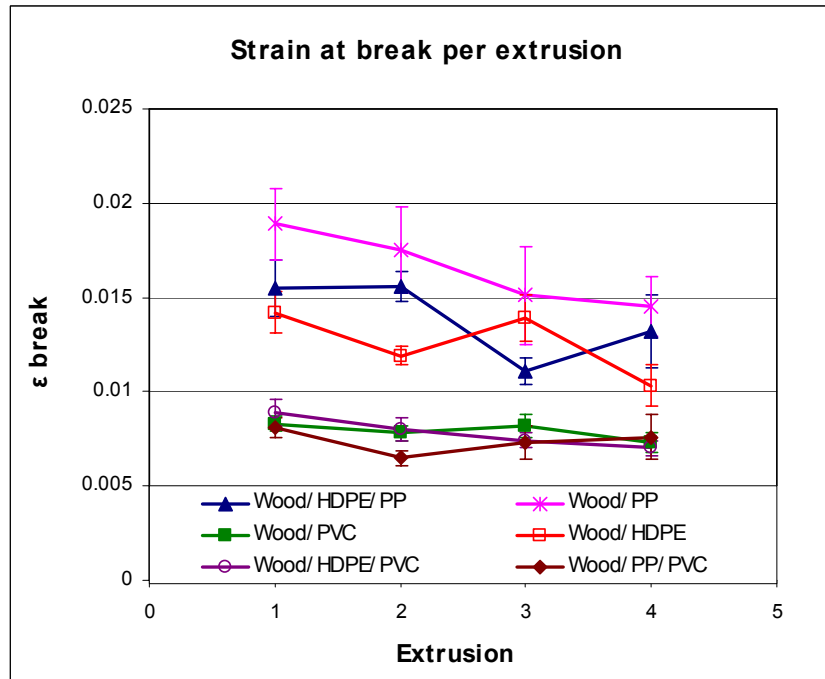
Figure 2-8 Strain at break of the blends, using representative curves.

26
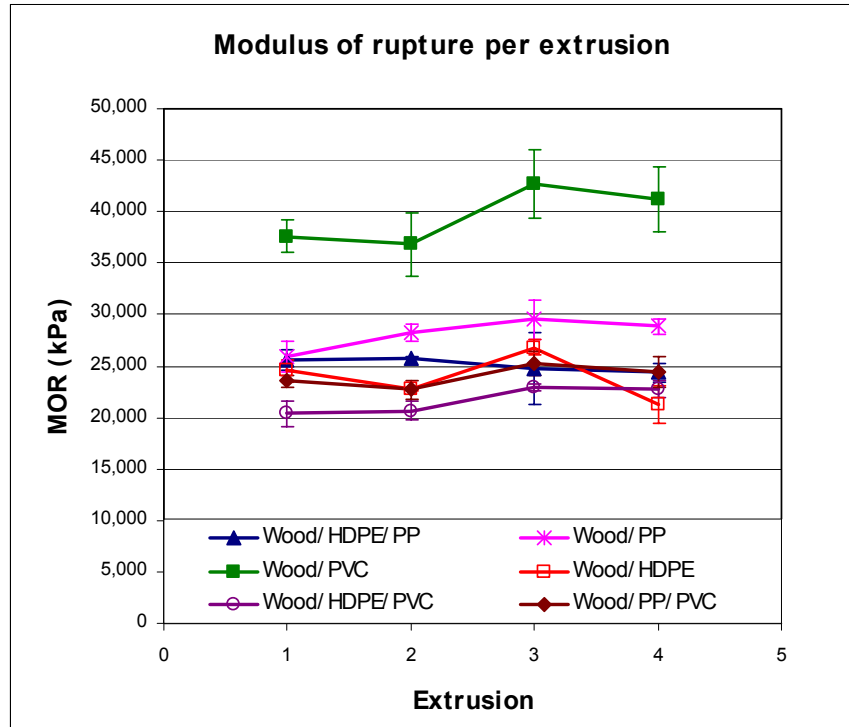
Figure 2-9 Modulus of rupture applied on the blends, using representative curves.

In addition to all these observations, the rule of mixture seems to apply to the MOE's found here. Here is the expression of this rule applied to the calculation of the MOE of a composite in function of the MOE and the volume of its components:

$$E_c = E_f V_f + E_m V_m$$

In this expression, E is the modulus of elasticity, V is the volume and the subscripts c, f and m stand for composite, fiber and matrix respectively. For WPC's, the matrix corresponds to the thermoplastic while wood is the fiber [33]. Since the composition of the composites is known, determining the MOE of composites made of polymer blends using the MOE of composites containing a single polymer is possible. For example, in the case of wood/HDPE/PP, the MOE is approximately the average of the MOE's of wood/HDPE and wood/PP.

Calculations can be found in Appendix A, Table A.7. Apparently, Wood/HDPE/PP followed this rule very closely but PVC introduced errors in the evaluation of the MOE. Interestingly, when the number of extrusions increased, the calculations became more accurate in the case of wood/HDPE/PP and wood/HDPE/PVC. On the contrary, the results obtained from the rule of mixture became less accurate in the case of Wood/PP/PVC. This loss of accuracy is possibly due to a degradation of the fiber during processing, especially because of fiber shortening. On the other hand, the enhance dispersion of the components might have improve the accuracy of the results for wood/HDPE/PP and wood/HDPE/PVC.

3. Moisture resistance

Kazemi-Najafi et al. clearly explained the water sorption mechanics in 2007 [8], stating that sorption usually occurs by capillarity because of gaps and flaws at the interface between wood and polymers, in addition to the natural sorption of the wood particles themselves. Studying the sorption properties of WPC's made of flour and virgin and recycled HDPE and PP, they found that the water sorption (ΔW) and the thickness swell (ΔT) increased with immersion time and reached a saturation point. In their analysis, they pointed out that composites made of HDPE showed a longer saturation time than those containing PP and that the ΔW of composites with PP was generally higher than that of composites from HDPE. They understood the poor water resistance of PP blends as a consequence of the incomplete adhesion of the components, creating gaps and flaws at the interfaces between polymers and wood.

In this investigation, wood/PE/PVC blends usually presented the shortest saturation time and the highest ΔW. ΔW and ΔT values were high for wood/PP/PVC as well. In general, the blends containing PVC presented the most important ΔW and ΔT, highlighting the poor water resistance of blends of PVC.

Even if all the blends experienced some sorption during the test, the water resistance of the WPC's was still better than that of solid wood. When the composites contained polymer blends, they did not react in any recognizable manner that could be due to the use of these polymer blends.

Water sorption

The values of the ΔW were calculated with the following formula:

$$\Delta W(t) = \frac{(W(t) - W_0) * 100}{W_0}$$

In this equation, $\Delta W(t)$ is the percentage of water absorption at given time t of immersion, $W(t)$ represents the weight of the specimen after the time t and W_0 is the conditioned initial weigh.

For the diverse extrusions, the blend of wood/HDPE/PVC usually was the one absorbing the most water, closely followed by wood/PP/PVC (Figures 2-10 to 2-13). After that, wood/HDPE/PP and wood/HDPE showed more ΔW than wood/PVC and wood/PP, except after the first extrusion.

The repeated extrusions obviously influenced the structure of the blends, leading to a reduction of ΔW. As noticed during the flexural tests, the extrusions changed the structure by re-mixing the blends. Since ΔW diminishes, it would make sense that the

29

structure gets more compact, with less gaps and a better adhesion between the components.

The curves of the water absorption all plateau around 20% because of the fiber saturation of the wood. The fiber saturation point is around 30% in most wood species [34]. Since the composites contained approximately 60% of wood, the fiber saturation point of the composites would be around 60%*30% = 18%. Then, by additioning the free water present in the voids, the final plateau values can be obtained.
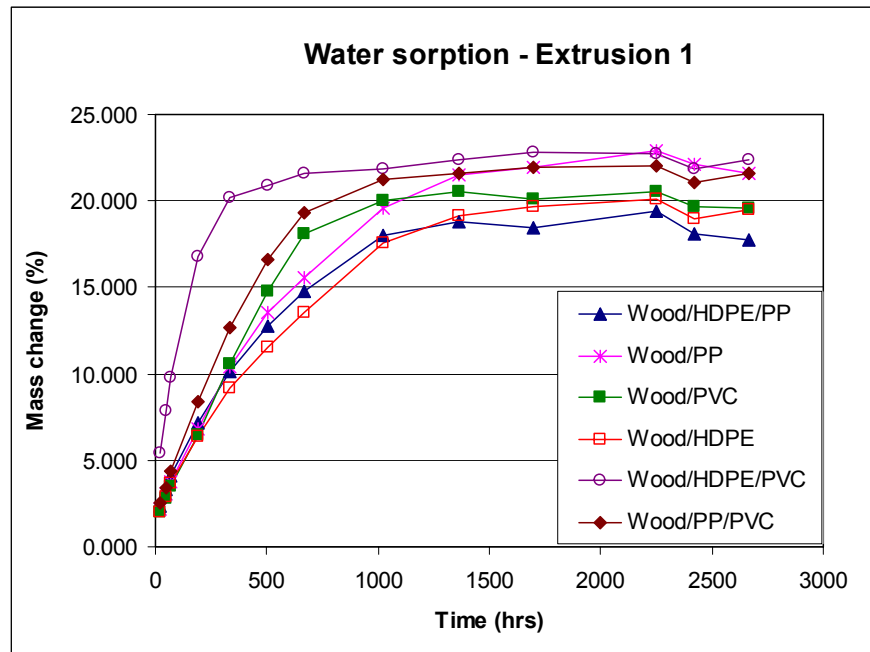
Figure 2-10 Plot of the water sorption, for the first extrusion.
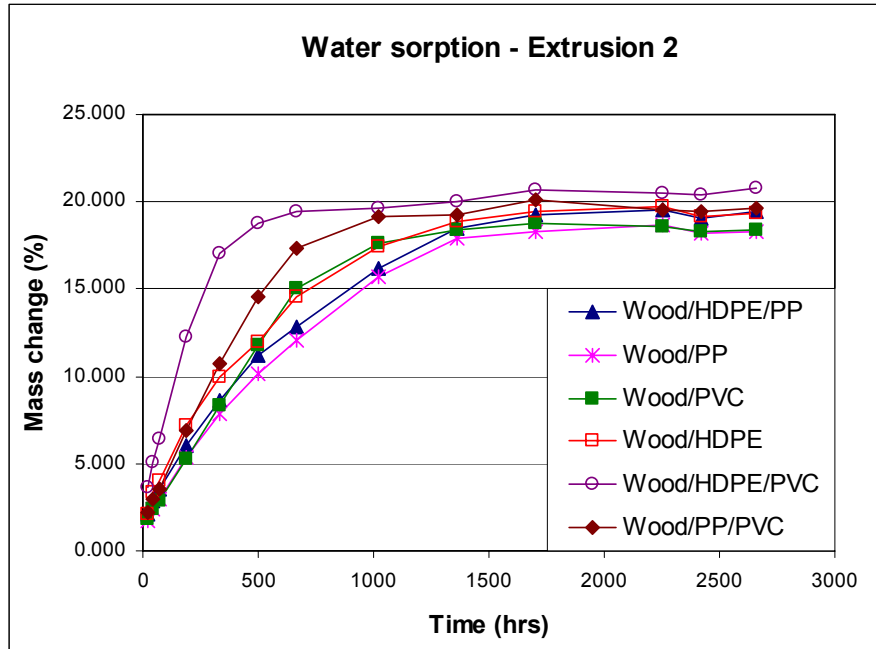
Figure 2-11 Plot of the water sorption, for the second extrusion.
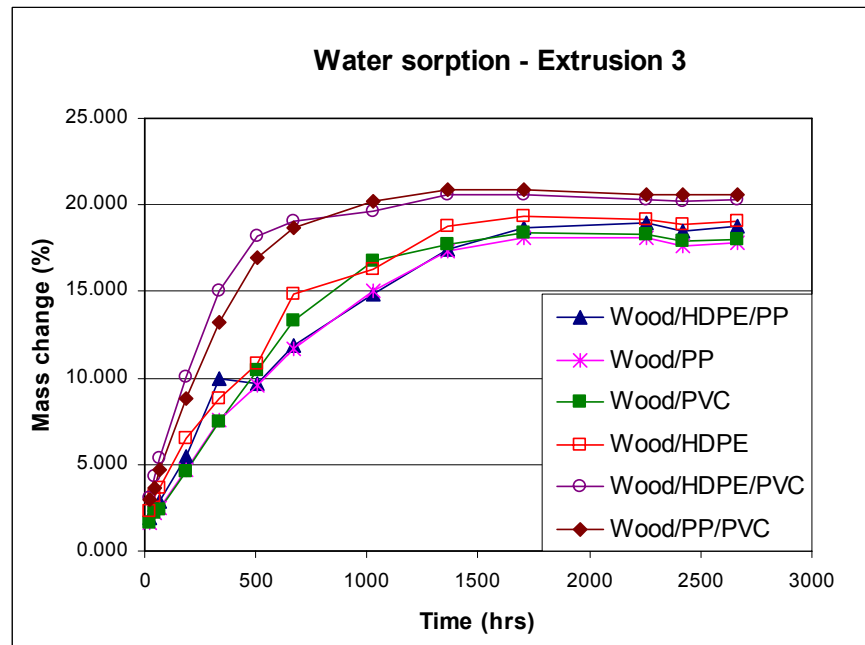
Figure 2-12 Plot of the water sorption, for the third extrusion.

31
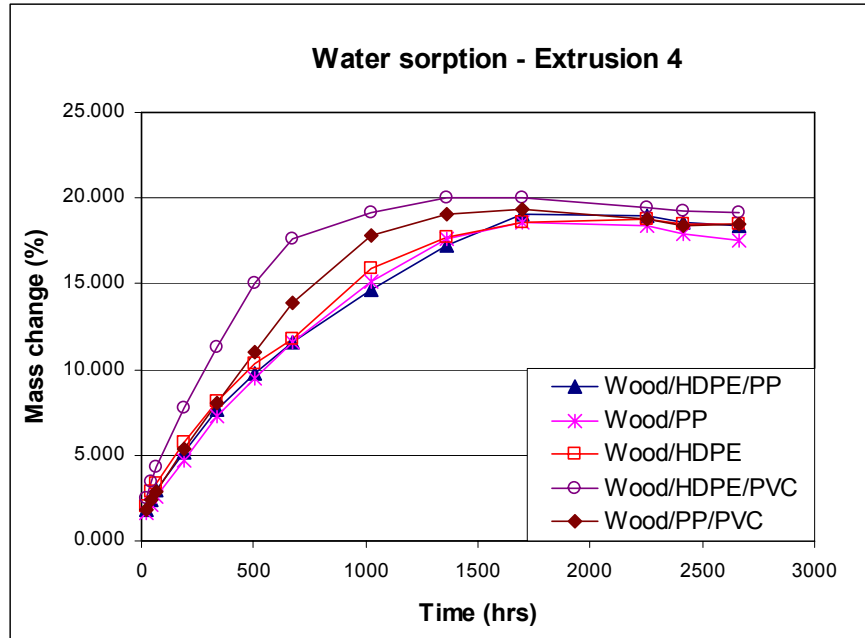
Figure 2-13 Plot of the water sorption, for the fourth extrusion.

Thickness swelling

ΔT values were calculated with the following equation:

$$\Delta T(t) = \frac{(T(t) - T_0)*100}{T_0}$$

In this equation, ΔT(t) is the percentage of thickness swelling at a given time t of immersion, T(t) is the thickness of the specimen at the time t and T_0 is the conditioned initial thickness.

Very similar observations and conclusions can be made on ΔT. Again, the samples that experienced the highest ΔT were wood/HDPE/PVC and wood/PP/PVC. The ΔT of wood/PVC was very high as well, once more demonstrating PVC blends' weakness to water. Perhpa, PVC did not adhere well to the wood and left gaps at the interface. Another explanation would be that, since PVC is denser, there is more wood flour in the

PVC-based WPC's (the composition was calculated by mass, not by volume). Besides, ΔT decreased as well when the samples underwent multiple extrusions. The results in terms of ΔT are indicated Figure 2-14 while the graphs of the other extrusions can be found in Appendix C.
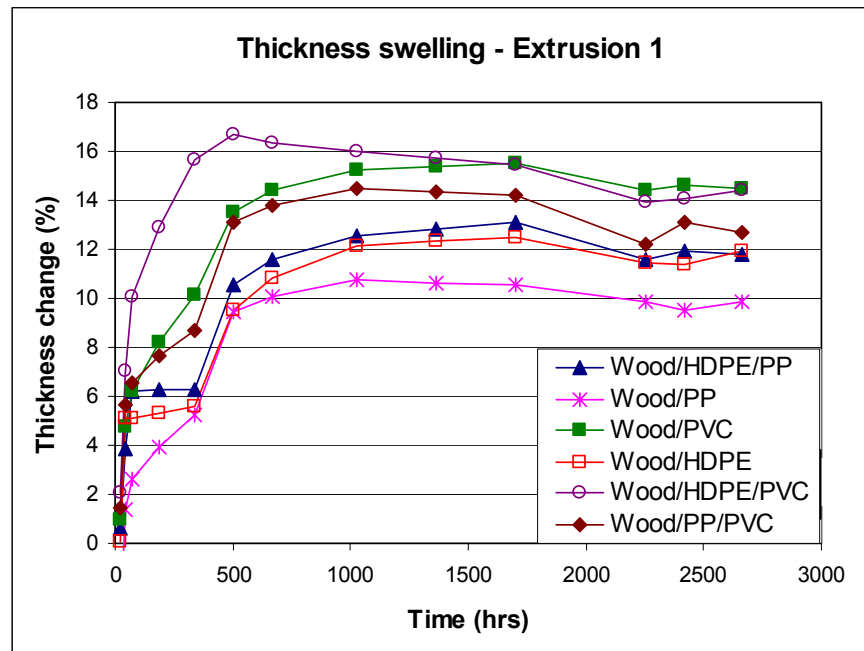
Figure 2-14 Plot of the thickness swelling versus immersion time, first extrusion.

Impact of the number of extrusions

As noticed before, the number of extrusions had an influence on the water resistance of the composites. To verify that observation, ΔW and ΔT curves were compared for each formulation in function of the number of extrusion, Figures 2-15 to 2-20. Apparently, the water resistance greatly increased between the first two extrusions, except in the cases of wood/HDPE and wood/HDPE/PP blends whose ΔW diminished less noticeably.

