

Recycling of Crosslinked High Density Polyethylene Through  
Compression Molding

by

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## ABSTRACT

Crosslinkable high density polyethylene (XHDPE) is used to manufacture large and rigid products such as fuel tanks using a rotomolding process. Currently, defective and post-consumer parts are not recycled and sent to landfills. Hence, recycling of this material through compression molding is the objective of this study. Thermal analysis revealed that the extent of crosslinking varied across the thickness of the rotomolded part due to the role played by air. Due to limited crosslinking, the recycled XHDPE (RXHDPE) could be remelted with higher viscosity than the virgin XHDPE (VXHDPE). Consolidation studies using rheometer indicated that both RXHDPE and VXHDPE could be compression molded to a density of  $0.952 \text{ g/cm}^3$ . However, higher consolidation stress is required for RXHDPE when compared to VXHDPE to realize the same density. RXHDPE, compression molded at 1.6 MPa and  $230^\circ\text{C}$ , had properties similar to those of VXHDPE molded at 0.321 MPa, demonstrating the recyclability.

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## **CHAPTER 1. INTRODUCTION**

Rotational molding or rotomolding is a common manufacturing process used to produce hollow one-piece plastic parts. The main advantage of this process, when compared to blow molding, thermoforming and injection moulding, is the possibility of producing strong and complex parts with uniform thickness. One of the main plastics used for rotomolding is the high density polyethylene (HDPE). For some applications, the HDPE must be crosslinked to make the parts stronger and increase the barrier resistance.

### **1.1 Background**

Rotomolding uses the rotation of the mold along two axes to distribute uniformly the plastic powder against the inner wall of the mold while the temperature is increased above the melting point of the material. The process has four main steps [1], presented in Figure 1-1, which are: (a) loading the mold, (b) heating, (c) cooling and (d) unloading the mold. The mold rotates during heating and cooling.

The principles used in this technique were introduced centuries ago to process ceramics and metals, but only in 1940 the technique was used to process polymers [2]. Some of the advantages and disadvantages of this process are presented in Table 1-1.

The grinding or pulverization of the raw material, before loading, is an essential step to achieve these advantages. Typically, 0.6 mm or 0.5 mm (28 or 35 mesh respectively) is enough to obtain a powder that can reach the inner details of the mold (i.e. cavities), as well as has a good residence time on the walls of flat surfaces, characteristics that pellets cannot achieve very well [3]. Now-a-days, the most versatile material for rotomolding is the HDPE. This thermoplastic polymer has low cost and is easy to process.

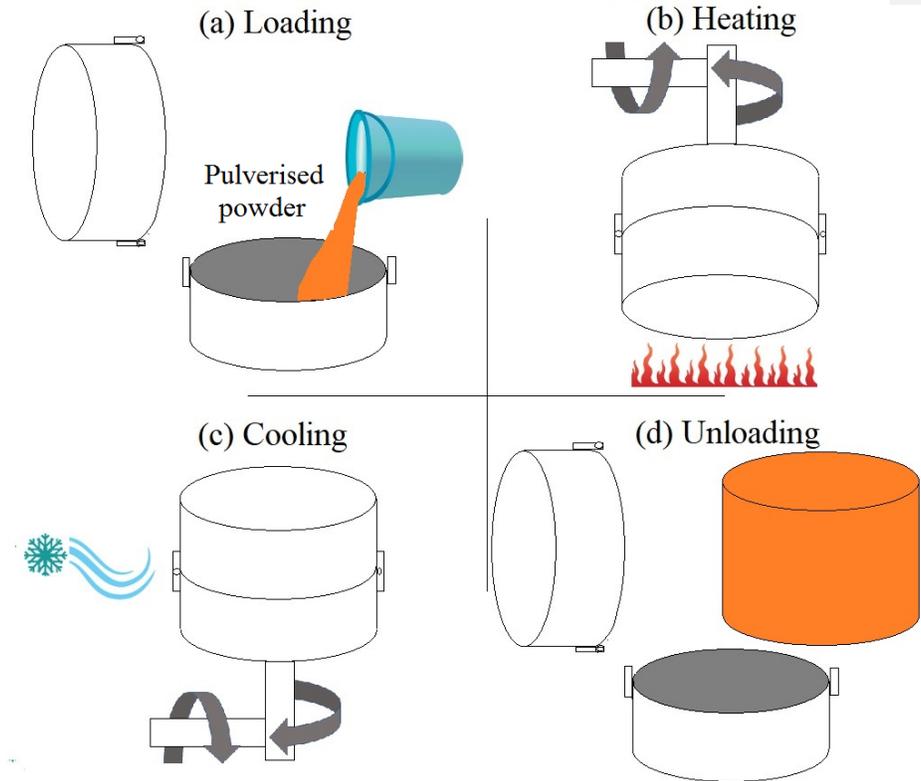


Figure 1-1: Illustration of rotomolding process

HDPE has a density of 0.940 - 0.965 g/cm<sup>3</sup> [5] and melting between 128°C and 138°C [6]. Mechanical properties of HDPE are superior, when compared with low-density polyethylene (LDPE). This is due to the catalysts used to reduce branching and create long chains, with the best performance given by the metallocene catalyst [7].

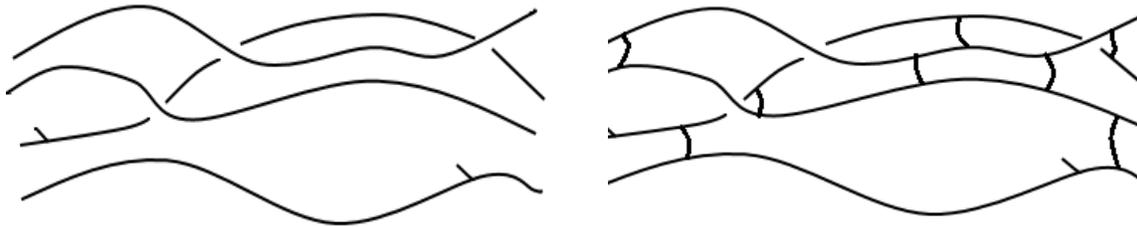
Despite the strength of the HDPE, some rotomolding applications require crosslinking of the HDPE to increase the toughness and barrier resistance properties. These qualities are essential for fuel tanks, as they are required to comply with emission regulations of fuel fumes. The crosslinked high density polyethylene (XHDPE) is a result of the bonding of the chain to itself and to other chains [8], as presented in Figure 1-2.