The plots Figure 2-15 to Figure 2-20 confirm that the additional extrusions decreased ΔW and ΔT for all the blends. The multiple processing apparently improved the structure of

the WPC's by their mixing action. Less voids, a better interfacial adhesion and more

dispersed phases might have resulted from this additional blending and improved the

water resistance of the composites.
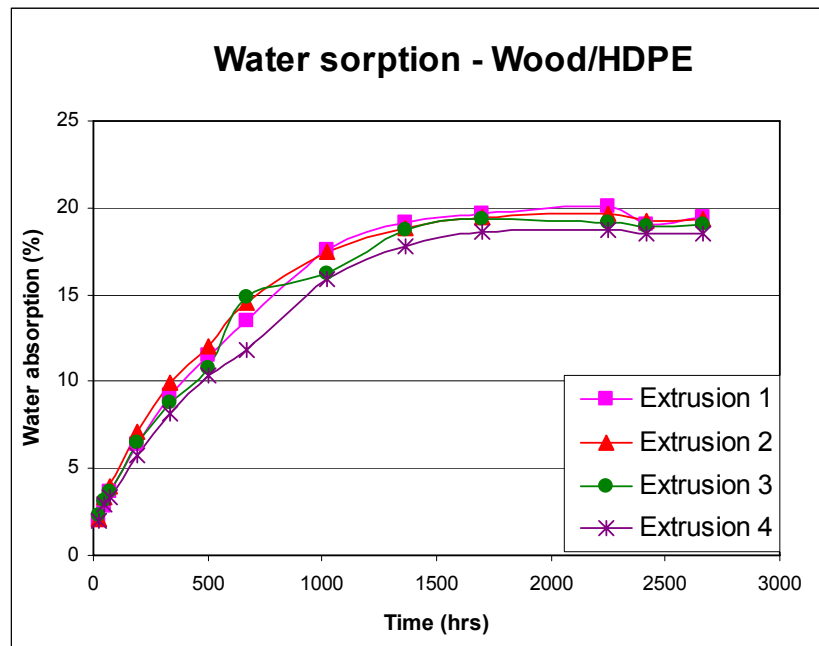
Figure 2-15 Plot of the water sorption versus the number of extrusions for wood/HDPE, after 2660 hours of immersion.
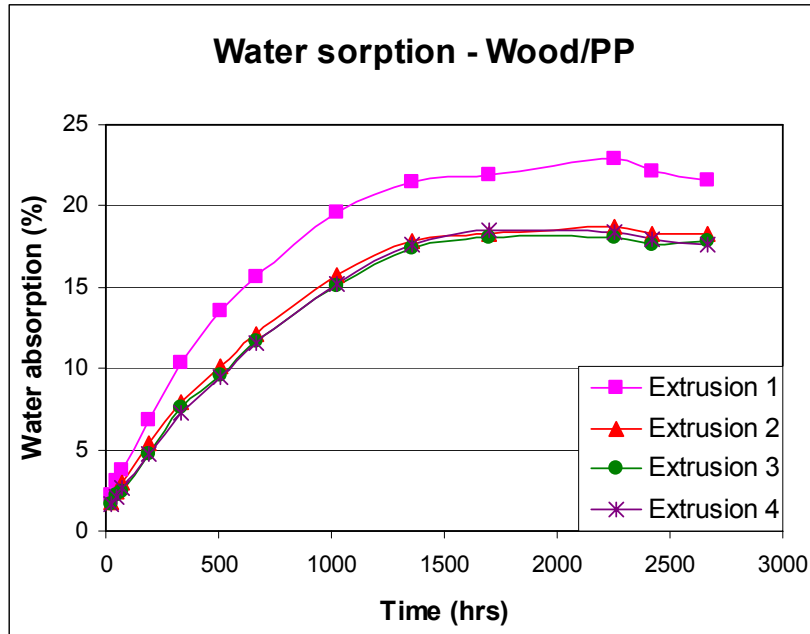
Figure 2-16 Plot of the thickness swelling versus the number of extrusions for wood/PP, after 2660 hours of immersion.
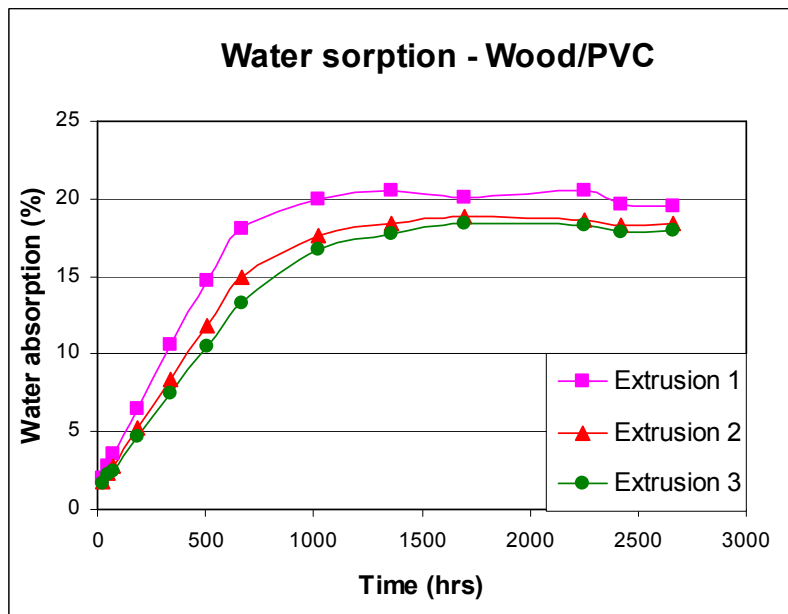
Figure 2-17 Plot of the thickness swelling versus the number of extrusions for wood/PVC, after 2660 hours of immersion.

35
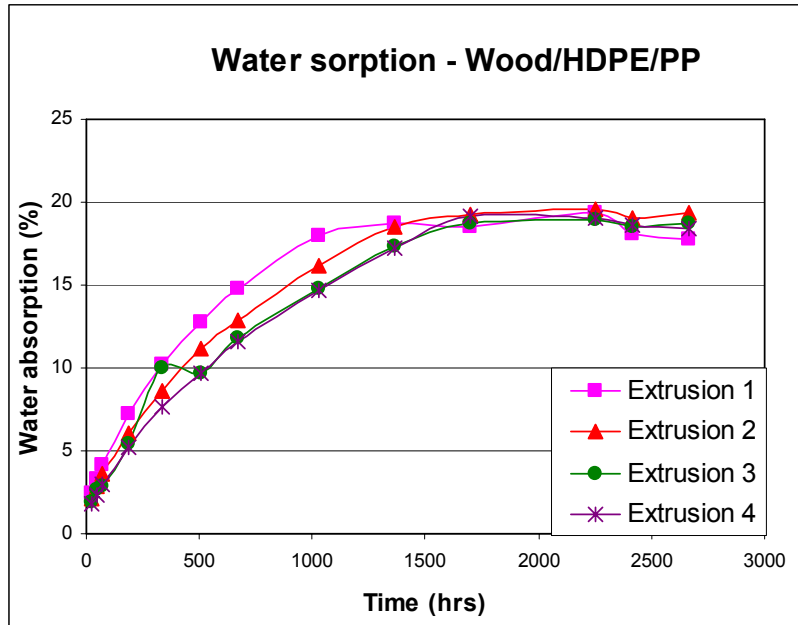
Figure 2-18 Plot of the thickness swelling versus the number of extrusions for wood/HDPE/PP, after 2660 hours of immersion.
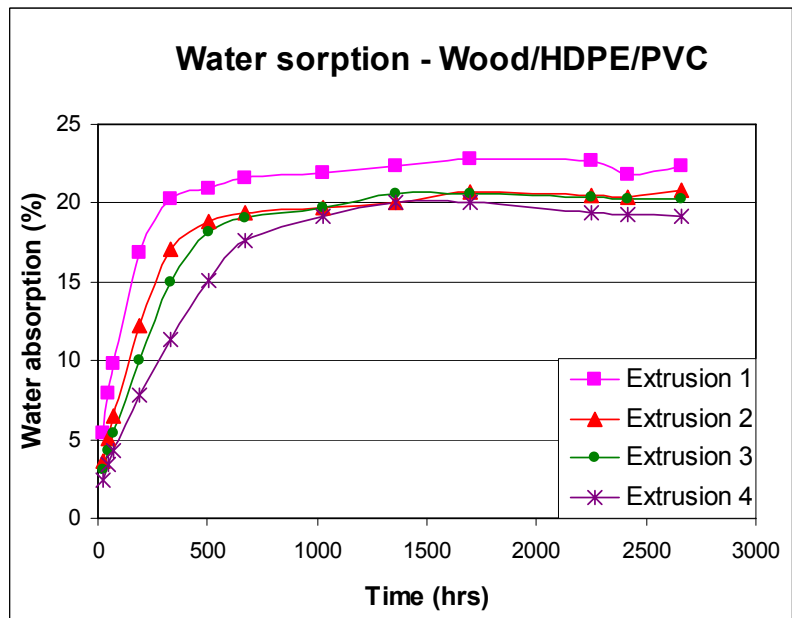
Figure 2-19 Plot of the thickness swelling versus the number of extrusions for wood/HDPE/PVC, after 2660 hours of immersion.
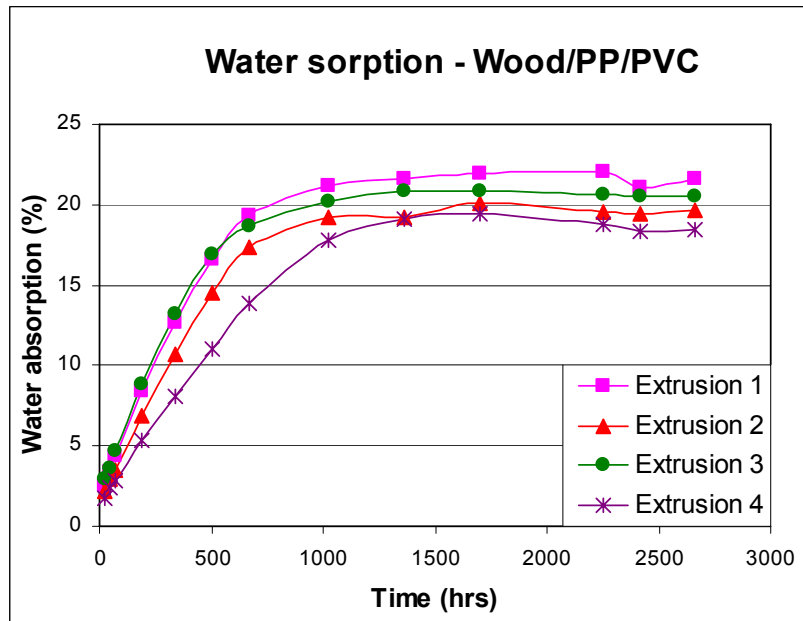
Figure 2-20 Plot of the thickness swelling versus the number of extrusions for wood/PP/PVC, after 2660 hours of immersion.

IV. Conclusion on the effect of re-processing and polymers blends on WPC's mechanical behavior

Blends containing PVC were the easier to process, stiffer and more brittle than the other blends, but their water resistance was not as effective. For its part, PP has a high T_m which made this polymer more difficult to process. Nevertheless, blends of PP were more ductile than PVC blends and presented the best water resistance. Finally, HDPE made ductile WPC's that had an average water resistance and an average processability.

Using polymer blends to create the WPC's did not show any particular disadvantage. The mechanical and physical properties observed depended on the components of the blends, not the fact that polymer blends were used. WPC's containing polymer blends often exhibited intermediate properties that depended on the blends they were made of, leaving no real objection to the use of several polymers to manufacture a WPC.

Repeated extrusions increased the stiffness, the brittleness and the water resistance of the composites. Possibly, the molecular structure of the samples was changed during these extrusions. The re-mixing impacted the structure and the morphology of the composites, certainly improving the homogeneity and reducing the occurrence of flaws and gaps. Other possibilities are that some degradation occurred, increasing the brittleness. Eventually, an increase in crystallinity cannot be excluded since the molecular flexibility of a polymer is related to X_c [27], but that assumption need to be proven. In the end, multi-processing has advantages as well as disadvantages and the future application of the processed material needs to be taken in account before applying this technique.

38

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CHAPTER III – CRYSTALLIZATION, MELTING AND OXIDATION ASPECTS

Abstract

The thermal and structural characteristics of WPC's made of polymer blends were evaluated by differential scanning calorimetry. These composites were also extruded four times to experiment extensive mixing on these products. Transition temperatures such as the melting point and the crystallization temperature were calculated, as well as the degree of crystallinity, the rate of crystallization and the oxidation induction times (OIT) of the samples. Results show that wood increased the melting point of most blends and reduced the crystallization temperature of HDPE-based composites. On the other hand, PVC diminished the melting point of PP-based blends. The different components were deemed immiscible and melted and crystallized separately. Re-mixing increased the degree of crystallinity, the half-time of crystallization and temperature of crystallization, but decreased the melting temperature, which might indicate structural degradation. Blends containing PVC experienced much higher OIT than PP or HDPE. The number of extrusions did not change the OIT of the composites tested.

I. WPC's and polymers blending issues

Polymers can be complex materials to deal with. They can be divided in two main categories: the amorphous and the semicrystalline [1][2][3][4]. Amorphous polymers are usually atactic polymers, copolymers or highly branched polymers. Their irregular structure prevents them to crystallize and melt. Instead, as they cool down they will experience a glass transition. Below their glass transition temperature (T_g), amorphous polymers are in a glassy state and become hard and brittle. Above T_g, they are in a rubbery state and soft and flexible, showing viscoelastic behavior. On the contrary, semicrystalline polymers can crystallize at a crystallization temperature (T_c). They consist of two components; one is crystalline and composed of thin lamella-shaped crystals. The other one is amorphous. The degree of crystallinity C can vary substantially from one polymer to another. As semicrystalline polymers have an amorphous and a crystalline component, they can have both T_g and T_c (the crystals will be melting and the amorphous components will be undergoing a glass transition).

Some of the most common polymers in the WPC's industry are HDPE, PP and PVC. HDPE has a linear morphology and is relatively strong. This thermoplastic polymer is highly crystalline and usually presents a T_m ranging from 128°C to 130 °C and a T_c of between 112°C and 116°C [6][7][8][13][17]. PP is a polyolefin similar to HDPE, the only difference being that on every other carbon atom in the backbone chain has a methyl group attached to it. PP is a thermoplastic that crystallizes from 112°C to 130°C and melts around 159-165°C [6][7][8][17][21]. Additionally, PVC is a vinyl polymer known for its capacity to resist both fire and water. This thermoplastic is often highly amorphous and

experiences a T_g around 81°C [20]. As the PVC used here is amorphous, this polymer will not melt but may soften to a point of viscous flow similar to melting when heated.

Most polymers are immiscible with each other and their blends will give a phase-separated solution. This kind of substance is called an immiscible blend, even if the word "blend" is supposedly reserved to miscible materials. Immiscible blends can show interesting properties. The morphology of the blend depends on the concentration of each polymer, usually showing either co-continuous or spherical shaped phases. The processing method plays also an important role on the morphology. Blend morphology is directly linked to its mechanical properties. In immiscible blends, phases are not bound very efficiently but using compatibilizers can solve this problem, improving the transfer of stress and energy throughout the blend. Properties of polymer blends mainly depend on morphology and thermal stability, for example a blend with dispersed phases will be stronger. In heterogeneous systems, the components preserve some of their individual properties because the polymers are incompatible. When the blends contain crystalline components, the crystallinity strongly influences the properties of the components [1][2][3][4][5][6][7].

Many researchers have taken interest in polymer blends of HDPE and PP. Qin et al. [8] investigated PP and linear bimodal polyethylene (LBPE) blends and showed that PP and LBPE were miscible to a certain extent and that there was no obvious separation of phases in the blend. LBPE is a new polyolefin that contains both a high-molecular-weight and a low-molecular-weight component. Good rheological properties, thermal stability and aging resistance characterize this polymer. They looked at the non-isothermal crystallization kinetics of the blends and found that the crystallization nucleation was

homogeneous, that the growth of spherulites was three-dimensional and that the crystallization mechanism of PP was hardly affected by LBPE. All DSC traces showed two crystallization peaks for the blends of LBPE/PP, indicating that two crystallizable components co-exist in the blends. Observing the influence of LBPE on the crystallinity of PP, Qin et al. found that for an 80% PP / 20% LBPE blend, the crystallinity was much higher than that of pure PP because the LBPE molecules had entered the PP crystal. On the other hand, for a 60% PP / 40% LBPE blend, the crystallinity was a little lower than that of pure PP because some PP chains dissolved in the LBPE melt.

For their part, Shanks and Li et al. [7] investigated blends of PP and different kinds of polyethylene in various studies. The polyethylenes in question were high density (HDPE), low density (LDPE), linear low density (LLDPE), very low density (VLDPE) and ultra low density polyethylene (ULDPE). Each blend contained 20% PP by mass. They used the Avrami equation to determine the crystallization rates of the blends. To determine the miscibility of the polymers, they compared the isothermal crystallization half-times ($t_{1/2}$) of the blends. When $t_{1/2}$ was the same as pure PP, they concluded that the components of this blend were immiscible. PP was found immiscible with HDPE, LDPE and VLDPE, miscible with LLDPE. With the immiscible polyethylenes, among them HDPE, the two phases of the blend crystallized independently. Under these conditions, the $t_{1/2}$ of PP was very similar to that of pure PP. In the case of LLDPE, The crystallization took place from a solution in the molten polyethylene and the crystallization rate of PP was decreased. Broad diffuse spherulites formed and PP crystallized as a homogeneous phase. They also found that the crystallization of PP occurred at varying T_c, depending on the blend's miscibility, even if the polymer always melted between 159°C and 163°C. HDPE crystallized at 112°C, which was the highest T_c

among the polyethylenes. The blend of PP/HDPE crystallized at 114.8°C and had two melting peaks at 131.1°C and 159.5°C. Several crystallization peaks were recorded for blends containing VLDPE, ULDPE or LDPE but only one for blends containing LLDPE or HDPE. In the PP/HDPE blend, PP appeared as large droplets dispersed in the HDPE melt. From the dimension of those droplets and the crystallization curves recorded, they understood that heterogeneous nucleation dominated in this blend, as well as in the other immiscible blends. Microscopy analysis showed that the bond between PP and HDPE was mechanically weak and easily penetrated. The phases were not continuous.

Martuscelli [17] also investigated the morphology and crystallization behavior of PP/HDPE blends and explained that even if these blends generally formed a multiphase system, the interphase adhesion could be sufficient to determine good properties. For some blend composition, a certain synergy existed because of interfacial effects and partial miscibility of HDPE and PP chains in the molten state. Co-crystallization was impossible because of the molecular structure differences between the polymers, and the presence of individual T_m indicated their incompatibility in the solid state. In his studies, he showed that the kinetics of crystallization of HDPE were delayed by the addition of a small amount of PP (10% by weight), and found a significant increase in the Avrami coefficient from 2.3 for pure HDPE to 3.2 for PP/HDPE (10/90), attributing this increase to a change from instantaneous to sporadic nucleation. He finally concluded that, even indirectly, PP and HDPE were immiscible but had a certain degree of compatibility in the melt.

A correctly mixed blend will have co-continuous or dispersed phases, with good interfacial adhesion to prevent voids that would weaken the blend and insure correct

stress transfer. But, mixing need to be done carefully because the heat and the shear developed during processing might damage the materials. To watch for oxidative degradation on the blends, understanding the oxidation properties of the processed materials is necessary. In 2009, Camacho and Karlsson [9] studied the oxidation and thermal stability of multi-extruded blends of recycled PP, HDPE and a blend of 20% PP / 80% HDPE. They showed that the OIT and the temperature of oxidation of the polymers and their blend decreased with the number of extrusion cycles. Because the thermal stability of the HDPE decreased with the number of extrusions, they concluded that the shear forces applied on the polymer during processing might induce the chain scission of the polymer backbone and shorten the chains. In the case of PP, however, the decrease in thermal stability was recorded until the third extrusion only. For both PP and HDPE, chain scission occurred during all the extrusions while no cross-linking nor chain branching were observed. The behavior of a blend of those two polymers, with 20% of PP, showed a synergetic tendency and two peaks appeared on the DSC curves, one for HDPE and the other for PP. The PP seemed to oxidize first and accelerate the oxidation of HDPE due to the presence of oxidation sites in the HDPE-PP interfaces. The blend appeared to be a two-phase blend.

However, concerning the oxidation of the blends, Schmidt et al. [14] compared the data obtained from three round robin tests campaigns and showed that the determination of OIT on several species of polyethylene (low and high density) were associated with a high degree of uncertainty, especially for low values (up to 70% for OIT = 3 minutes, around 15% for OIT ≥ 20 minutes).

Objectives

Even if immiscible, polymers can be mixed into useful blends. Using polymer blends to create WPC's is not common but would offer great development opportunities for the industry. Having the possibility to use polymer blends instead of pure polymers should give more manufacturing flexibility and mixed plastic extrusion of WPC's could lower the price point, open up new recovered polymer sources, which can potentially extend the range of WPC products already on the market and maybe open the doors to new applications of these products. Moreover, the use of polymer blends can find the greatest benefit within the single-stream recycling markets. In post-consumer single-stream recycling, polymers are not separated curbside, resulting in added processing costs to separate the polymers. Using several types of polymers together, without prior separation or treatment would be very economical. This project focus is to evaluate the potential of using polymer blends to manufacture WPC's and the impact of multiple extrusions on those same composites with respect to their thermal and oxidative properties

The objectives were:
- To identify the crystallization characteristics of the composites,
- To estimate the impact of processing and polymer blends on the WPC's melting point,
- To evaluate the changes in oxidative resistance of the WPC's in function of the presence of polymer blends and the number of applied extrusions,
- To determine the impact of repeated processing on those thermal properties of and look for any degradation of the structure of the composites.

II. Materials and testing methods

To study typical WPC's, common thermoplastic materials were chosen: HDPE, PP and PVC with wood floor. HDPE, PP and PVC constitute the main components of most WPC's and wood floor is easier to process and cheaper than wood fibers. As the same materials and formulations were used to tests thermal and physical, please refer to Chapter Two for the exact designation of the components used and Table 2-1 for the blends' compositions.

All the composites had to be mixed in a drum blender before being extruded into solid profiles of 38x10 mm (1.5×0.4 inches). The polymer blends without wood floor or lubricants, for their part, were blended utilizing a torque rheometer.

1. Extrusion

The same WPC's than in chapter two were investigated to determine their thermal propertes. The details of the extrusion processed can be found in the previous chapter. A 35 mm twin-screw extruder was used to process the blends. A series of four extrusions were applied on the WPC's. The samples were extruded as thin boards that were cut and granulated between each extrusion to serve as samples for the DSC analysis or to be re-extruded. As PP has the highest T_m, 160 ºC, the die and extruder temperatures of the extruder were set on 180ºC. At this temperature, all the blends could melt without inducing wood degradation. The screws rotated at 20 rpm for the first extrusion, and 10 rpm for following three extrusions due to the higher feeding capacity of the pelleted material.

2. Thermal transitions and crystallization

The non-isothermal crystallization of the WPC's was examined and T_c, T_m, C and $t_{1/2}$ were determined by using DSC. After each extrusion, some of the boards were ground into powder with a 20 mesh screen and conditioned in hermetic containers to protect them against moisture. Then, they were placed in 40μl aluminum crucibles, those pans were sealed and the samples could be tested in the DSC. Each pan contained approximately 5 mg of powdered material. Three samples were scanned for each specimen from each extrusion.

Two cycles of heating and cooling were applied on the specimens, with a starting temperature of 40ºC. The samples were heated up to 220ºC, kept at this temperature for 3 minutes and then cooled and heated again at a heating rate of 20ºC/min, creating seven thermal segments as shown Table 3-1. In these seven segments, only two were meaningful: the third and the fifth. The exothermic reaction due to the crystallization of the samples appeared on the third segment, when the temperature cooled down form 220 ºC to 40 ºC. The second cooling, segment 7, was not used because the multiple temperature changes could have affected the structure of the blend and degraded it. On the fifth segment the samples were heated and melted. Two heating cycles were performed to first erase the thermal history of the samples (in segment #1) and obtain more accurate results on segment #5, when the next endothermic reaction occurred.

Table 3-1 Heating segments used on the differential scanning calorimter (DSC)

	Seg. 1	Seg. 2	Seg. 3	Seg. 4	Seg. 5	Seg. 6	Seg. 7
Start temp.	40ºC	Isotherm – 3 min	220ºC	Isotherm – 3 min	40ºC	Isotherm – 3 min	220ºC
End temp.	220ºC		40ºC		220ºC		40ºC
Heating rate	20ºC/min		20ºC/min		20ºC/min		20ºC/min

T_c and T_m correspond on the curve to the peak heat flow recorded by the DSC, as shown on Figure 2. Even if T_g could theoretically be determined as well, this thermal transition did not appear during this investigation because of the crystalline nature of most blends. Even tests on PVC, which is amorphous, did not show any recognizable glass transition.

The degree of crystallinity X_c was evaluated using the heat of fusion and according to the following formula [24][25];

$$X_c = \frac{\Delta H}{\Delta H_{100\%}} . 100$$

In this equation, X_c represents the percentage of crystallinity of the semicrystalline material, ΔH is the measured heat of fusion in J/g , $\Delta H_{100\%}$ is the heat of fusion of 100% crystalline material. The following enthalpy values were provided by Mettler Toledo and used for the thermoplastics: $\Delta H_{100\%}$ of HDPE = 293.6 J/g and $\Delta H_{100\%}$ of PP = 207.1 J/g.

3. Oxidation Induction

Determination of the thermal oxidation behavior of the wood-filled and unfilled polymers and there blends were conducted according to ASTM D 3895-02 requirements and carried out on a DSC. Three samples of 6 mg ± 0.1 were run for each sample of each

series of extrusions, again with the ground material from the extruded boards. These samples were placed in unsealed aluminum pans.

Like illustrated on Figure 3-1, nitrogen and oxygen were alternatively used on the DSC. The samples of were heated in a nitrogen environment, which is an inert gas, up to 200°C. After that, the gas was switched from nitrogen to oxygen and the temperature of 200°C was maintained. The time when the gases switched was recorded and served as point zero time (t_0) for the experiment. When the oxidative reaction occurred, the test was then terminated.

The recorded baseline before the oxidative exotherm needs to be extended while the steepest linear slope of this exotherm is extrapolated and intercepts the extended baseline at the interception time t_i. The OIT is defined as the time measured from point zero time t_0 to this intercept point t_i:

$$OIT = t_i - t_0.$$
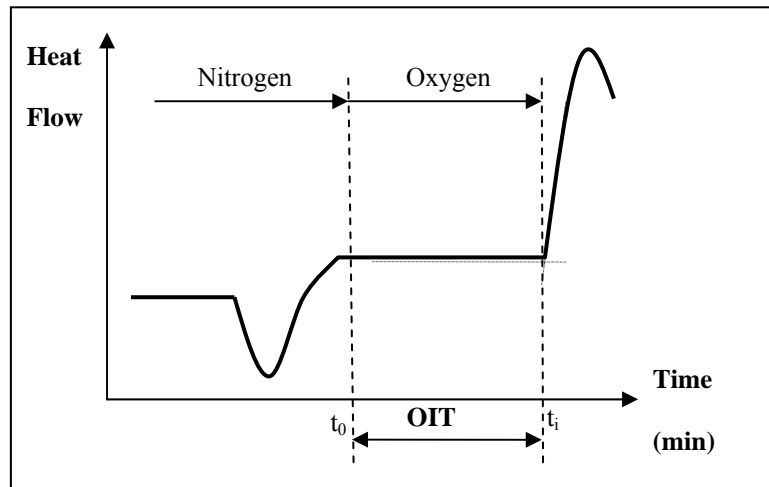
Figure 3-1 Principle sequence of OIT according to ISO 11357-6 (Schmitt et al. [10]).

III. Thermal and morphological response of the tested WPC's

1. Thermal transitions and crystallization

The curves presented are representative curves. All curves of a same set of tests (corresponding to an extrusion) are very similar, their general shapes are identical. T_m and T_c were evaluated when the heat flow peaks occurred, the endothermic reaction corresponding to the melting and the exothermic reaction corresponding to the crystallization of the blends. These calculations seem very accurate since the coefficients of variation between the results were remarkably small, except when the degrees of crystallinity were evaluated. This is mostly due to the difficulties to identically draw a straight baseline for all the blends.

Neat polymers and polymer blends

Table 3-2 Thermal properties of neat polymers and polymer blends.

	Crystallization temperature		Melting temperature				Degree of Crystallinity	
	T_c (°C)	% cov	T_{m1} (°C)	% cov 1	T_{m2} (°C)	% cov 2	X_c(%)	% cov
HDPE	115.2	0.25	129	0.22	/	/	44.40	7.10
PP	106.7	0.07	/	/	159.4	1.69	35.70	4.90
HDPE/PP	114.1	1.35	130.8	2.01	160.4	2.0	39.64	39.64
HDPE/PVC	115.2	0.92	130.2	0.94	/	/	23.11	15.74
PP/PVC	109.9	2.07	/	/	155.5	0.08	20.15	11.12
HDPE/PP /PVC	114.2	0.92	129.3	0.10	156.8	0.77	26.71	4.50

In Table 3-2, the term "cov" corresponds to the coefficient of variation between the results of each sample of a blend. Peaks occurred around 115°C for virgin HDPE and 107°C for PP (Table 3-2 and Figure 3-3). These T_c's are backed up by the literature [6][7][13][14] where authors usually found temperatures between 112°C and 115°C for HDPE and 106°C for PP. The T_c's of polymer blends and WPC's containing HDPE were very close to the T_c of HDPE: 114.1°C for HDPE/PP and 114.2°C for HDPE/PP/PVC for example (Figure 3-3). In the case of the HDPE/PVC blend, the same temperature as virgin HDPE was found, 115.2°C. PP apparently tended to reduce the T_c of HDPE by 1%; PVC did not affect the T_c of HDPE.
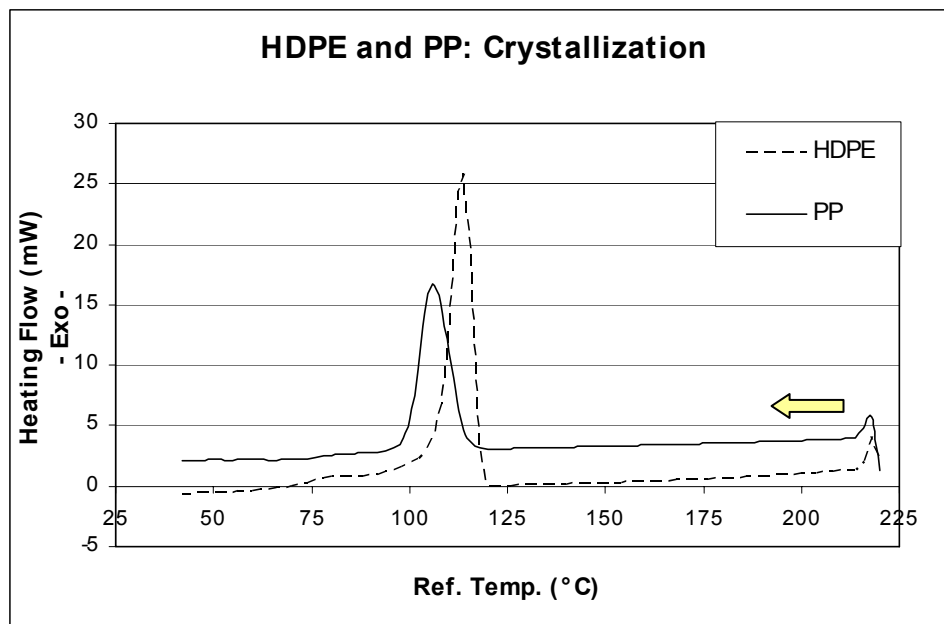
Figure 3-1 Crystallization of neat polymers.
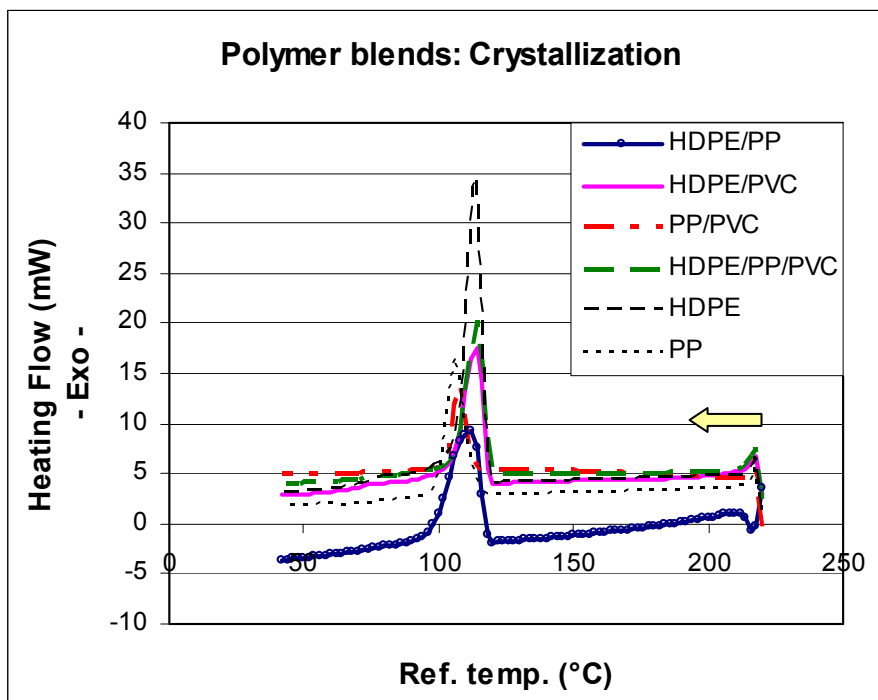
Figure 3-2 Crystallization of polymer blends during their cooling in DSC.

Concerning the melting behavior, the tests on virgin HDPE and PP displayed in Figure 3-4 revealed T_m's of 129°C for HDPE and 159°C for PP, confirmed by several authors [6][7][13][14] who usually found temperatures around 130°C for HDPE and 160°C for PP. Blends containing HDPE melted around the T_m of this polymer while blends that contained PP melted around that of PP (Figure 3-5).
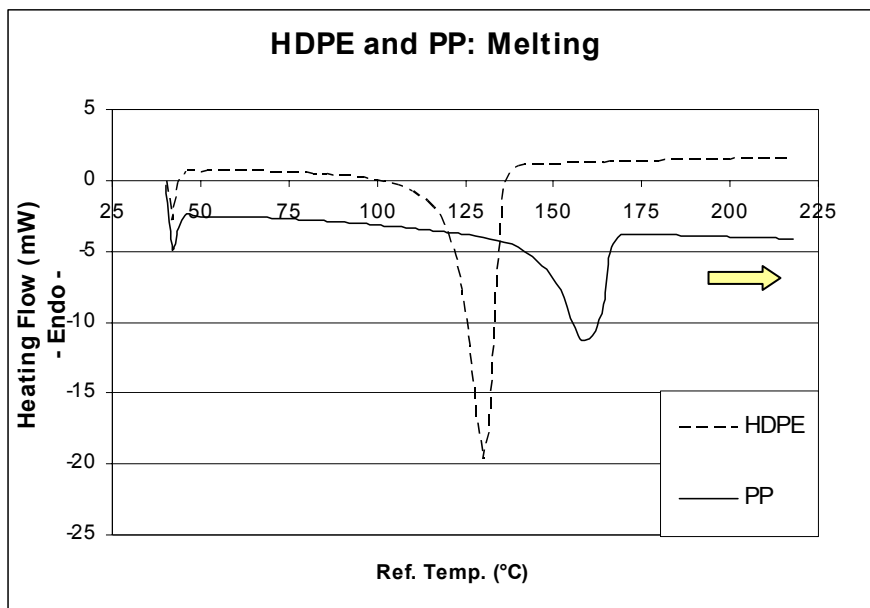
Figure 3-3 Melting of neat polymers.
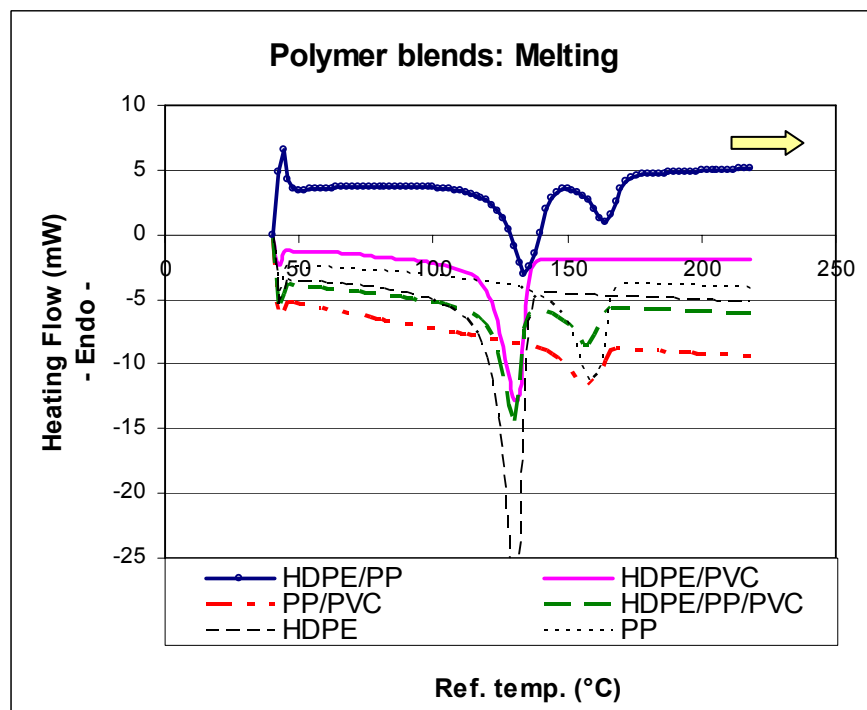
Figure 3-4 Melting of polymer blends during their heating in DSC.