The crosslinking of polyethylene is prepared using either a crosslinking agent (peroxide or silane) or electron beam radiation. During rotomolding, the crosslinking caused by the peroxide initiator increases the gel content (>80% as claimed by a rotomolder using this material), which reduces the flow of the material when heated above the melting temperature.

The main disadvantage of XHDPE for rotomolding is that the defective and post-consumer parts cannot be reprocessed using rotomolding, and the waste is currently sent to the landfill. Published studies on recycling this material, discussed in Chapter 2, involves degrading the material to low molecular components and blending them with other thermoplastic polymers to manufacture parts. This methodology has not found much traction. Few published studies have attempted recycling / reusing this material without degrading or blending, but these are not comprehensive and do not provide any insight into the success of these attempts. Thus, recycling this material through other processing methods or reusing in rotomolding without degrading and blending would be of immense importance to rotomolders of North America.

Table 1-1: Advantages and disadvantages of the rotomolding process [3, 4]

<b>Advantages</b>	<b>Disadvantages</b>
- Parts with uniform thickness	- Slow cycle time
- Strong one-piece parts	- Intensive labour
- Low residual stress	- Material must be grinded before process
- Uses low pressure	- Limited plastics available
- Able to make large or small parts	- Hard to achieve dimensional accuracy
- Multi-layer option	- Large flat surfaces present warpage
- Inserts can be molded during process	- Requires release agents



**HDPE (0.94 – 0.97 g/cm<sup>3</sup>)**

**XHDPE**

Figure 1-2: Comparison between HDPE and XHDPE structure

## **1.2 Thesis scope**

Hence, this research is focused on the reuse of this material, without degrading and blending, through compression molding. The thermal and consolidation behavior of the recycled XHDPE (RXHDPE) was characterized and compared with the virgin XHDPE (VXHDPE) to understand the issues in recycling / reusing this material. Based on this, the compression molding conditions were chosen to manufacture tensile specimens. The tensile properties of RXHDPE are compared with VXHDPE to demonstrate the former's recyclability through compression molding.

## **1.3 Organization of thesis**

Chapter 2 comprises a detailed review of the published work on recycling of crosslinked polyethylene to highlight the knowledge gaps. Based on this review, the objectives of this thesis are defined to address the knowledge gaps. Chapter 3 presents details on the experimental procedure. Experimental results are presented and discussed in Chapter 4. Conclusions and recommendations for further work in this field are presented in Chapter 5.

## **CHAPTER 2. LITERATURE REVIEW**

This chapter provides a concise review of published literature on the recycling of XHDPE. Initially, the major discoveries related to the XHDPE are presented. Subsequently, available recycling technologies are presented and discussed. Based on this, current knowledge gaps in the area of recycling of XHPDE are highlighted. Based on these knowledge gaps, the scope and objectives of this thesis are defined.

### **2.1 Introduction**

Since the discovery of the first polymer in 1907 [9], the world has seen several industrial and scientific revolutions with the development of products with increasingly specific and improved properties.

Considering the increasing volume of plastics produced annually, the main challenge is to develop sustainable products, which can be easily recycled. That is not the case with XHDPE. Despite its advantages over HDPE, XHDPE cannot be re-melted, under the same process conditions used for the virgin material, due to crosslinks [10]. Thus, the current solution, chosen by manufacturing companies, for defective products is to discard them to the landfill.

Figure 2-1 presents an overview of key innovations directly related to XHDPE. Published research on recycling of XHDPE is very limited. Most of the recycling technologies, reviewed in the next section, are applied to crosslinked low density polyethylene (XLPE). Depending on the following parameters, these technologies may require additional development before application to XHDPE:

- a) Molecular weight of polyethylene (LDPE, HDPE, etc.);
- b) Type of crosslinking process: peroxide, silane or electron beam radiation;
- c) The amount of crosslinking.

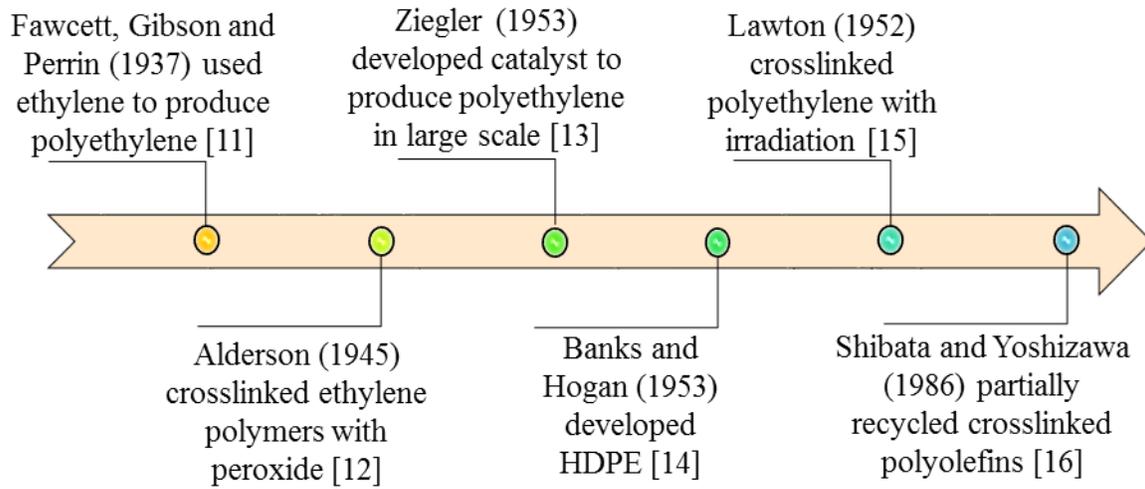


Figure 2-1: Timeline of major discoveries related to XHDPE

## 2.2 Recycling technologies

While discussing recycling of crosslinked rubber waste, Thakur [17] had proposed to decrease the amount of waste in the landfill by adopting and pursuing the following methodologies in that order: reduce, reuse, recycle, energy recovery, and finally disposal in a landfill if all other methods fail. The same order can be recommended for XHDPE. Table 2-1 presents a summary of these technologies, which can be divided into five main groups.

As Table 2-1 shows, most part of the available publications discuss the recycling process for XLPE (crosslinked low density polyethylene). Although the properties and process parameters can differ, the techniques can still be applied to crosslinked HDPE (XHDPE).

The first documented effort to recycle XHDPE was made in 1986 to recycle partially crosslinked polyolefins [16]. The recycling solution proposed was to use a solvent to dissolve the non-crosslinked content, remove the crosslinked content, and then evaporate the solvent to obtain the non-crosslinked content for reuse. However, the crosslinked content, which usually is the majority, was not recycled.

Alternative technology developed to recycle XHDPE is the solid state shearing followed by melt processing, which can be a solid or molten state shearing. In solid state shearing, the partially crosslinked material waste is chipped and ground in a mill, below the melting temperature, into a fine powder. Sekiguchi and Corp [10] showed that the solid state shearing of silane crosslinked XLPE resulted in the reduction of the gel content from 65% to 52%. Using the powder, 0.3 mm in size obtained from solid state shearing, in a twin-screw extruder at 200°C, consolidated material was obtained through melt state shearing for mechanical properties testing.

<b>Recycling technologies</b>	<b>Material</b>	<b>References</b>
1. Selective dissolution	XLPE	[16]
2. Milling + Melt processing:		
2.1. Extrusion	XLPE	[10, 18, 22]
2.2. Injection molding	XLPE	[18]
2.3. Compression molding	XLPE	[18, 19]
3. Decrosslinking methods		
3.1. Supercritical	XLPE	[20, 21, 22]
3.2. Ultrasonic	XHDPE	[23, 24]
4. Blend	XHDPE	[25, 26, 27]
5. Energy recovery	XLPE	[28, 29, 30]

Table 2-1: Recycling technologies available for XLPE and XHDPE

Comparing the tensile tests results of virgin and recycled samples prepared under low and high shearing (extruder screw speed), the melt process with low shearing presented the best mechanical properties with a tensile strength of 9.6 MPa and elongation at break of 180%, which were still inferior to those of virgin material (20.9 MPa and 510%).

Following the same strategy, other researchers used the powdered recycle into a melt process, studying other extrusion parameters and other processes as injection molding, compression molding.

Using XLPE waste from electrical cables ground to 1.2 mm crumbs, White, Wagenblast and Shaw [18] compared the properties of specimens molded using compression molding, extrusion and injection molding. The specimens from the compression molding process, prepared under a stress of 3 MPa, presented poor appearance and properties when compared to virgin material. The single-screw extrusion did not yield a solid specimen. Applying 135 MPa at 190°C, the injection molding was able to produce good parts with tensile strength of 16.2 MPa and elongation to break of 44%, which were still inferior to virgin material properties (18.8 MPa and 550%).

Wu, Liang and Canhui [19] studied the recycling of XLPE cables (melting peak 103°C and gel content 70%) through compression molding. After 20 milling cycles, the gel content of the powder decreased to 14.5%. The powder was compression molded at 10 MPa and tested. Optimal compression molded product was obtained after 15 milling cycles, with a tensile strength of 16.4 MPa and elongation to break 449%, which were superior to raw XLPE (5.8 MPa and 27 MPa). However, the study did not compare mechanical properties with the virgin material.

Another technology to recycle the crosslinked polyethylene involves the use of supercritical fluids. Watanabe et al. [20] used supercritical water in a high-pressure vessel to decrosslink XLPE (LDPE crosslinked with gel content of 80%) in a batch process. The decrosslinked material was subsequently crosslinked presenting physical and electrical properties similar to the material before recycling. However, mechanical properties were not studied. Baek et al. [21], compared the gel content reduction as a function of temperature and methanol content in a supercritical process. Despite claiming that the material was fully converted into a thermoplastic when achieving 0% gel content, the mechanical properties of the recycled material were not tested.

Goto et al. [22] combined a supercritical environment while applying molten state shearing in an extruder. The crushed silane crosslinked XLPE was treated using supercritical alcohol in a twin-screw extruder. Results show that the gel content decreased to 0% from 30% at temperatures above 270°C and pressure above 5 MPa. Best mechanical properties were achieved after 15 hours with tensile strength of 25.2 MPa and elongation to break of 642%. Despite presenting results very similar to the virgin material properties (32.8 MPa and 648%), this research used a XLPE with very low gel content, which means that the results might be different for high gel content.

Another method involves the use of an extruder along with an ultrasonic system to decrosslink without using fluids. Isayev and Huang [23] used 4 mm chunks of peroxide crosslinked HDPE and compared the effect of different ultrasonic amplitudes in a single-screw extruder at 200°C. Best mechanical properties were achieved when the amplitude of 10  $\mu\text{m}$  was applied, resulting in a tensile strength of 22.8 MPa and elongation at break of 565%, which were very similar to the virgin properties (20.7 MPa and 620%).

In another ultrasonic application, Huang, Isayev and Zhong [24], used a decrosslinking screw design and different ultrasonic amplitudes to reduce gel content from 80% to almost 0%, with mechanical properties very similar to the virgin material [24].

Blending recycled crosslinked polyethylene with virgin polymer is another technology available. Sekiguchi and Corp [10] showed that blend of LDPE with up to 50% of recycled XLPE presented tensile strength 20% lower and elongation to break 20% higher than the new XLPE. Then, increasing % of recycled XLPE decreased mechanical properties.

Navratil et al showed, in another blending research, that using irradiated-XHDPE (tensile strength of 26.2 MPa, modulus of 977 MPa and gel content of 60%) as a filler in LDPE (tensile strength 10.5 MPa, modulus 239.2 MPa) with a volume fraction of 60% through injection molding increased the tensile strength of LDPE by 47.6% and modulus by 87.3% [25]. Sirisinha and Chuaythong [26] blended recycled silane XHDPE with virgin HDPE (33.7 MPa and 965%), with volume fraction of 50% in a twin-screw extruder achieving tensile strength of 24.5 MPa and elongation to break of 402% which are properties similar to the virgin silane XHDPE (21.6 MPa and 472%). Qudaih, Janajreh and Vukusic [27] went further, blending LDPE with silane XHDPE in a conic twin-screw extruder and then preparing the tensile specimens in an injection molding process. Best results were obtained using 15% of silane XHDPE obtaining a tensile strength 37% higher when compared with LDPE.