Wood-plastic composites

- Temperature of crystallization

For the HDPE-based composites in Table 3-3, after the first two extrusions, adding wood to the polymer blends reduced T_c by approximately 4°C. For the next extrusions, this reduction in T_c diminished greatly. The difference between the T_c's of the polymer blends and the WPC's almost disappeared. Wood appeared to have an impact on the crystallization of HDPE-based blends. When the number of extrusions increased, this impact diminished, possibly because of the degradation of the material's structure and an alteration of the wood or the polymers.
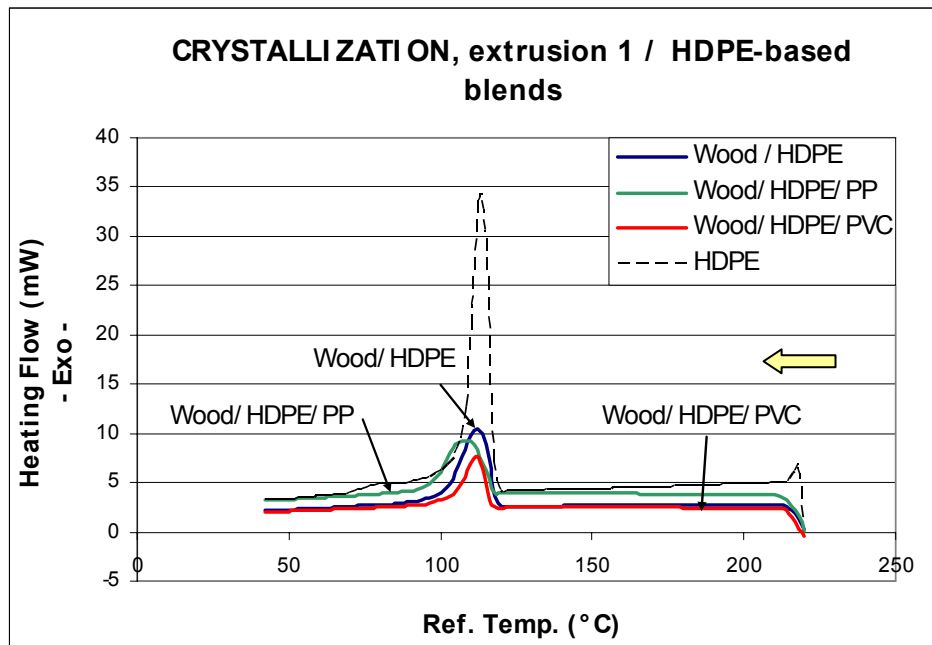
Figure 3-5 Crystallization of HDPE-based composites after one extrusion.

56

When PP was a component, the addition of wood had a different impact on the crystallization of the blends, as shown in Table 3-4. In the case of wood/PP composites, adding wood to the PP increased its T_c. For the wood/HDPE/PP blend, concerning the two first extrusions, T_c was closer to the temperature of PP. For the next couple of extrusions, T_c was closer to the temperature of HDPE. In fact, for the extrusions number 1 and 2, T_c was between those of PP and HDPE. The T_c of the wood/PP/PVC blend regularly increased after each extrusion. For the two first extrusions, T_c was smaller than that of PP/PVC but higher than that one of PP alone. For the third and fourth extrusions, T_c became almost the same as that of PP/PVC.
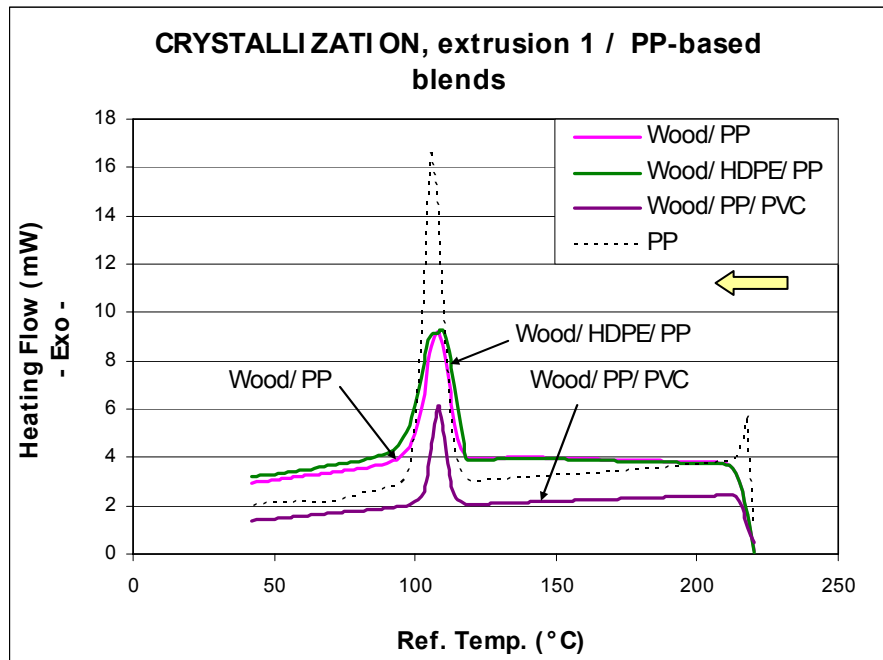
Figure 3-6 Crystallization of PP-based composites after one extrusion.

On one hand, the blends of HDPE/PP and PP/PVC crystallized at a higher T_c than PP, which could mean that PVC increased T_c and HDPE/PP crystallized at HDPE's T_c. But, on the other hand, T_c was also increased by the addition of wood (contrarily to HDPE-based composites) as explained earlier, except in the case of wood/PP/PVC. This proves that PP's crystallization behavior changed in the presence of wood or PVC, and in a different way than HDPE. Besides, increasing the number of extrusions always increased the T_c of the WPC's in the cases of both HDPE and PP based blends.

In the literature, several authors pointed out that the introduction of cellulose fiber in a PP melt changed the morphology and the crystallization behavior of this melt [28][29]. The cellulose fibers formed a larger surface for the crystals to nucleate, helping the crystallization. With enough nucleation density, the nucleating crystals could invade one another and grow in a radial direction from the cellulosic surface. As a result, a particular form of interphase was created: a transcrystalline layer. Possibly, T_c increased here for PP-based composites because the wood floor helped the nucleation, leading crystallization to happen earlier.

Table 3-3 Crystallization temperatures for HDPE-based WPC's tested in DSC.

	Crystallization temperature T_c (°C) for HDPE-based blends and composites					
	HDPE	wood/HDPE	HDPE/PP	wood/HDPE/PP	HDPE/PVC	wood/HDPE/PVC
Extrusion 1	115.2	111.8	114.1	109.7	115.2	111.6
% cov	0.25	1.01	1.35	1.03	0.92	1.09
Extrusion 2	-	110.4	-	109.7	-	113.0
% cov	-	1.86	-	2.18	-	2.04
Extrusion 3	-	114.5	-	113.7	-	114.4
% cov	-	0.05	-	1.00	-	0.05
Extrusion 4	-	114.6	-	113.2	-	114.4
% cov	-	0.00	-	0.94	-	0.10

Table 3-4 Crystallization temperatures for PP-based WPC's tested in DSC.

	Crystallization temperature T_c (°C) for PP-based WPC's					
	PP	**wood/PP**	**HDPE/PP**	**wood/HDPE/PP**	**PP/PVC**	**wood/PP/PVC**
Extrusion 1	106.7	109.0	114.1	109.7	109.9	107.6
% cov	0.07	1.09	1.35	1.03	2.07	1.10
Extrusion 2	-	110.3	-	109.7	-	108.4
% cov	-	2.04	-	2.18	-	0.05
Extrusion 3	-	112.4	-	113.7	-	110.3
% cov	-	0.00	-	1.00	-	0.05
Extrusion 4	-	112.5	-	113.2	-	110.4
% cov	-	0.00	-	0.94	-	0.05

- <u>Degree of crystallinity X_C</u>

When observing the results found for X_c, it appears that X_c was almost proportional to the amount of HDPE and PP. For example, in the wood/PE blend, there was 40% of HDPE. That same HDPE had a X_c of about 44.4%: 40% * 44.4% = 17.8 %, which is close to the degrees shown for the four runs.

The same observation could be made for the other blends, coming down to the following generalized formula:

$$X_{cpol}(\%) = Conc_{pol} * X_{c100\%\_pol}$$

In this formula, X_{cpol} would represent the crystallinity due to a polymer in particular, either PP or HDPE, $Conc_{pol}$ would be the concentration of this polymer in the blend and $X_{c100\%\_pol}$ would correspond to the crystallinity found for the virgin polymer.

Table 3-5 Average degrees of crystallinity of the WPC's tested in DSC.

	Degrees of crystallinity X_c						
	HDPE	PP	wood/HDPE	wood/PP	wood/HDPE /PP	wood/HDPE /PVC	wood/PP /PVC
Extrusion 1	44.4%	35.7%	19.5%	15.6%	15.1%	8.6%	8.2%
% cov	7.07	4.90	6.28	7.12	3.38	4.13	7.43
Extrusion 2	-	-	18.2%	13.8%	14.9%	8.6%	7.7%
% cov	-	-	7.11	11.83	8.85	11.03	2.50
Extrusion 3	-	-	18.9%	15.9%	13.5%	9.6%	6.9%
% cov	-	-	6.58	4.95	1.52	5.84	11.64
Extrusion 4	-	-	22.3%	16.2%	15.2%	10.2%	8.6%
% cov	-	-	5.46	8.47	11.53	9.14	3.89

On figure 3-8, X_c apparently increased slightly from an extrusion to another but that change is not obvious. Keeping in mind that the measure of X_c can lack of accuracy and that the coefficient of variability associated vary from 3% and 12% (Table 3-5), the real impact of the extrusions on the crystallinity is still doubtful.
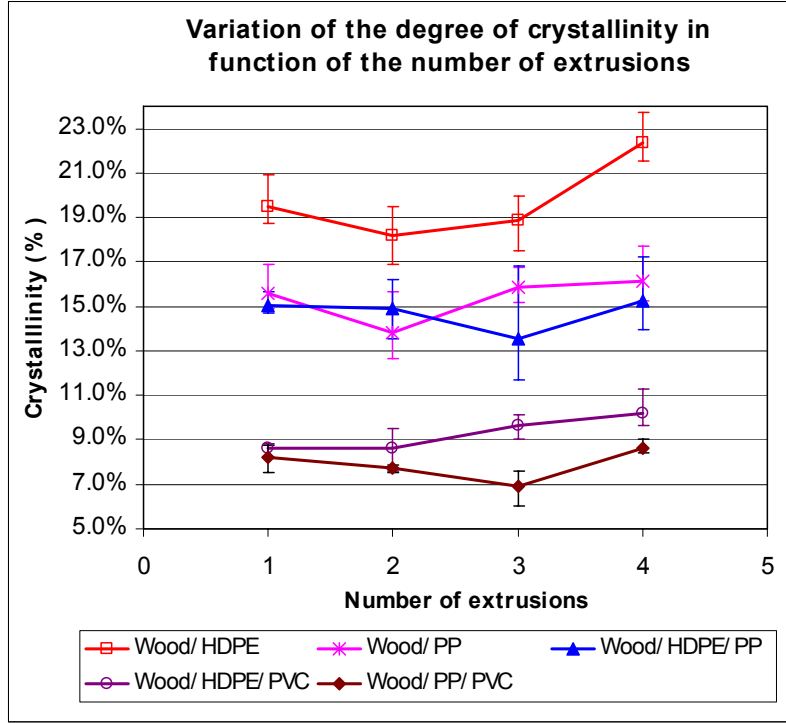
Figure 3-7 Degree of crystallinity versus number of extrusions.

- Half time of crystallization $t_{1/2}$

The half time of crystallization $t_{1/2}$ is a measure of the crystallization rate and used by many authors [6][8][22][23], represents the length of time required for a blend to complete 50% of the crystallization, corresponding to a relative crystallinity X(t) of 50%. The relative crystallinity was calculated in function of the time t with this formula [1][6][8][22][23]:

$$X(t) = \frac{\int_{t_0}^{t} \frac{dH_c}{dt}.dt}{\int_{t_0}^{t_\infty} \frac{dH_c}{dt}.dt} * 100$$

In this equation, X(t) is the percentage of completion of the crystallization, t_0 and t_∞ represent respectively the onset and end times of the crystallization and dH_c/dt is the rate of heat evolution. After plotting X(t), $t_{1/2}$ was calculated.

61

Table 3-6 Average times of half crystallization of the WPC's tested in DSC.

	Half times of crystallization $t_{1/2}$ (in seconds)						
	HDPE	PP	Wood/HDPE	Wood/PP	Wood/HDPE /PP	Wood/HDPE /PVC	Wood/PP /PVC
Extrusion 1	275.0	321.6	305.3	315.6	309	309.8	323.0
% cov	0.21	0.26	0.23	0.50	0.08	0.49	0.72
Extrusion 2	-	-	306.8	310.0	309.9	307.7	321.2
% cov	-	-	0.33	0.02	0.69	0.66	0.56
Extrusion 3	-	-	302.9	307.1	304.0	304.5	318.6
% cov	-	-	0.15	0.16	0.53	0.21	0.13
Extrusion 4	-	-	302.5	306.2	303.5	304.3	319.1
% cov	-	-	0.15	0.36	0.28	0.19	0.13

$t_{1/2}$ increased greatly when wood was added to HDPE but decreased when wood was mixed with PP, except in the case where PVC was also in the blend. PVC apparently increased the time of crystallization as well, or in other terms, the blends took more time to crystallize in the presence of PVC (and wood in the case of HDPE).

Interestingly, $t_{1/2}$ decreased of a few seconds after every extrusion. Thus, not only the repeated extrusions seem to have increased the degree of crystallinity but they also reduced the time needed to crystallize. Extruding apparently facilitated crystallization.
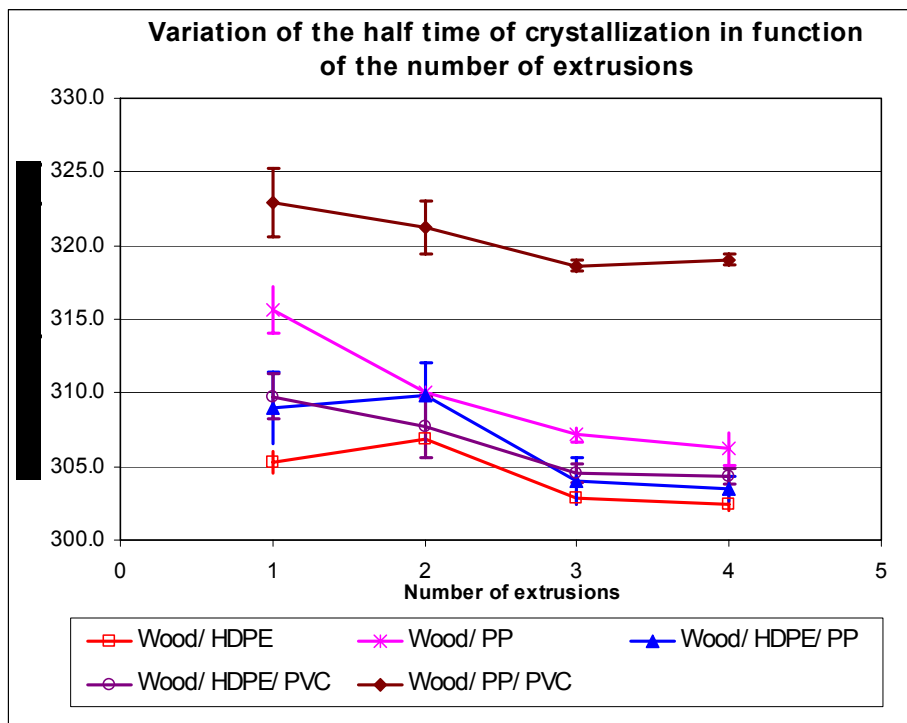
Figure 3-8 Half time of crystallization versus number of extrusions.

- Melting point

Wood/HDPE/PP, HDPE/PP/PVC and HDPE/PP blends showed two endothermic peaks because the blends were immiscible and the phases of PP and HDPE did not melt at the same time. The first heating flow peak occurred at the T_m of HDPE, around 130°C. The second peak occurred at the T_m of PP, around 160°C.
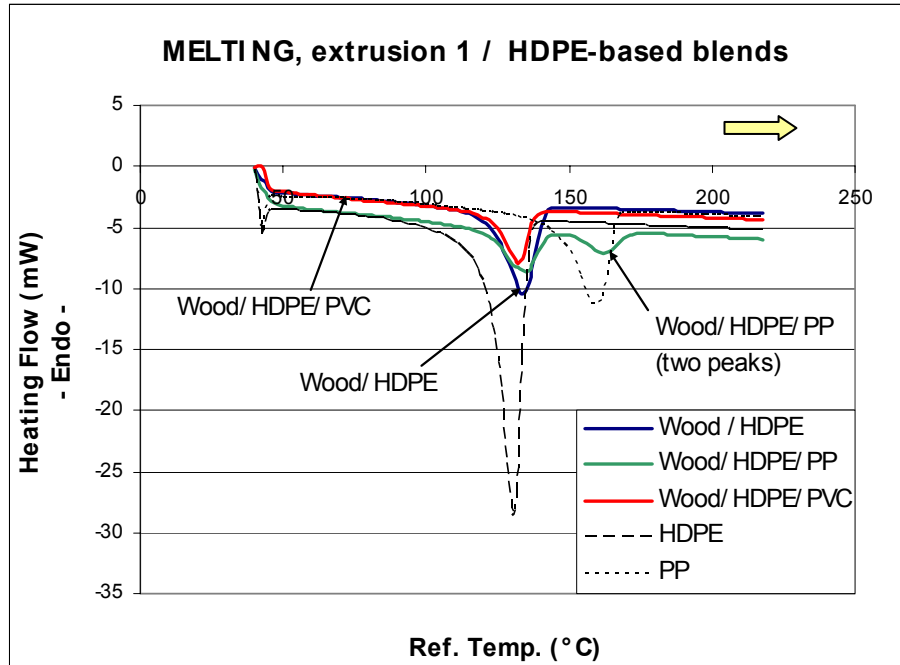
Figure 3-9 Melting of HDPE-based composites after one extrusion.
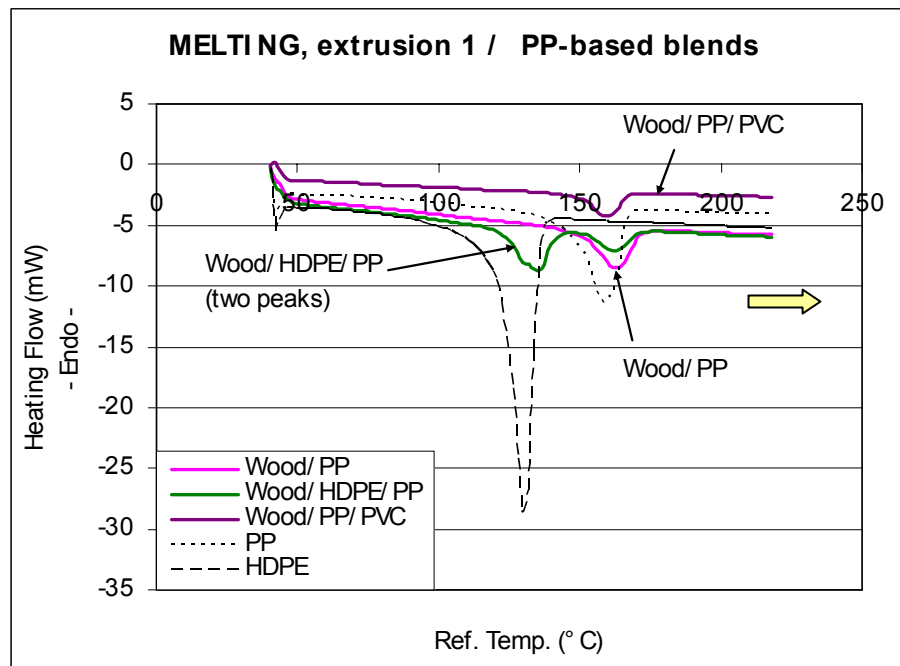
Figure 3-10 Melting of PP-based composites after one extrusion.