Finally, energy recovery is one alternative technology which can be applied to the crosslinked material. Boss et al. discussed the importance of low content of metals and chlorine in the crosslinked material to avoid coating and corrosion, respectively, of the furnace during energy recovery processes [28]. Du et al. studied the pyrolysis of XLPE, under nitrogen, which happened from 395°C to 503°C with an activation energy of 365.3 kJ/mol [29].

Comparing the thermal and catalytic degradation at 430°C of XLPE into fuel, Uddin et al. [30] showed that the thermal process yielded 63.1% of fuel, 20.6% of wax, 7.2% of gases and 9.1% of residues, while the catalytic process, using silica-alumina catalyst, yielded 78.6% of fuel, 11.2% of gases and 10.2% of residues. The rate of degradation using the catalyst was 3 times faster and the resulting fuel had properties similar to commercial gasoline.

### **2.3 Summary of literature review and knowledge gaps**

Reusing and/or recycling of crosslinked polyethylene through melt state processing, using processes like rotomolding, compression molding, extrusion, and injection molding, is the focus of this study due to their simplicity and low cost. There is no published study on recycling using rotomolding and published studies on recycling using other processes are very few. These studies were focused on XLPE. There is no published study on XHDPE although the results from XLPE could be adopted. These studies confirm that XLPE could be melt processed after milling the XLPE into powder, despite the high gel content. The reason for this has not been explored. However, the properties of the recycled material were inferior to those of the virgin material. No attempts have been made to study the effect of processing conditions, such as temperature, stress, and shear rate (in case of extrusion and injection molding) on properties to optimize the properties.

Based on the above summary, the following gaps in the knowledge are identified, and are required to be filled, to successfully reuse and / or recycle XHDPE through melt processing.

- The extent of crosslinking in the crosslinked XHDPE product and its relation to subsequent melting during recycling must be quantified.
- The effect of powder size on the melting behavior

- The effect of processing conditions, such as temperature, stress, and shear rate, on flow and consolidation into a dense product
- The effect of processing conditions on properties.

## **2.4 Thesis objectives**

Hence, the main goal of the thesis is to address the knowledge gaps, identified in the previous section, to aid in the development of robust recycling process for XDPE. However, this study will be limited to compression molding. Moreover, the effect of powder size will not be studied at this time.

In order to achieve this goal, the following objectives are proposed.

1. To study the thermal properties of the RXHDPE using Thermal Gravimetric Analyser (TGA) and Differential Calorimeter Scanning (DSC) and then compare with those of VXHDPE to understand the extent of crosslinking during manufacturing and its relation to melting of pulverized powders of RXHDPE. Results of this objective will help define the testing conditions for objective 2.
2. To study the effect of temperature, stress, and time on flow and consolidation behavior of the VXHDPE and RXHDPE and select optimal compression molding conditions
3. Manufacture, through compression molding, RXHDPE and VXHDPE test specimens using the optimal molding condition derived in objective 2.
4. Compare the mechanical properties of RXHDPE with those of VXHDPE to demonstrate the recyclability of XHDPE through compression molding.

## **CHAPTER 3. EXPERIMENTAL DETAILS**

### **3.1 Introduction**

This chapter presents a description of the material and experimental methods used to achieve the objectives of the thesis.

### **3.2 Material**

The XHDPE used in this study was supplied by the rotomolder, Acrylon Plastics, Winkler, MB. The virgin material is manufactured by Exxon Mobil and distributed as Paxon 7000<sup>TM</sup> series of crosslinkable mHDPE resins. The “m” in mHDPE specifies that the HDPE was prepared using a metallocene catalyst which increases the toughness of the polyethylene.

According to the datasheet, this material is recommended when there is a demand for high environment stress-crack resistance (ESCR), toughness, thermal and impact resistance. Some applications include automotive parts, agriculture products, chemical storage tanks, large refuse containers, marine fuel tanks, and recreational vehicles – fuel tanks [31]. A summary of the mechanical properties, from the manufacturer’s data sheet, is presented in Table 3-1.

ExxonMobil recommends a rotomolding process at temperatures between 248°C and 343°C, but the crosslinking can be reached when the internal air temperature exceeds 210°C for more than a minute [32]. Acrylon Plastics supplied both the virgin (VXHDPE) and recycled (RXHDPE) materials after pulverizing them, using the same solid-state grinding process, which yields a powder size of 0.6 mm (28 mesh). The VXHDPE is received by Acrylon as pellets. RXHDPE is prepared from the defective rotomolding parts (RP), whose gel content as claimed by the supplier is above 80%. Figure 3-1 presents the current rotomolding process flowchart.

Table 3-1: Properties of the XHDPE rotomolded product

<b>Mechanical Properties</b>	<b>XHDPE (Paxon™ 7000 series)</b>
Tensile strength at Yield *	19 MPa
Elongation at Yield *	10%
Flexural Modulus (1%) **	760 MPa
Elongation at Break ***	390%

\*ASTM D638      \*\* ASTM D790B      \*\*\*ExxonMobil Method  
(3mm rotomolding samples tested at 50mm/min)

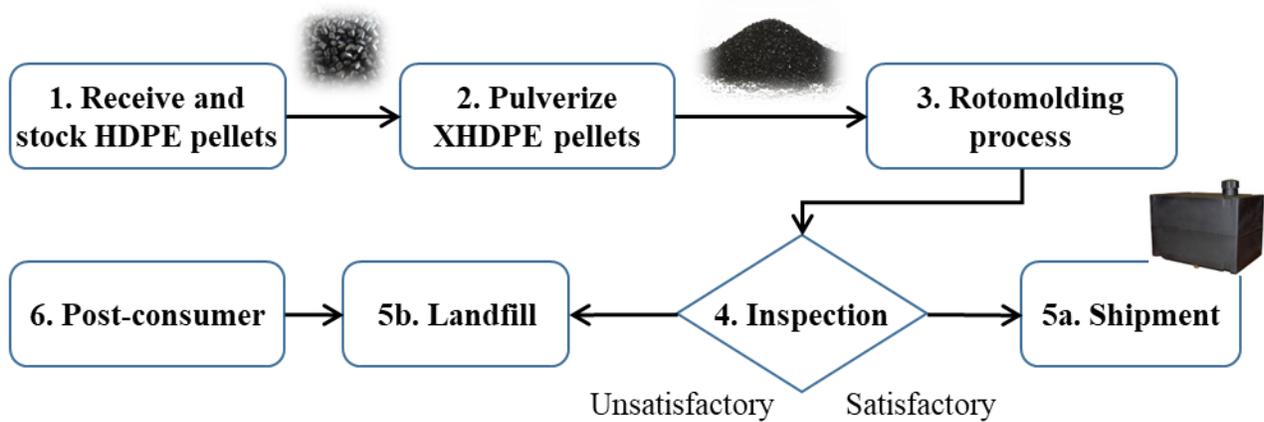


Figure 3-1: Current rotomolding process for XHDPE

The rotomolding process flowchart shows that the defective and the post-consumer products are sent to the landfill, which has an environment impact and has costs involved, especially considering that most part of Acrylon products are large in size. Previously, Acrylon tried to reuse the RXHDPE powder in the rotomolding process without success.

### **3.3 Thermal property characterization**

#### ***3.1.1 Melting and crosslinking***

Preliminary tests were performed using TA Instruments' Q2000 DSC (Differential Scanning Calorimeter) to observe the melting characteristics of both VXHDPE and RXHDPE, using nitrogen as the sample purge gas. In TA Instrument's 2920 DSC (shown in Figure 3-2), was used with air as the purge gas, to study the effect of air present during the rotomolding process. Temperature was ramped up and cooled down at a rate of 10°C/min from -30°C to 300°C under a purge gas flow of 50 mL/min. Some experiments, under nitrogen, used isothermal conditions at 300°C for 1 hour, following the ramping, to detect any crosslinking under nitrogen, before cooling down.

Additional experiments were performed to understand the crosslinking kinetics of RXHDPE and VXHDPE powders using isothermal tests at 185°C, 195°, 205°C and 220°C under flow of air at the rate of 50 mL/min. Isothermal temperatures were reached using a ramp rate of 5°C/min. The DSC sample lids were perforated to allow the purge gas to reach the sample.

#### ***3.1.2 Thermal-degradation***

The degradation characteristics were studied using TA Instruments' Q500 TGA (Thermogravimetric Analyzer) shown in Figure 3-3. Temperature was ramped at a rate of 10°C/min from 25°C to 550°C using nitrogen and air as the purge gas.



Figure 3-2: TA Instruments` DSC 2920 with RCS cooling system

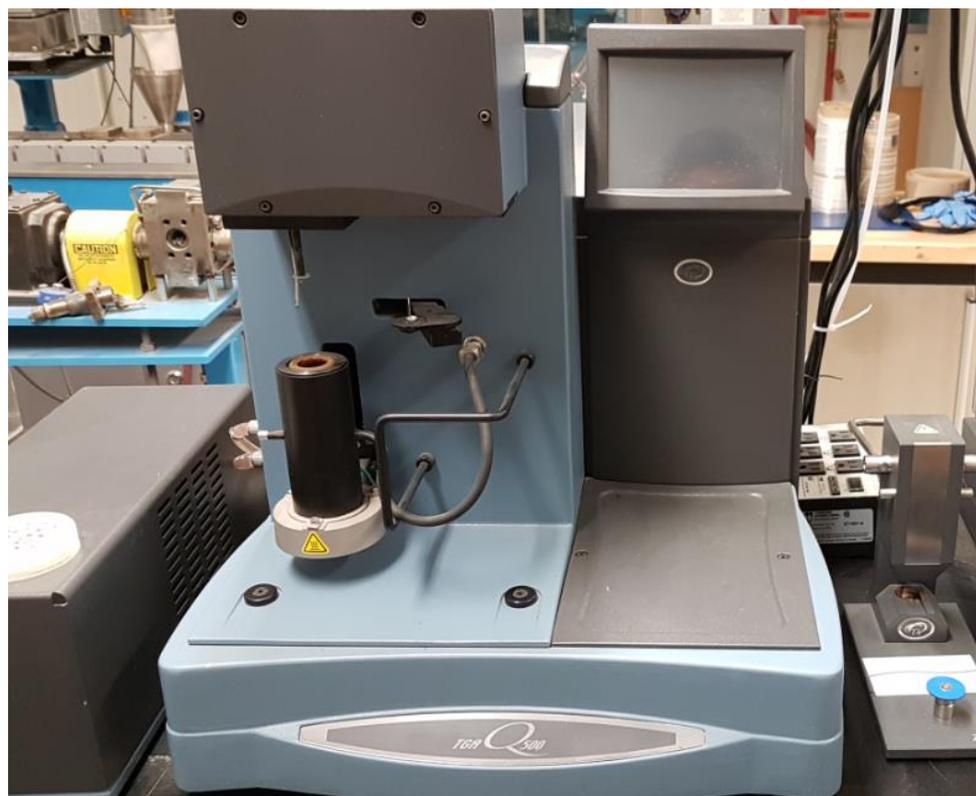


Figure 3-3: TA Instruments` TGA Q500

The TGA sample lids were perforated to allow the purge gas to access the XHDPE sample. In addition, isothermal experiments were completed at 185°C, 195°C, 205°C and 225°C using air as the purge gas.

### ***3.1.3 Consolidation behavior***

Since the goal of this thesis is to recycle the RXHDPE through compression molding, the consolidation behavior of the pulverized powders of the RXHDPE and VXHDPE was studied using the TA Instruments' AR 2000ex (Rheometer). A mold, as shown in Figure 3-4, was designed and manufactured for the research. The bottom mold had a cavity with diameter of 12.62 mm and the top plate had a diameter of 12.60 mm. The cavity had a depth of 0.8 mm. The cavity was filled with the powder and the two molds halves were assembled within the rheometer.