Composites containing HDPE as a component were compared in Table 3-7. In the cases of wood/PE and wood/PE/PVC blends, when compared to the temperature of the associated polymer blends, T_m increased for the two first extrusions (+6°C for wood/PE and +2°C for wood/HDPE/PVC) and decreased for the last extrusions. Wood/PE melted at a higher temperature than HDPE, but the difference diminished when the number of extrusions increased. Wood/HDPE/PP also showed variations of T_m when the number of extrusions increased: for the first two extrusions, this temperature increased but for the last extrusions T_m decreased and settled around that of PP and HDPE.

Table 3-7 Melt temperature of the HDPE-based WPC's tested in DSC.

	Melting point T_m (°C) for HDPE-based WPC's							
	HDPE	wood/HDPE	HDPE/PP		wood/HDPE/PP		HDPE/PVC	wood/HDPE/PVC
Extrusion 1	129.0	134.2	130.8	160.4	133.0	161.1	130.2	132.4
% cov	*0.22*	*0.86*	*2.01*	*2.04*	*0.78*	*0.63*	*0.94*	*0.92*
Extrusion 2	-	136.2	-	-	133.6	162.3	-	132.4
% cov	-	*0.89*	-	-	*1.50*	*0.68*	-	*0.85*
Extrusion 3	-	132.1	-	-	130.4	160.5	-	131,0
% cov	-	*0.90*	-	-	*0.86*	*0.69*	-	*0.84*
Extrusion 4	-	131.3	-	-	130.9	159.6	-	129.6
% cov	-	*0.04*	-	-	*0.79*	*0.06*	-	*0.09*

Composites containing PP as a component were compared in Table 3-8. In the case of wood/PP blend, the addition of wood to the polymer seemed to increase T_m but with increasing extrusions, the temperature difference lessened. For wood/PP/PVC, T_m was higher than that of PP/PVC and closer to PP's T_m. PVC seemingly diminished the T_m of PP when those polymers were mixed, but adding wood eventually increased T_m.

When the number of extrusions increased, T_m decreased and the effect of wood became less important and the T_m of the wood/PP/PVC blend got closer to the one of PP/PVC.

Table 3-8 Melting points of the PP-based WPC's tested in DSC.

	Melting point T_m (°C) for PP-based WPC's							
	PP	wood/PP	PE/PP		wood/HDPE/PP		PP/PVC	wood/PP/PVC
Extrusion 1	159.4	162.3	130.8	160.4	133.0	161.1	155.5	159.7
% cov	*1.69*	*0.69*	*2.01*	*2.04*	*0.78*	*0.63*	*0.08*	*1.25*
Extrusion 2	-	161.7	-	-	133.6	162.3	-	160.2
% cov	-	*0.89*	-	-	*1.50*	*0.68*	-	*0.67*
Extrusion 3	-	161.0	-	-	130.4	160.5	-	158.4
% cov	-	*1.42*	-	-	*0.86*	*0.69*	-	*0.77*
Extrusion 4	-	160.1	-	-	130.9	159.6	-	157.0
% cov	-	*0.70*	-	-	*0.79*	*0.06*	-	*0.75*

Synthesis on the effects of repeated extrusions on the crystallization

The Table 3-9 synthesizes the results obtained from DSC testing of the WPC's and are related to the crystallization mechanisms of the composites.

Table 3-9 Synthesis of the impact of the number of extrusions of the crystallization parameters of the WPC's (↑ indicates an increase, ↓ indicates a decrease)

	Wood/HDPE	Wood/PP	Wood/HDPE/PP		Wood/HDPE/PVC	Wood/PP/PVC
T_c	↑	↑	↑		↑	↑
X_c	↑	↑	-		↑	-
$t_{1/2}$	↓	↓	↓		↓	↓
T_m	↓	↓	↓	↓	↓	↓

With T_c increasing, and since crystallization is an exothermic reaction that doesn't require any energy absorption to occur, crystals can form earlier in time. The increase in X_c clearly indicates that more crystals have been formed after several extrusions, except in the cases of wood/HDPE/PP and wood/HDPE/PVC where no increase is apparent.

Moreover, $t_{1/2}$ decreased for all the blends, showing that the number of extrusions decreased the time of crystallization, or in other words, increased the crystallization rate. The rate of crystallization is known to show strong temperature dependence. Usually, a

decrease in T_m is believed to increase the rate of crystallization [4]. Also, a decrease in the melting point might indicate smaller crystals, meaning that crystallization should be facilitated.

These parameters agree on the fact that extensive mixing helped the crystallization and increased the crystallinity. This increase might be due to the formation of particles of smaller size. Possibly, extensive mixing dispersed better the wood flour within the composite and extended the contact surface of the wood with the polymers. This extended surface might have sustained the nucleation and growth of crystals. Besides, more transcrystalline layers might have be created during mixing, again increasing the crystallinity of the composites [30-31].

2. Oxidation Induction Time (OIT)

The OIT is the time taken by a material to begin an exothermic oxidation and degrade. The tests evaluate the changes induced by different treatments on the specimen's OIT and determine wether the repeated extrusions reduced or increased the material's resistance to oxidative decomposition. An increased OIT means that the material becomes more stable and will need more time to degrade [15][26][27].

All formulations were tested but the wood/PVC samples did not show any oxidation peak, so no OIT was recorded for this blend. When the number of extrusions applied to a sample increased, no obvious drop in the times of oxidation was noted, which indicates that the samples did not particularly degrade after these four extrusions, at least in terms of resistance to oxidation (see Figure 3-12 and Table 3-10). Nevertheless, the high coefficients of variation introduce some uncertainty about the influence of the repeated

extrusions, especially for composites containing PP or HDPE whose OIT are very short. Schmitt et al. did several investigations on the determination of OIT and found that the obtained data often showed a certain degree of variation [10][15].

Table 3-10 Oxidation Induction Times (OIT) obtained by DSC.

		wood/HDPE	wood/PP	wood/HDPE/PP	wood/HDPE/PVC	wood/PP/PVC
Extrusion 1	Average OIT (min)	2.77	1.16	2.90	22.20	4.20
	% cov	13.31	28.64	8.88	7.78	7.63
Extrusion 2	Average OIT (min)	3.98	1.29	1.12	25.94	6.06
	% cov	16.07	23.87	17.50	5.77	17.20
Extrusion 3	Average OIT (min)	3.22	1.91	2.48	21.32	6.02
	% cov	27.29	20.95	37.21	4.59	2.26
Extrusion 4	Average OIT (min)	2.68	0.72	1.53	25.17	4.81
	% cov	30.92	28.61	23.89	6.54	3.31

Whereas the blend of wood/PVC did not show any oxidation peak during the tests, when polymers blends of PVC and HDPE were used in the WPC's, the samples exhibited a peak and recorded longer OIT than the others WPC's. The longest OIT were found for wood/HDPE/PVC (between 15 to 20 minutes more than for the other blends). Here, PVC-based composites exhibited a better resistance to oxidation, which could make them more reliable than the other composites in an oxidative environment.

Blends of HDPE seemed to have a slightly longer OIT than that of PP. No obvious diminution of the different samples' OIT was noticed when several extrusions were

applied, meaning that the WPC's did not change the reaction to oxidation of the composites. This last observation might be interesting for recycling purposes.
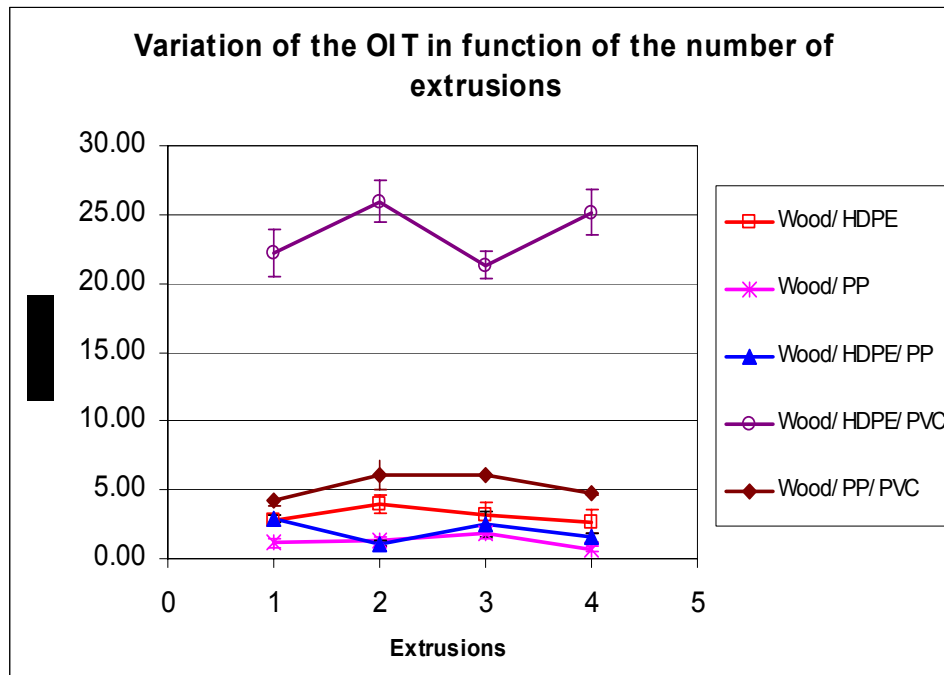
Figure 3-11 Oxidation induction times in function of the number of extrusions.

IV. Conclusion on the effects of mixing and polymer blends on WPC's structural and thermal properties

Even if PVC and wood neither melt nor crystallize, they still influence the thermal behavior of the other elements. The WPC's components being immiscible, HDPE and PP melted and crystallized separately. Repeated extrusions seemed to increase X_c and T_c, but decrease the T_m and $t_{1/2}$. In other words, processing apparently facilitated crystallization. The increase in X_c is a significant change of the structure of the blends and must be overseen because it might harden the composites and increase their brittleness.

In comparison with the composites containing PP or HDPE, blends of PVC showed the longest OIT. Moreover, multi-processing did not change the OIT of the composites tested, meaning that apparently, recycling those materials should prove possible without degradation. That said, the poor accuracy of the results in terms of OIT must be remembered. After more extrusions cycles, degradation might take place but no proof of that potential damage could be found during this investigation. Others researchers [9] found proof of increased oxidative degradation after repeated processing on PP, HDPE and their blend.

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CHAPTER FOUR – CONCLUSIONS

Composites made of wood and thermoplastics have been tested mechanically, physically and thermally to determine the impact of extensive mixing and the introduction of polymer blends on the structure and the macroscopic behavior of these WPC's. Four extrusions were applied on the composites in order to create additionnal blending and try to improve the components dispersion. These repeated extrusions on the WPC's had impacts on the structure of the composites in seevral ways. First, they slightly increased the MOE and the MOR of the tested samples. They also decreased the capacity of deformation of those samples, leading to more brittle specimens. Brittle materials are characterized by a low ductility and break suddenly, leaving these products potentially more dangerous than ductile materials. The increase in the brittleness is a serious issue that needs overseeing and might interfere with a WPC's usefulness. A lifetime after which a WPC cannot be recycled anymore because this composite would get too brittle might even be defined.

During thermal testing, the crystallization was apparently being favored by the repeated extrusions and extensive mixing: X_c increased while $t_{1/2}$ decreased. The additional blending action probably helped the dispersion of the polymers and the wood flour, possibly improving the homogeneity of the blends and insure a better adhesion of the components to one another. This increased adhesion would have developed better stress tansfer, thus strenghening the composites. Improved blending could also have eliminated voids and increased the overall water resistance. However, another consequence of the crystallinity is the brittleness of the material. If the recorded increase in brittleness might

be due to structural degradation caused by repeated extrusions, it is also possible that the increase in crystallinity could have made the composites more brittle. The relationship between crystallinity, strength and brittleness is not completely clear but the crystallinity is believed to increase the brittleness and the stiffness in semicrystalline polymers.

During oxidation induction testing, the number of extrusions was not a factor in the OIT, meaning that extruding did not damage the WPC's by accelerating its oxidative degradation. That said, other researchers that investigated the OIT of multi-processed PP and HDPE found contrary results. Knowing that the coefficients of variation of the OIT tests were rather high, these conclusions must be made with precaution.

Finally, the polymer blends did not influence the behavior of the composites, in fact this behavior was strongly linked to the nature of the polymer used. No disadvantage in using blends of polymers appeared during the different tests, should these tests be on the strength of the composites or on their morphology. Using blends of polymers presents many advantages and opportunities that need to be investigated and evaluated during future investigations. Certainly, new applications of WPC's might be found with polymer blends and this new area of research needs more specific attention.

APPENDIX

A. Results of the bending tests for virgin WPC's

Table A-1 Bending tests results for the wood/HDPE blend.

	WOOD/HDPE							
	Max load (N)	% cov	MOR (kPa)	% cov	ε_{break}	% cov	MOE (MPa)	% cov
Extrusion 1	356	4.21	24,550	4.27	0.0142	7.75	3,347	2.31
Extrusion 2	334	0.56	22,705	0.48	0.0119	4.20	3,123	1.16
Extrusion 3	440	1.83	26,814	2.96	0.0139	8.63	3,504	1.77
Extrusion 4	329	8.86	21,278	8.54	0.0103	10.68	3,172	13.50
Average	365	3.87	23,837	4.06	0.0125	7.82	3,286	4.69

Table A-2 Bending tests results for wood/PP blend.

	WOOD/PP							
	Max load (N)	% cov	MOR (kPa)	% cov	ε_{break}	% cov	MOE (MPa)	% cov
Extrusion 1	489	5.77	25,936	5.76	0.0189	10.00	3,053	7.50
Extrusion 2	480	3.43	28,268	2.98	0.0175	13.14	3,276	2.31
Extrusion 3	516	5.70	29,537	6.40	0.0151	17.22	3,528	3.04
Extrusion 4	503	2.88	28,878	2.53	0.0145	11.03	3,731	5.06
Average	497	4.45	28,155	4.42	0.0165	12.86	3,397	4.48

Table A-3 Bending tests results for wood/PVC blend.

	WOOD/PVC							
	Max load (N)	*% cov*	**MOR (kPa)**	*% cov*	ε_{break}	*% cov*	MOE (MPa)	*% cov*
Extrusion 1	596	*4.13*	37,611	*4.12*	0.0083	*4.82*	5,553	*2.11*
Extrusion 2	600	*5.21*	36,801	*8.51*	0.0078	*5.13*	5,225	*6.13*
Extrusion 3	694	*6.36*	42,742	*7.71*	0.0082	*7.32*	6,206	*9.76*
Extrusion 4	667	*4.27*	41,260	*7.61*	0.0073	*6.85*	6,161	*4.03*
Average	639	*4.99*	39,603	*6.99*	0.0079	*6.03*	5,786	*5.51*

Table A-4 Bending tests results for wood/HDPE/PP blend.

	WOOD/HDPE/PP							
	Max load (N)	*% cov*	**MOR (kPa)**	*% cov*	ε_{break}	*% cov*	MOE (MPa)	*% cov*
Extrusion 1	405	*1.05*	25,819	*0.47*	0.0156	*5.13*	3,280	*3.37*
Extrusion 2	405	*1.05*	25,819	*0.47*	0.0156	*5.13*	3,280	*3.37*
Extrusion 3	365	*4.43*	24,797	*14.08*	0.0111	*6.31*	3,438	*14.45*
Extrusion 4	405	*2.62*	24,338	*3.63*	0.0132	*14.39*	3,460	*2.85*
Average	395	*2.29*	25,193	*4.66*	0.01388	*7.74*	3,365	*6.01*

Table A-5 Bending tests results for wood/HDPE/PVC blend.

	WOOD/HDPE/PVC							
	Max load (N)	*% cov*	**MOR (kPa)**	*% cov*	ε_{break}	*% cov*	MOE (MPa)	*% cov*
Extrusion 1	316	*6.25*	20,352	*6.26*	0.0089	*7.87*	3,628	*2.14*
Extrusion 2	320	*4.15*	20,675	*4.08*	0.008	*7.50*	3,655	*1.61*
Extrusion 3	365	*1.33*	22,938	*1.39*	0.0074	*5.41*	4,373	*3.06*
Extrusion 4	347	*3.78*	22,787	*3.44*	0.007	*5.71*	4,352	*3.17*
Average	337	*3.88*	21,688	*3.79*	0.00783	*6.62*	4,002	*2.50*

Table A-6 Bending tests results for wood/PP/PVC blend.

	WOOD/PP/PVC							
	Max load (N)	*% cov*	**MOR (kPa)**	*% cov*	ε_{break}	*% cov*	**MOE (MPa)**	*% cov*
Extrusion 1	383	*2.59*	23,508	*2.61*	0.0081	*6.17*	4,325	*2.34*
Extrusion 2	369	*4.07*	22,691	*4.25*	0.0065	*6.15*	4,393	*3.32*
Extrusion 3	427	*3.69*	25,270	*4.50*	0.0073	*12.33*	4,671	*3.37*
Extrusion 4	405	*6.45*	24,372	*6.11*	0.0076	*15.79*	4,247	*12.34*
Average	396	*4.20*	23,960	*4.37*	0.00738	*10.11*	4,409	*5.34*

Table A-7 Application of the rule of mixture on the MOE.

	Wood/HDPE	Wood/PP	Wood/PVC	Wood/HDPE /PP	Wood/HDPE/ PP	*Wood/HDPE/ PP*
	test	test	test	test	Rule mixture	*% error*
Extrusion 1	3 347	3 053	5 553	3 280	3200	*2.51%*
Extrusion 2	3 123	3 276	5 225	3 280	3199	*2.54%*
Extrusion 3	3 504	3 528	6 206	3 438	3516	*-2.22%*
Extrusion 4	3 172	3 731	6 161	3 460	3451	*0.27%*
Average	3 286	3 397	5 786	3 365	3342	*0.68%*

	Wood/HDPE/ PVC	Wood/HDPE/ PVC	*Wood/HDPE /PVC*	Wood/PP /PVC	Wood/PP /PVC	*Wood/PP /PVC*
	test	Rule mixture	*% error*	test	Rule mixture	*% error*
Extrusion 1	3 628	4450	*-18.47%*	4 325	4303	*0.51%*
Extrusion 2	3 655	4174	*-12.43%*	4 393	4251	*3.33%*
Extrusion 3	4 373	4855	*-9.92%*	4 671	4867	*-4.03%*
Extrusion 4	4 352	4666	*-6.73%*	4 247	4946	*-14.13%*
Average	4 002	4536	*-11.77%*	4 409	4592	*-3.99%*

DSC curves obtained for each WPC's

Results concerning crystallization

T_c corresponds to a peak toward a maximum positive heating flow in the 3rd segment.