Under constant normal force, the set-up was ramped-up followed by ramp-down between 30°C and 250°C under air atmosphere. The change in thickness of the powder sample was recorded as a function of temperature. Additional test was performed using empty mold set-up at the same ramp-up and ramp-down rate. The thickness change of the empty mold corresponds to change in dimension of the mold due to thermal expansion and contraction of the mold material. This was subtracted from the thickness data for the sample data to obtain the thickness change due to sample consolidation. This procedure is demonstrated in Figure 3-5. The ramp rates and normal forces used were 1°, 5° and 10°C/min and 1, 5, 20 and 40 N. As the top mold has a diameter of 12.6 mm, the uniaxial stresses applied were 0.008, 0.040, 0.160, 0.321 MPa, respectively. Additional isothermal consolidation testing was carried out to understand the difference in consolidation during ramping and isothermal holding. Tests were conducted at 0.321 MPa for 60 minutes at 140°C and 230°C.



Figure 3-4: Rheometer AR 2000EX and inset view of the mold

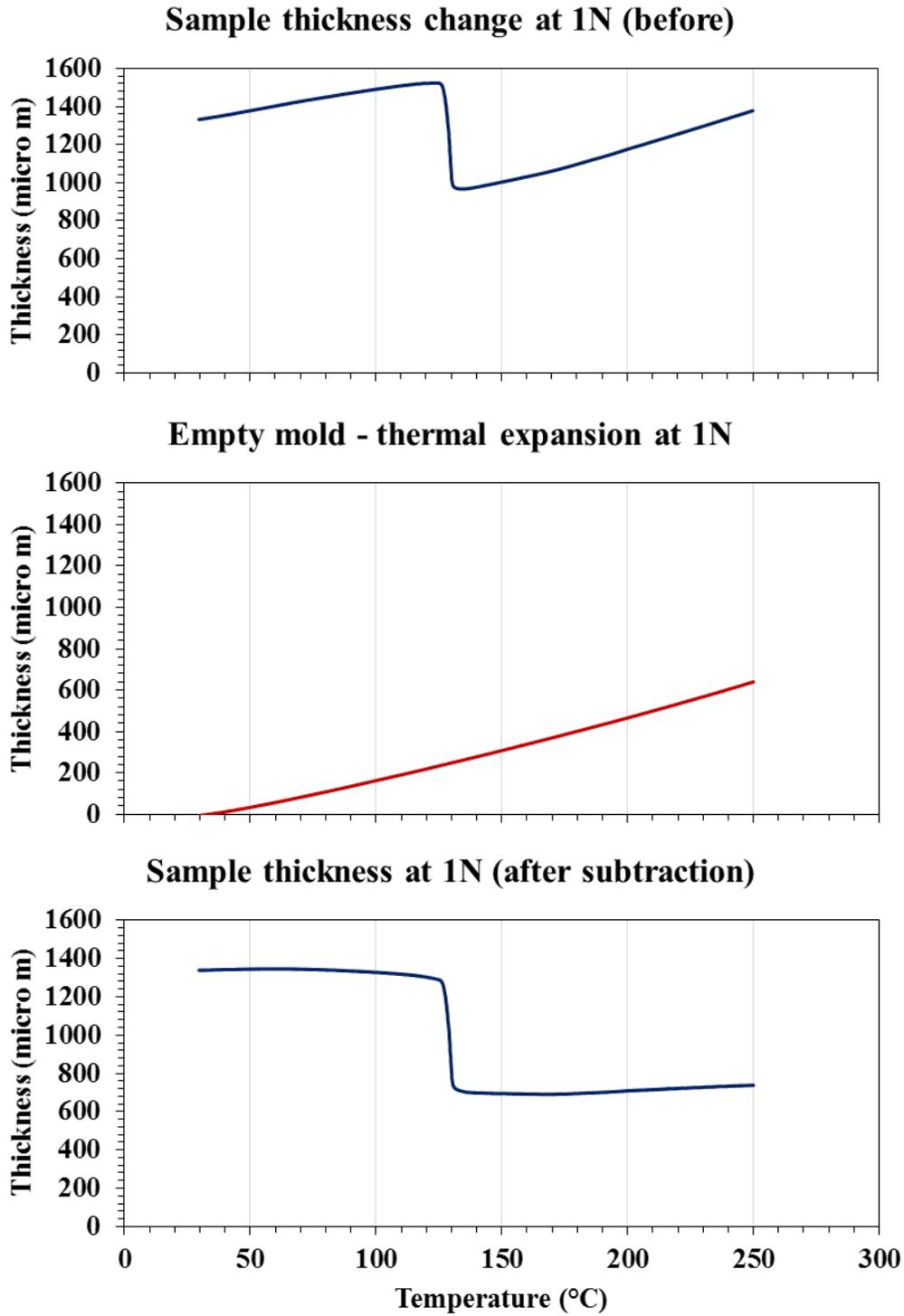


Figure 3-5: Consolidation data extraction method

After the test, the specimen was removed from the mold and trimmed of any lips formed due to squeeze flow in the clearance. The trimmed specimen was used to measure its density, which was subsequently used to study the effect of processing on consolidation.

#### ***3.1.4. Compression molding***

The compression molding was chosen as the process for recycling. A two-part mold as shown in Figure 3-6 was designed and manufactured. A draft angle of  $2^\circ$  between the walls of the top and bottom mold halves was chosen to allow the particle / melt flow under stress, venting of entrapped air, and the easy removal of the top plate / molded part. The initial drawing for the mold design is included in Appendix I. The initial clearance between the walls of the top and bottom halves of the mold was 1mm, but with the addition of aluminum foils the clearance was decreased to 0.2mm.

The bottom mold was filled with pulverized powder, covered with top mold, and held between the platens of the 50-ton Carver hydraulic hot press (WABASH 440H-42) shown in Figure 3-7. The set-up was subjected to the desired stress, heated at a ramp rate of  $10^\circ\text{C}/\text{min}$  to the desired temperature, held at the temperature for 30 minutes, and cooled at the rate of  $5^\circ\text{C}/\text{min}$ . The chosen temperature was  $230^\circ\text{C}$  for most part of the experiments; however,  $145^\circ\text{C}$  was tested using the highest stress used for  $230^\circ\text{C}$  to compare results. Three stresses were tested, starting with the highest stress applied during the rheometer test: 0.32, 1.60 and 4.80 MPa. These molding conditions were chosen based on the results from DSC, TGA and Rheometer. Plates were molded using both RXHDPE and VXHDPE powders. Density of these plates were measured and compared with those from rheometer experiment to evaluate any difference in consolidation during rheometer testing and compression molding since the draft angle used in the rheometer mold was different from that used in the compression mold.

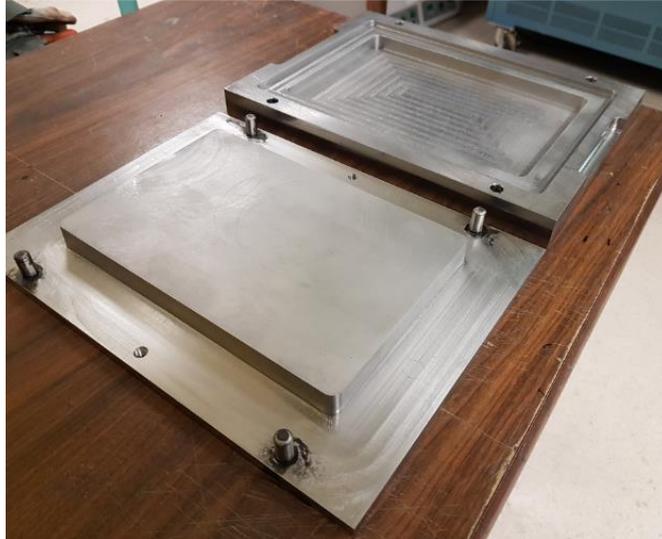


Figure 3-6: Two-part mold for compression molding



Figure 3-7: Carver hydraulic hot press (WABASH 440H-42)

### ***3.1.5 Mechanical testing***

ASTM standard tensile test coupons, with dimensions as shown in Figure 3-8, were machined from these compression molded plates and tested as per ASTM D638 (type I) using MTS Insight 30 test machine, shown in Figure 3-9. Extensometer was used to obtain the strain before yielding, which was subsequently used to determine the modulus of each sample. Test coupons were tested at extension rates of 50 mm/min, which corresponded to strain rates of  $0.005 \text{ s}^{-1}$ . Modulus, yield strength, strain at yield, strain at fracture, and tensile strength were determined from this test. Results for RXHDPE were compared with those for VXHDPE to evaluate the recyclability of RXHDPE through compression molding. A microscopy analysis of the tensile test coupons was performed using the microscope Nikon LV100.



Figure 3-8: XHDPE tensile samples – ASTM D638 (type I)



Figure 3-9: MTS Insight 30

## **CHAPTER 4. RESULTS AND DISCUSSION**

### **4.1 Introduction**

Initially, this chapter presents the results and discussion from DSC, TGA and Rheometer tests. Subsequently, the mechanical properties of the tensile specimens prepared through compression molding are presented and discussed.

### **4.2 Thermal properties**

#### ***4.2.1 Differential Scanning Calorimeter (DSC) results***

The melting, crystallization, and crosslinking characteristics were studied using the DSC. During ramping-up, the pulverized powders of the RXHDPE showed a melting endotherm during heating and a crystallization exotherm during cooling, as observed in Figure 4-1. This indicates that the XHDPE could be recycled through remelting. However, the heat of fusion for RXHDPE was lower than that for VXHDPE by 6.25%, as shown in Figure 4-2, suggesting that the RXHDPE was partially crosslinked.

During ramping in nitrogen environment, no exothermic reaction was observed in both VXHDPE and RXHDPE, during ramping and isothermal hold at 300°C after melting. Peroxide initiators used in this material should have resulted in crosslinking due to thermal activation. That VXHDPE did not show any crosslinking, is unexpected. In order to examine if the pulverization process had decrosslinked the RXHDPE, samples were taken from the surface (RPs) and the mid-thickness (RPc) of the rotomolded part and examined in the DSC. The results are shown in Figures 4-3 and 4-4 for RPc and RPs respectively. The heat of fusion for the RPs recorded during the first run, is less than that for the RPc, which is less than that for the VXHDPE.

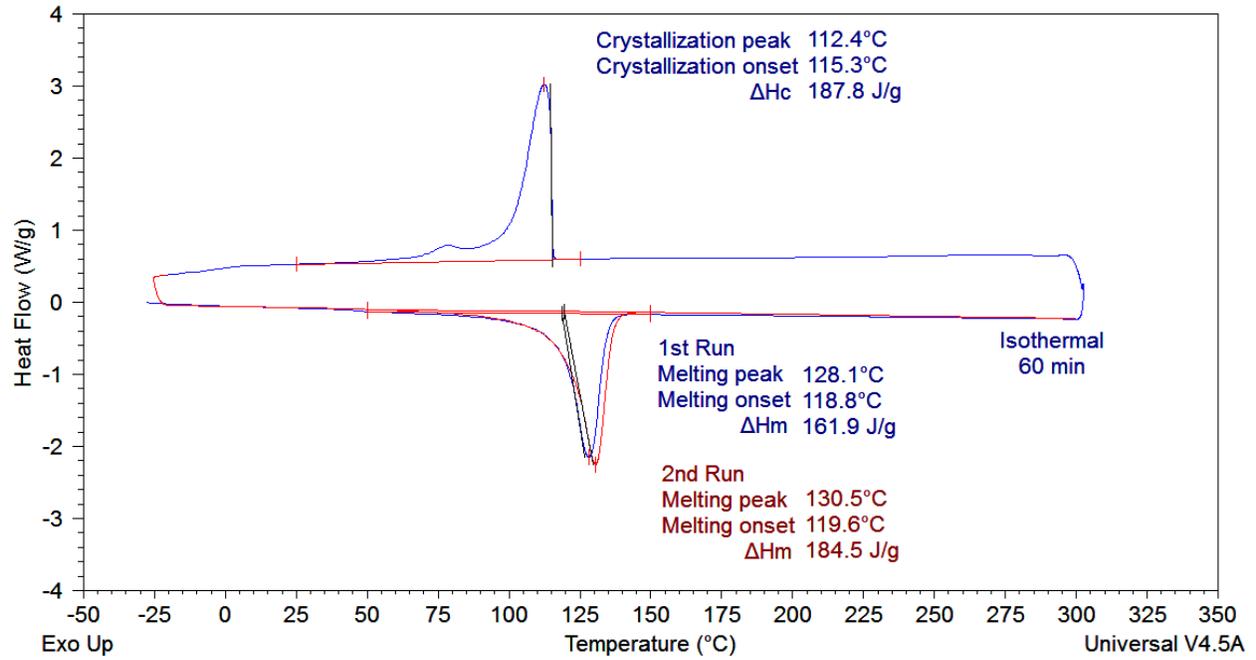


Figure 4-1: DSC result for RXHDPE (purge gas: nitrogen)