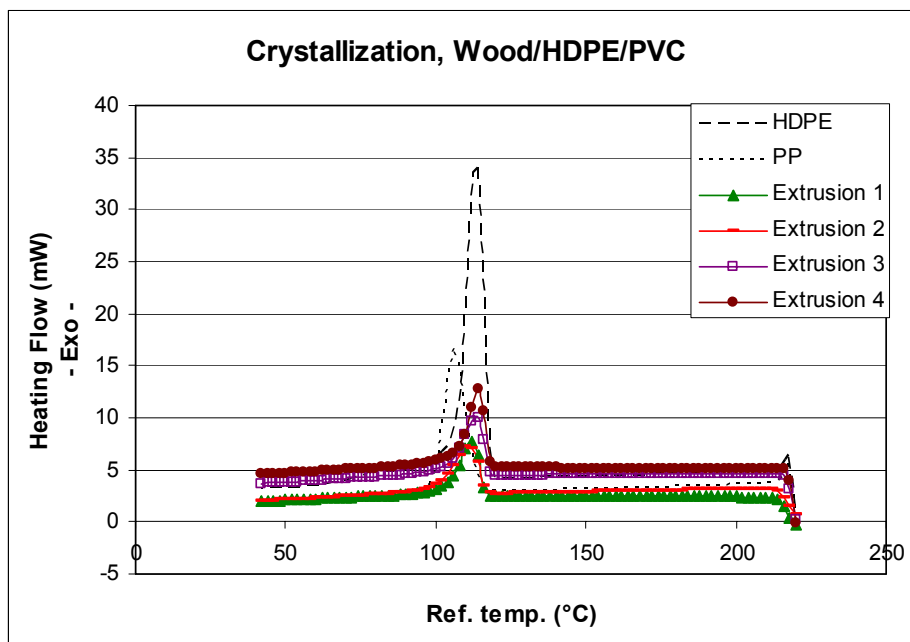- Effect of the number of extrusions on the crystallization, per blend
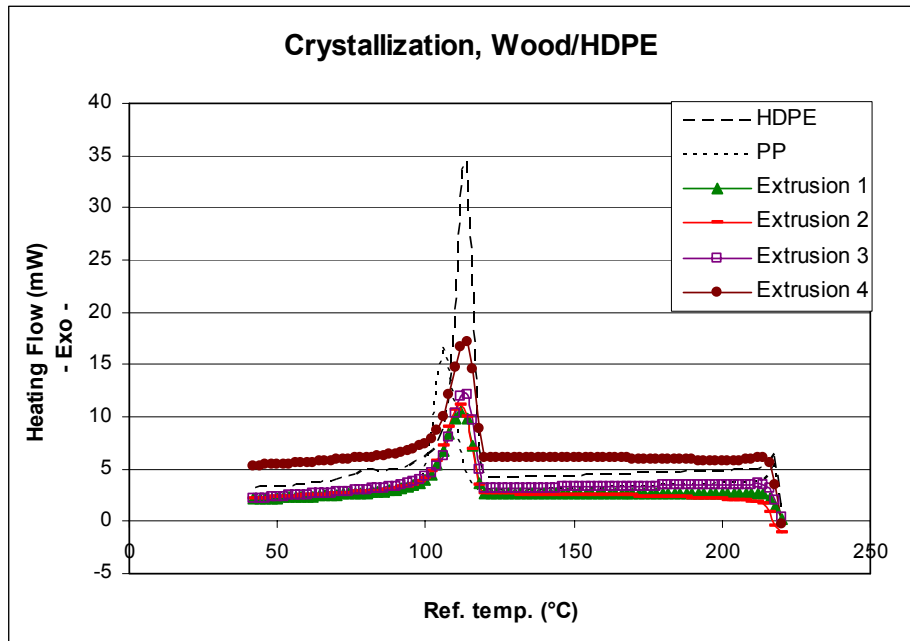
Figure A-1 Plot of the exothermic curves showing the crystallization for the wood/HDPE blends after every extrusion.
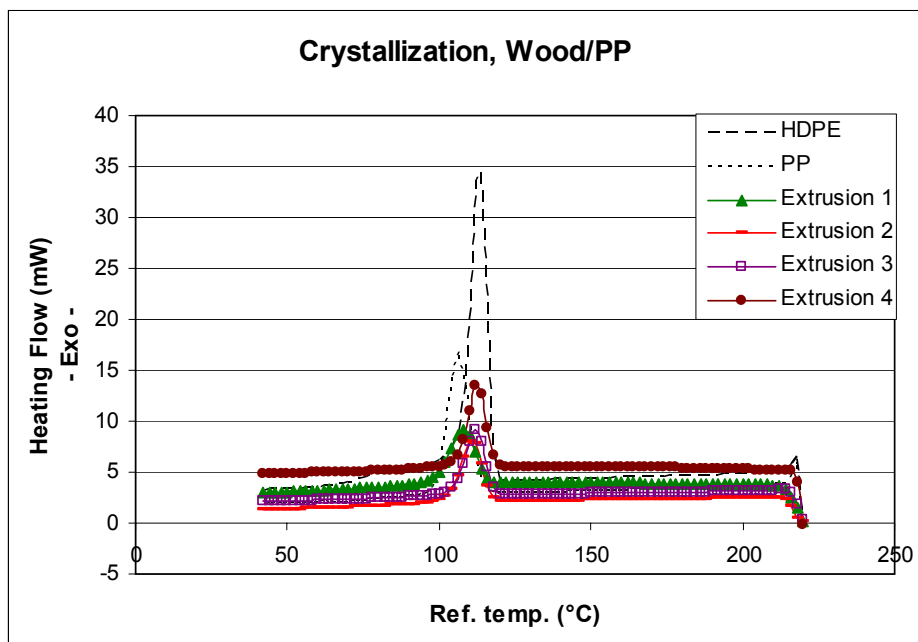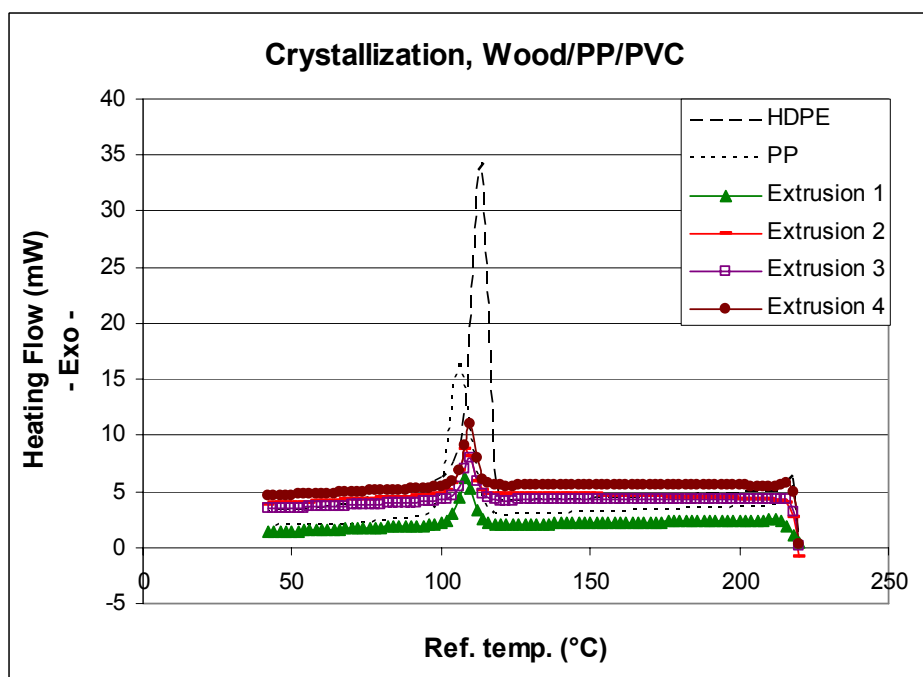
Figure A-2 Plot of the exothermic curves showing the crystallization for the wood/PP blends after every extrusion.
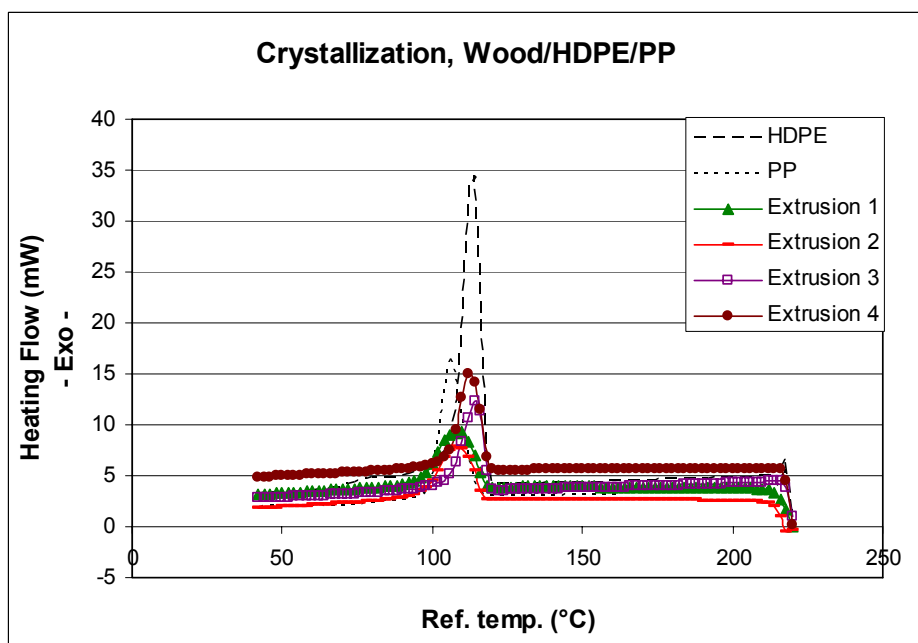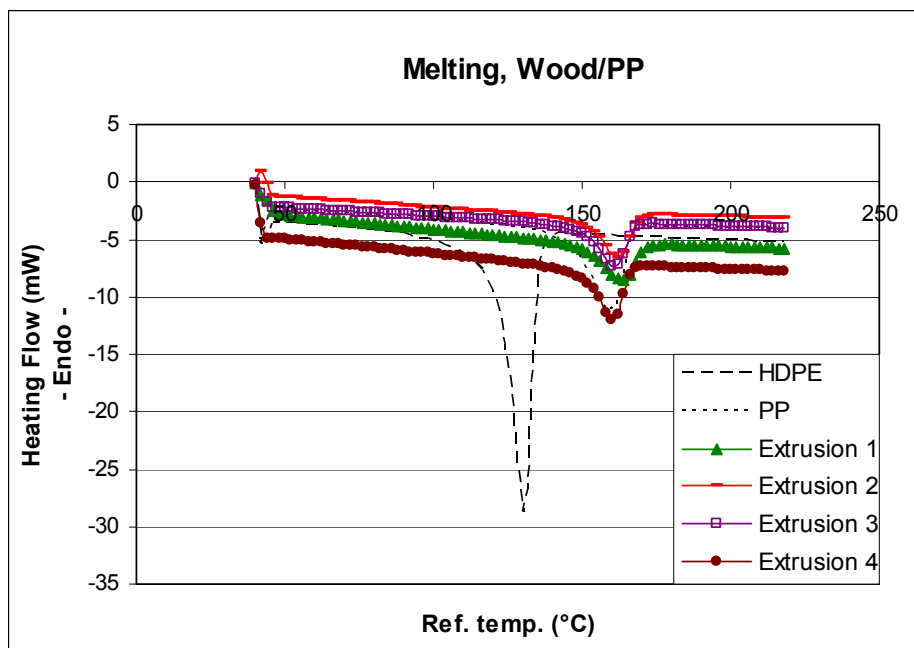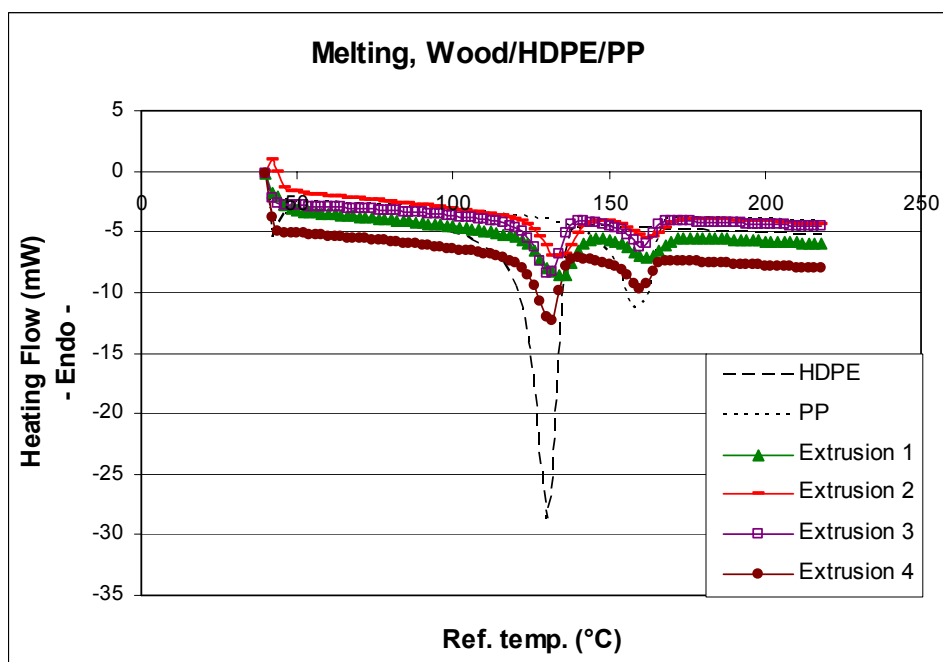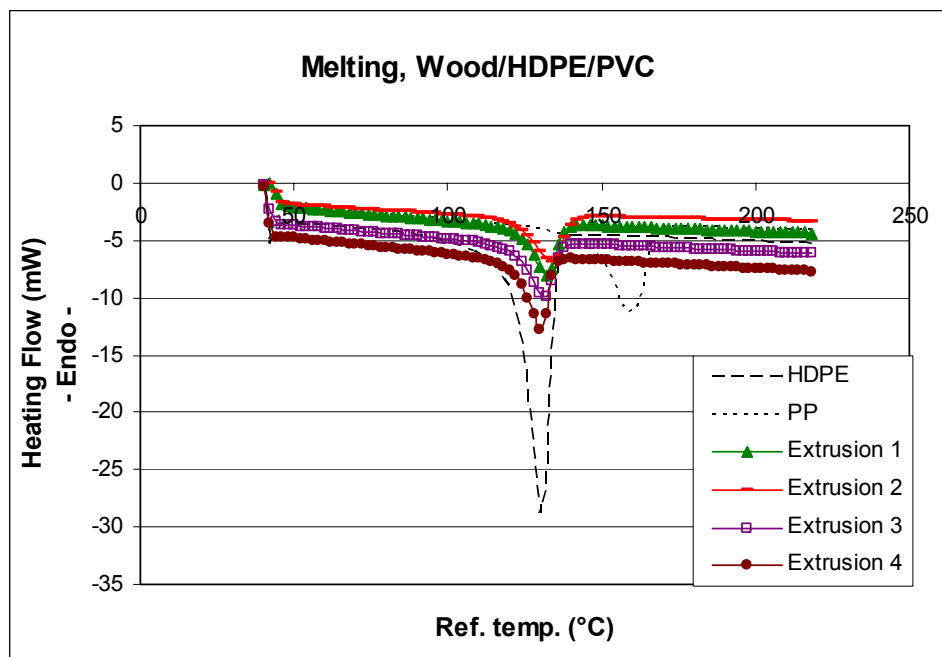

Figure A-3 Plot of the exothermic curves showing the crystallization for the wood/HDPE/PP blends after every extrusion.

Figure A-4 Plot of the exothermic curves showing the crystallization for the wood/HDPE/PVC blends after every extrusion.
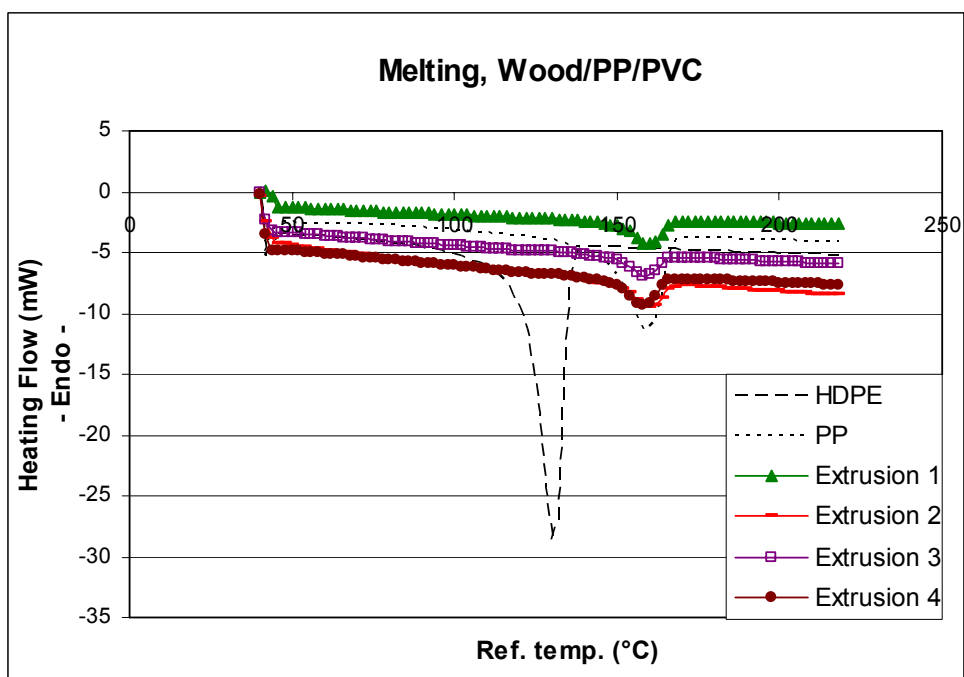

Figure A-5 Plot of the exothermic curves showing the crystallization for the wood/PP/PVC blends after every extrusion.
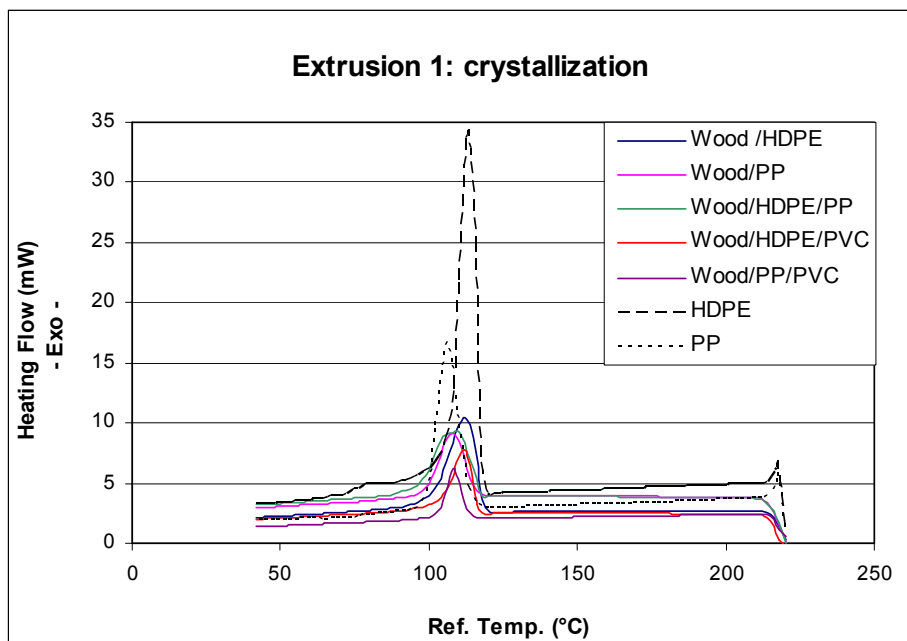
Figure A-6 Exothermic curves showing the blends crystallization after the 1st extrusion.
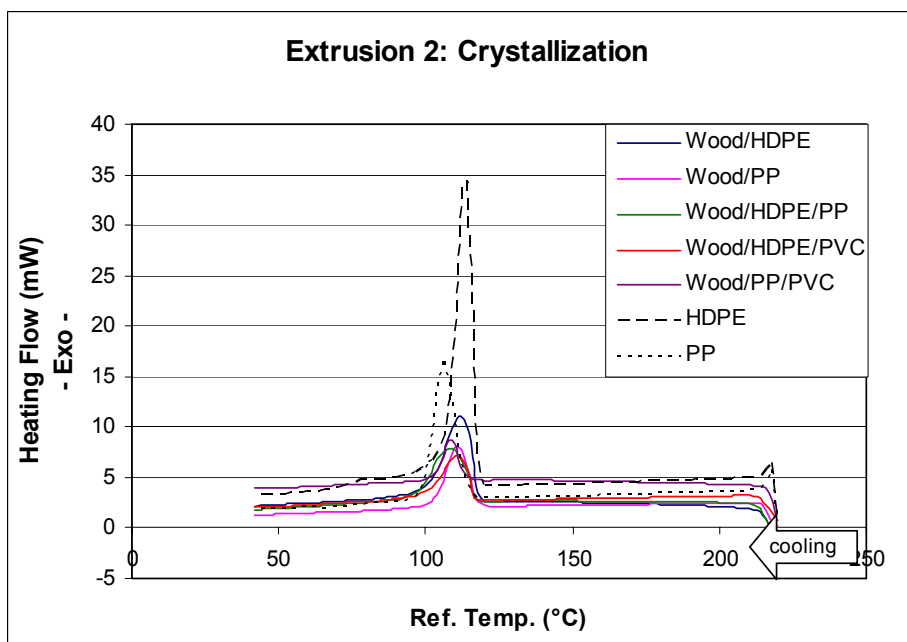
Figure A-7 Exothermic curves showing the blends crystallization after the 2nd extrusion.
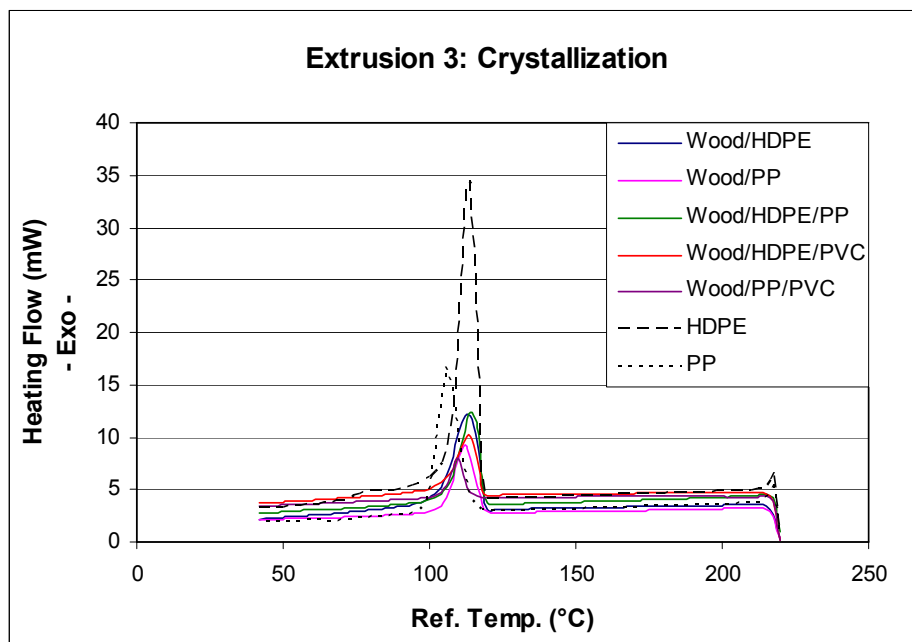
Figure A-8 Exothermic curves showing the blends crystallization after the 3rd extrusion.
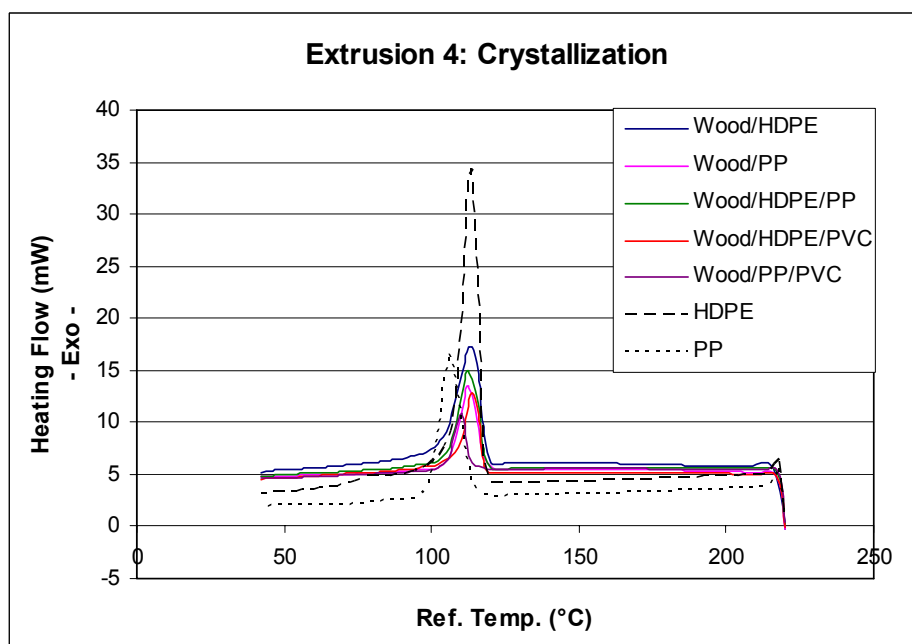
Figure A-9 Exothermic curves showing the blends crystallization after the 4th extrusion.

82

Results concerning melting

T_m corresponds to a peak toward a maximum negative heating flow in the 5th segment of a DSC cycle.

- Effect of the number of extrusions on the melting, per blend
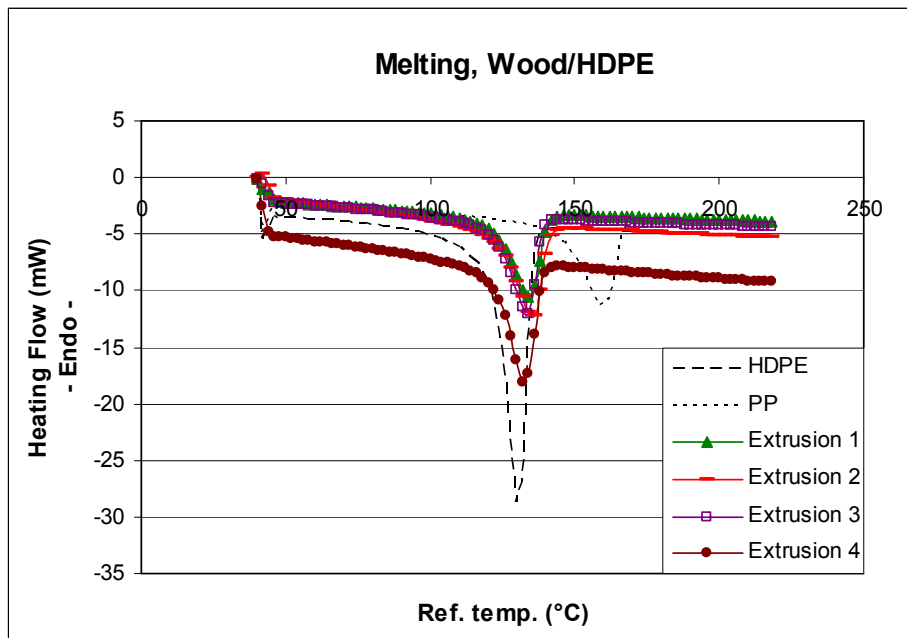
Figure A-10 Plot of the endothermic curves showing the melting for the wood/HDPE blends after every extrusion.

Figure A-11 Plot of the endothermic curves showing the melting for the wood/PP blends after every extrusion.

Figure A-12 Plot of the endothermic curves showing the melting for the wood/HDPE/PP blends after every extrusion.
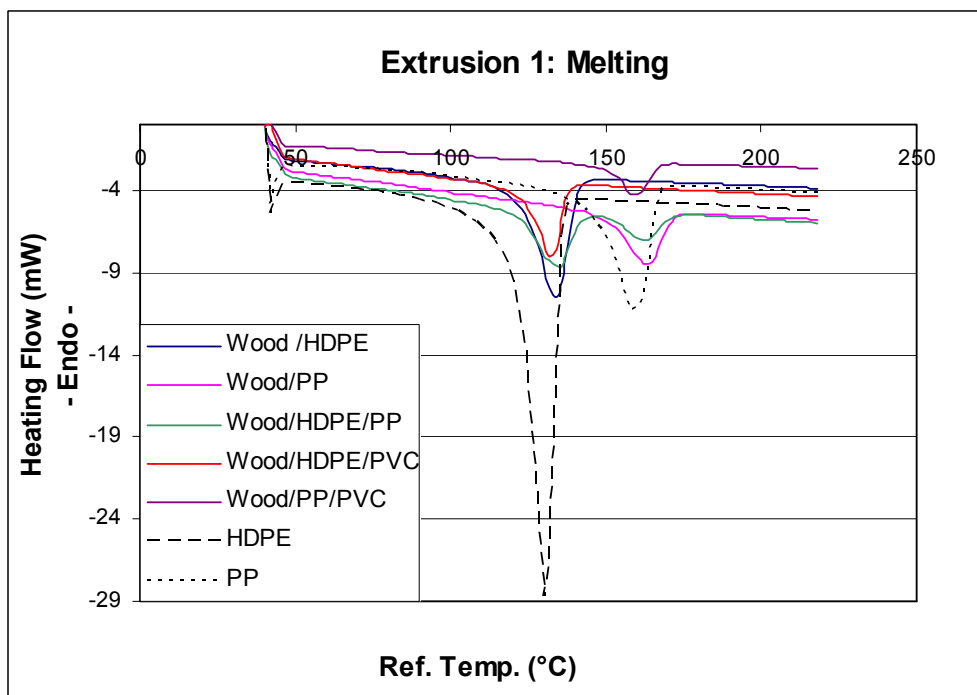
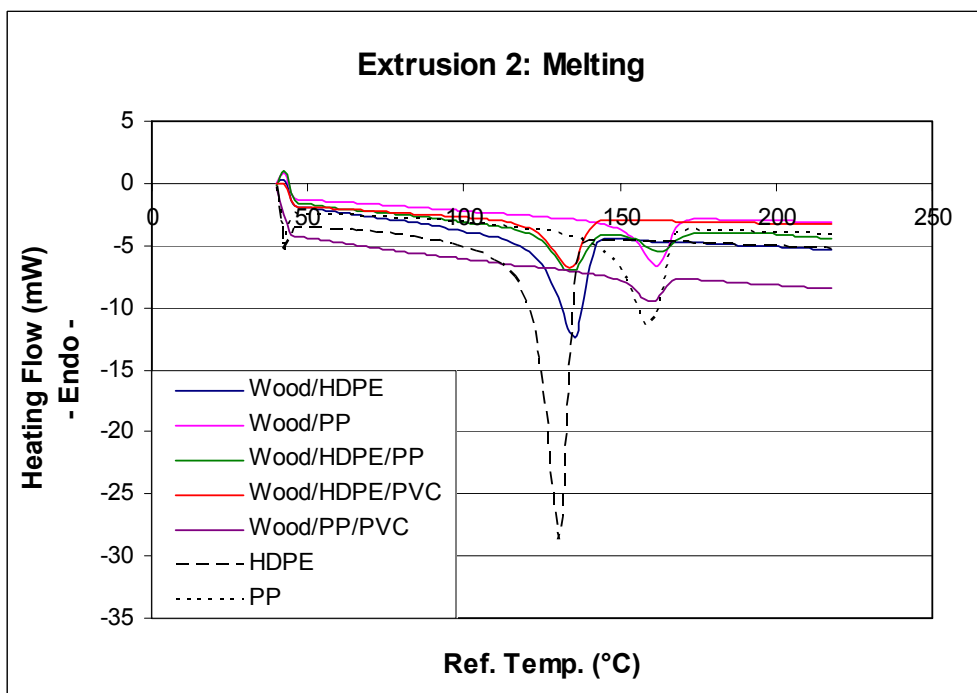**Figure A-13 Plot of the endothermic curves showing the melting for the wood/HDPE/PVC blends after every extrusion.**

Figure A-14 Plot of the endothermic curves showing the melting for the wood/PP/PVC blends after every extrusion.

Figure A-15 Endothermic curves showing the blends melting after the 1ˢᵗ extrusion.

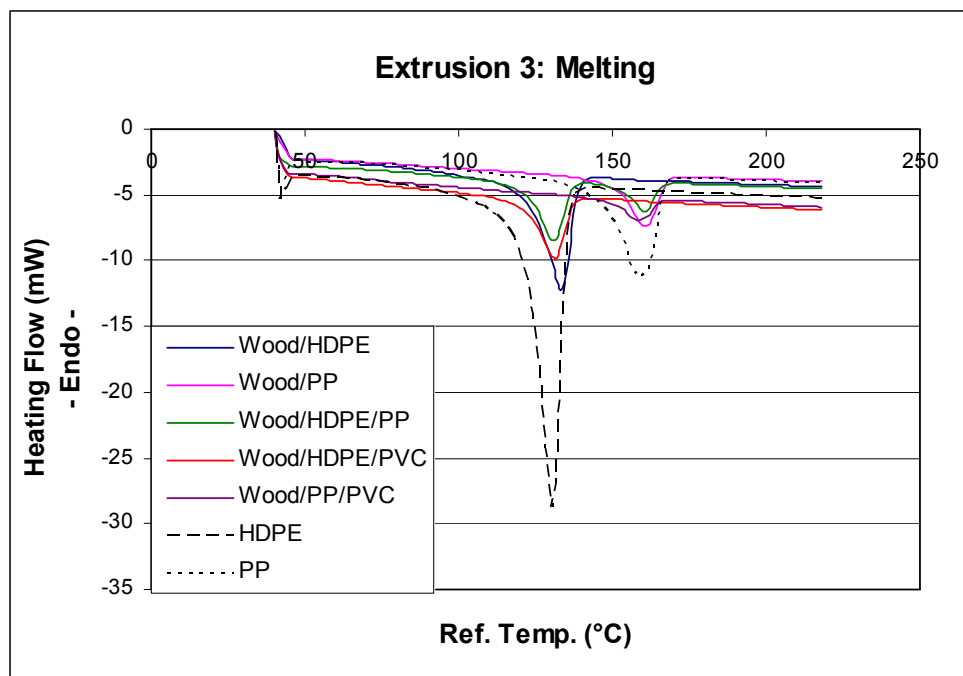**Figure A-16 Endothermic curves showing the blends melting after the 2ⁿᵈ extrusion.**

Figure A-17 Endothermic curves showing the blends melting after the 3rd extrusion.
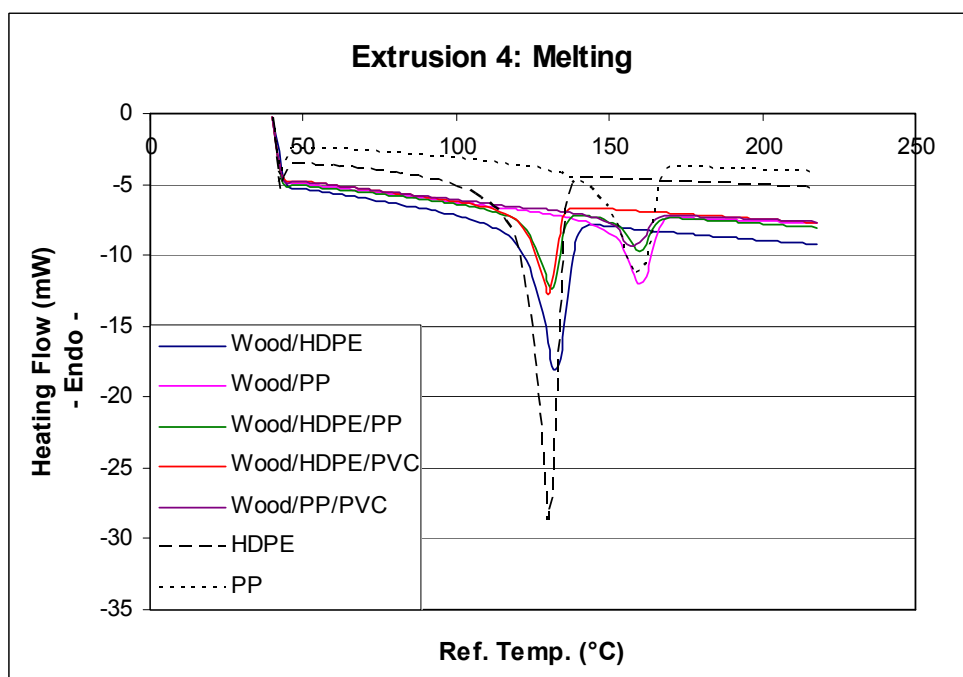

Figure A-18 Endothermic curves showing the blends melting after the 4th extrusion.

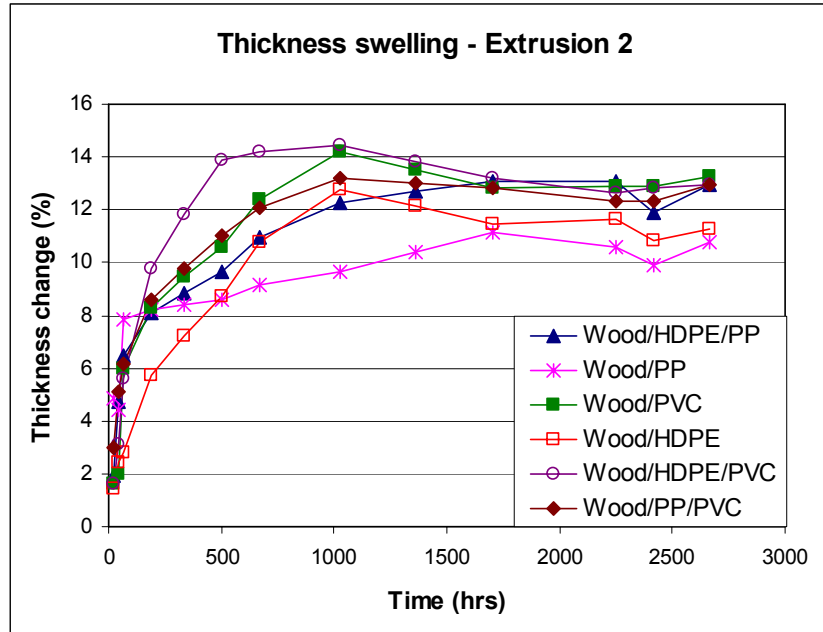## B. Thickness swelling for extrusions #2 to #4

Figure B-1 Plot of the thickness swelling versus immersion time, second extrusion.
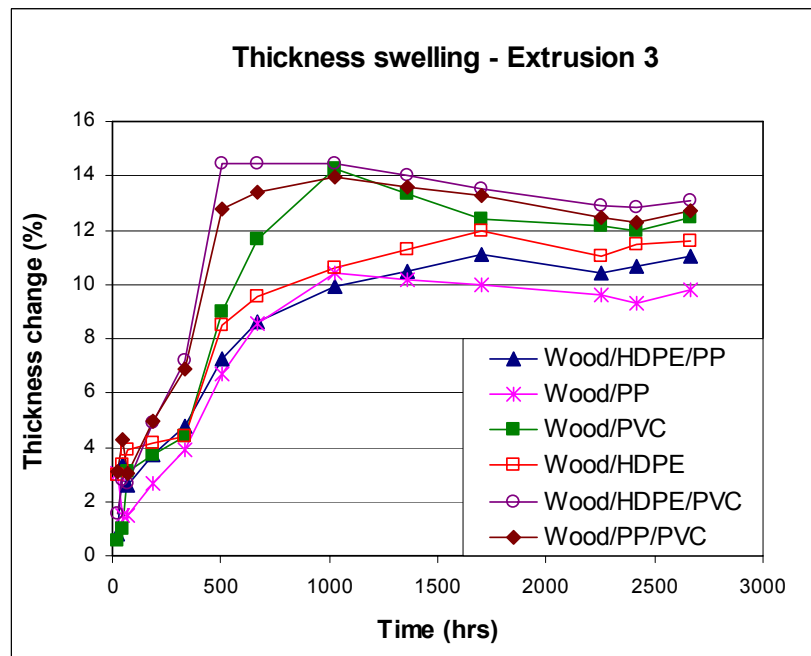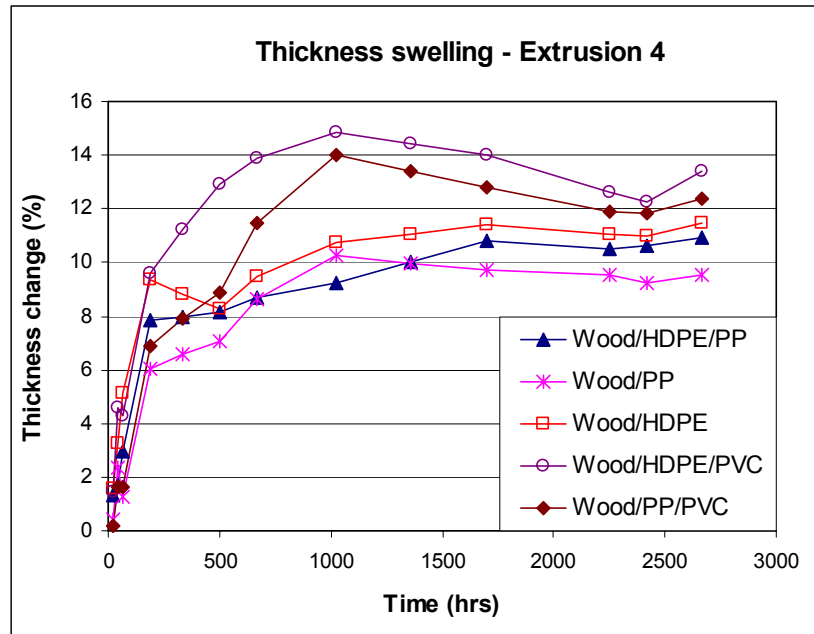

Figure B-2 Plot of the thickness swelling versus immersion time, third extrusion.

Figure B-3 Plot of the thickness swelling versus immersion time, fourth extrusion.

C. Thickness swelling vs. number of extrusions

Figure C-1 Plot of the thickness swelling after 2660 hours of immersion, for the different extrusions of the wood/HDPE blend.

Figure C-2 Plot of the thickness swelling after 2660 hours of immersion, for the different extrusions of the wood/PP blend.

Figure C-3 Plot of the thickness swelling after 2660 hours of immersion, for the different extrusions of the wood/PVC blend.

Figure C-4 Plot of the thickness swelling after 2660 hours of immersion, for the different extrusions of the wood/HDPE/PP blend.
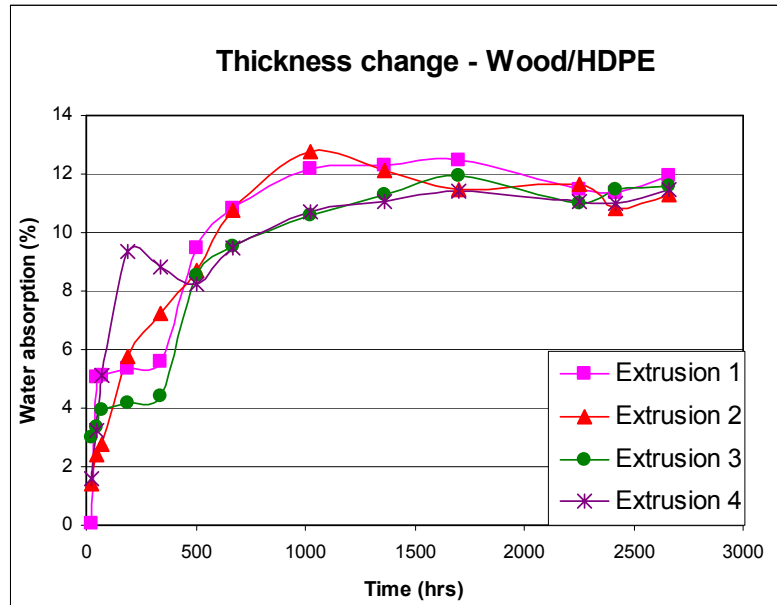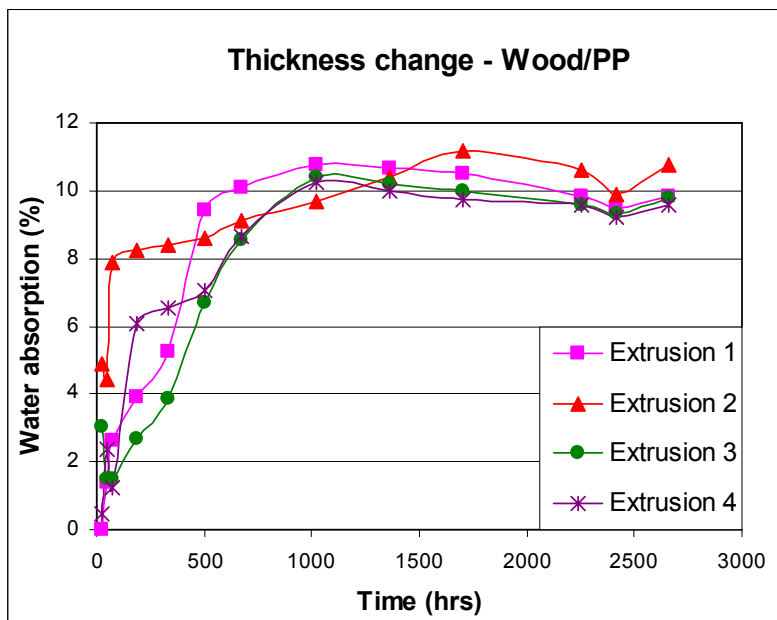
Figure C-5 Plot of the thickness swelling after 2660 hours of immersion, for the different extrusions of the wood/HDPE/PVC blend.
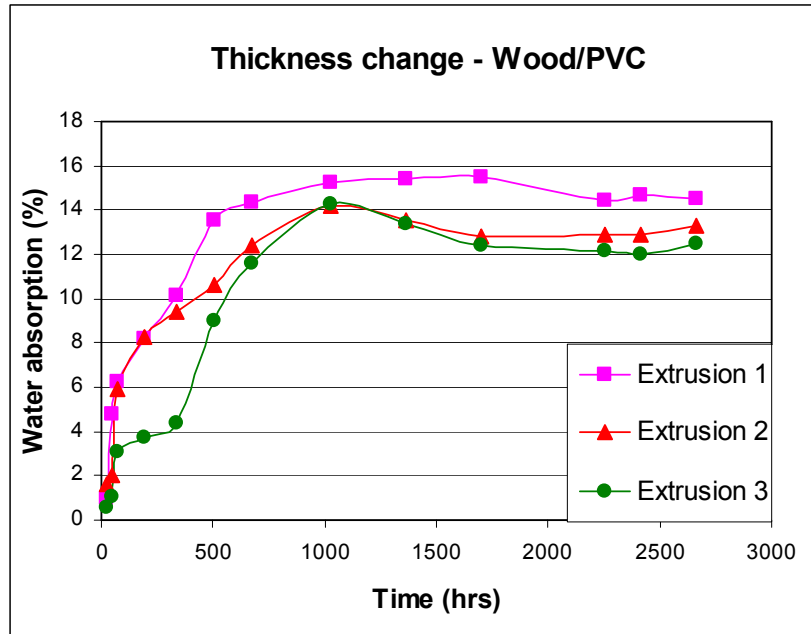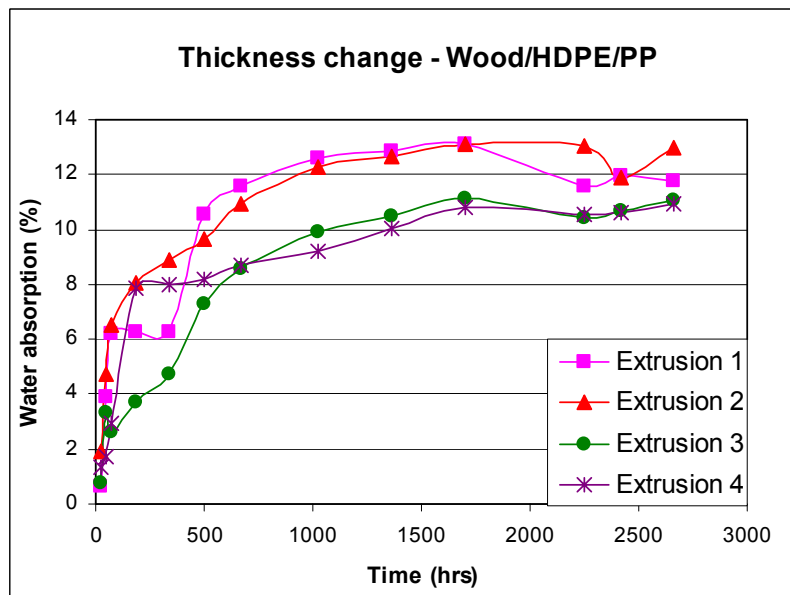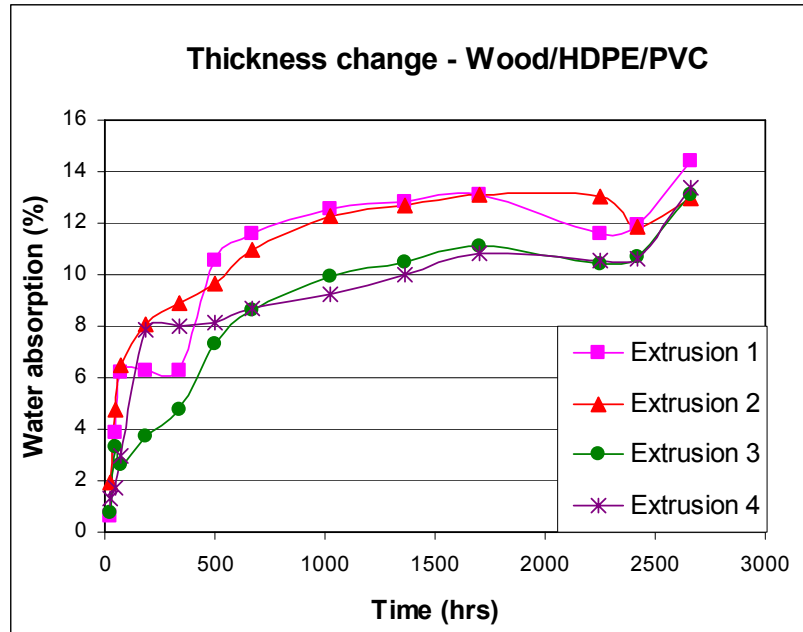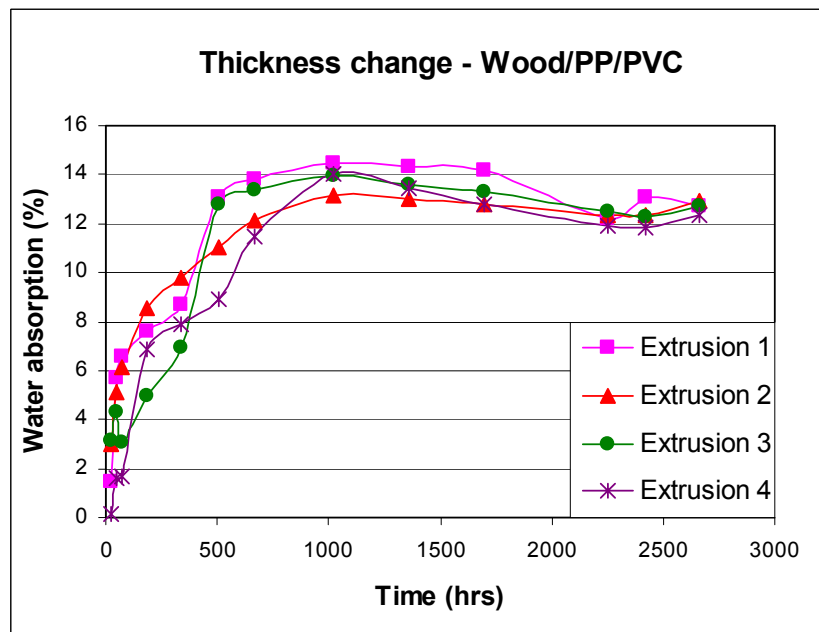

Figure C-6 Plot of the thickness swelling after 2660 hours of immersion, for the different extrusions of the wood/PP/PVC blend.

D. Extrusion processing parameters

Table D-1 Extrusion processing parameters for the first extrusion.

EXTRUSION #1	Extruder temperature	Die temperature
all zones	180° C / 356° F	180° C / 356° F

Blend	Screw speed (rpm)	Melt temperature	Melt stress	Electric charge (Amp)
1	20	180° C / 356° F	416 psi / 2868 kPa	8
2	20	180° C / 356° F	515 psi / 3551 kPa	7
3	20	180° C / 356° F	496 psi / 3420 kPa	6
4	20	180° C / 356° F	581 psi / 4006 kPa	7
5	20	180° C / 356° F	511 psi / 3523 kPa	6
6	20	180° C / 356° F	577 psi / 3978 kPa	6

Table D-2 Extrusion processing parameters for the second extrusion.

EXTRUSION #2	Extruder temperature	Die temperature
all zones	180° C / 356° F	180° C / 356° F

Blend	Screw speed (rpm)	Melt temperature	Melt stress	Electric charge (Amp)
1	10	180° C / 356° F	387 psi / 2668 kPa	7
2	10	180° C / 356° F	311 psi / 2144 kPa	11
3	10	180° C / 356° F	189 psi / 1303	11
4	10	180° C / 356° F		11
5	10	180° C / 356° F	311 psi / 2144 kPa	10
6	10	180° C / 356° F	320 psi / 2206 kPa	10

Table D-3 Extrusion processing parameters for the third first extrusion.

EXTRUSION #3	Extruder temperature	Die temperature
all zones	180° C / 356° F	180° C / 356° F

Blend	Screw speed (rpm)	Melt temperature	Melt stress	Electric charge (Amp)
1	10	180° C / 356° F	291 psi / 2006 kPa	11
2	10	180° C / 356° F	288 psi / 1917 kPa	11
3	10	180° C / 356° F	115 psi / 792 kPa	8
4	10	180° C / 356° F	194 psi / 1338 kPa	10
5	10	180° C / 356° F	236 psi / 1627 kPa	10
6	10	180° C / 356° F	262 psi / 1806 kPa	10

Table D-4 Extrusion processing parameters for the fourth extrusion.

EXTRUSION #4	Extruder temperature	Die temperature
all zones	180°C / 356°F	180°C / 356°F

Blend	Screw speed (rpm)	Melt temperature	Melt stress	Electric charge (Amp)
1	10	180°C / 356°F	364 psi / 2506 kPa	10
2	10	180°C / 356°F	335 psi / 2310 kPa	11
3	10	180°C / 356°F	262 psi / 1806 kpa	8
4	10	180°C / 356°F	266 psi / 1834 kPa	10
5	10	180°C / 356°F	322 psi / 2220 kPa	10
6	10	180°C / 356°F	324 psi / 2234 kPa	8

E. List of abbreviations and variables

PP   Isotactic polypropylene

PVC   Polyvinyl-chloride

HDPE   High density polyethylene

LDPE   Low density polyethylene

LLDPE   Linear low density polyethylene

VLDPE   Very low density polyethylene

ULDPE   Ultra low density polyethylene

EPDM   Ethylene-propylene-diene (copolymer)

EBS   Ethylene bis stearamide

T_e Equilibrium torque

MOE   Modulus of elasticity

MOR   Modulus of rupture or maximum stress

ε_{break} Strain at break

ΔW Percentage of water absorption or mass change

W_o Conditioned initial weight of a sample prior to water soaking tests

ΔT Percentage of thickness swelling

T_o Conditioned initial thickness of a sample prior to water soaking tests

EMC   Equilibrium moisture content

RH   Relative humidity

DSC   Differential scanning calorimeter/calorimetry

T_c Temperature of crystallization

T_m	Melting point
X_c	Degree of crystallinity
$X(t)$	Relative crystallinity
dH_c/dt	Rate of heat evolution.
$t_{1/2}$	Half-time of crystallization
OIT	Oxidation induction time
cov	Coefficient of variation (%)