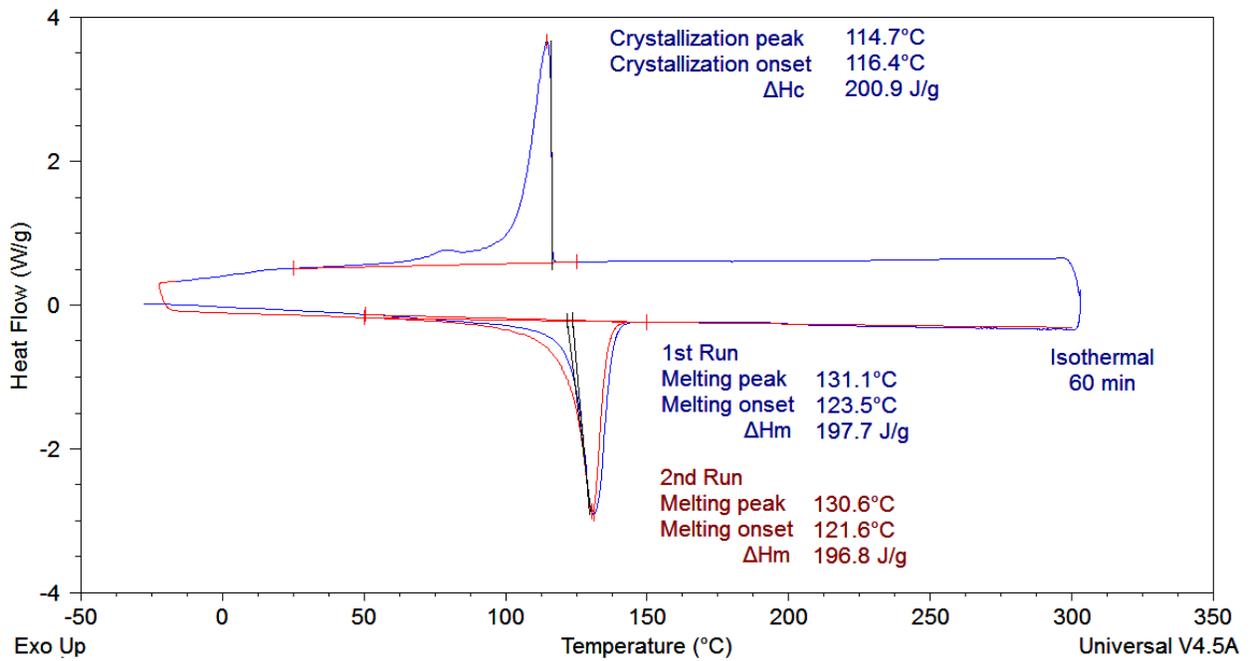


Figure 4-2: DSC result for VXHDPE (purge gas: nitrogen)

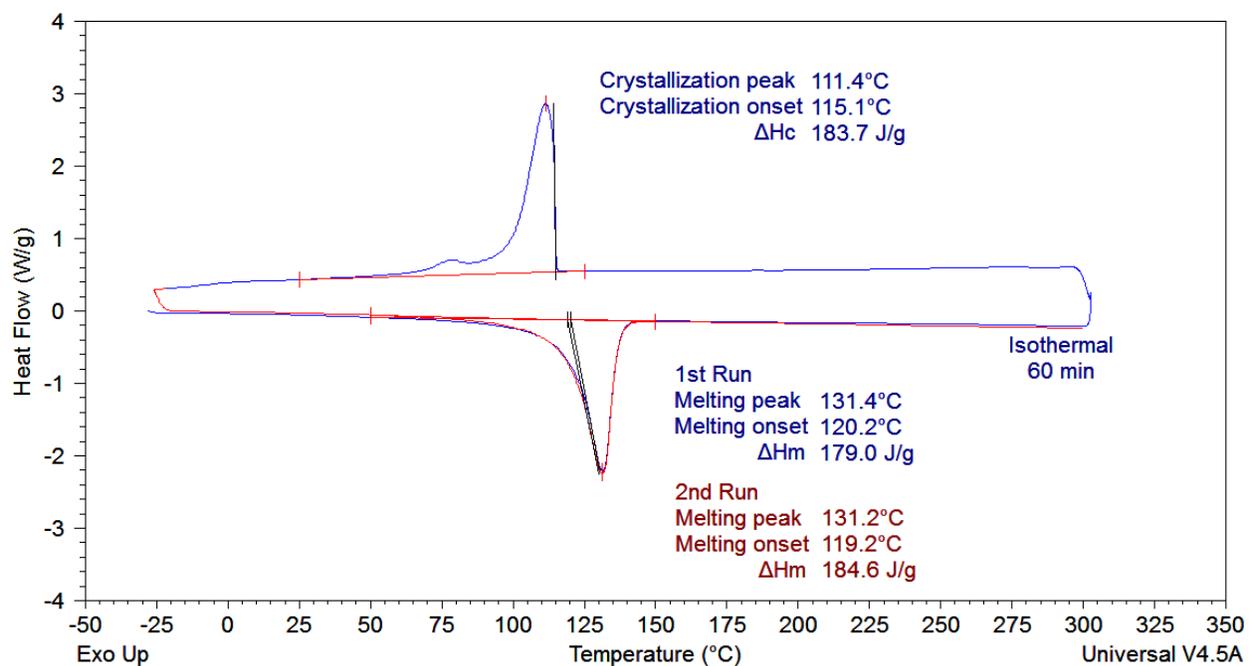


Figure 4-3: DSC results for the RPC (purge gas: nitrogen)

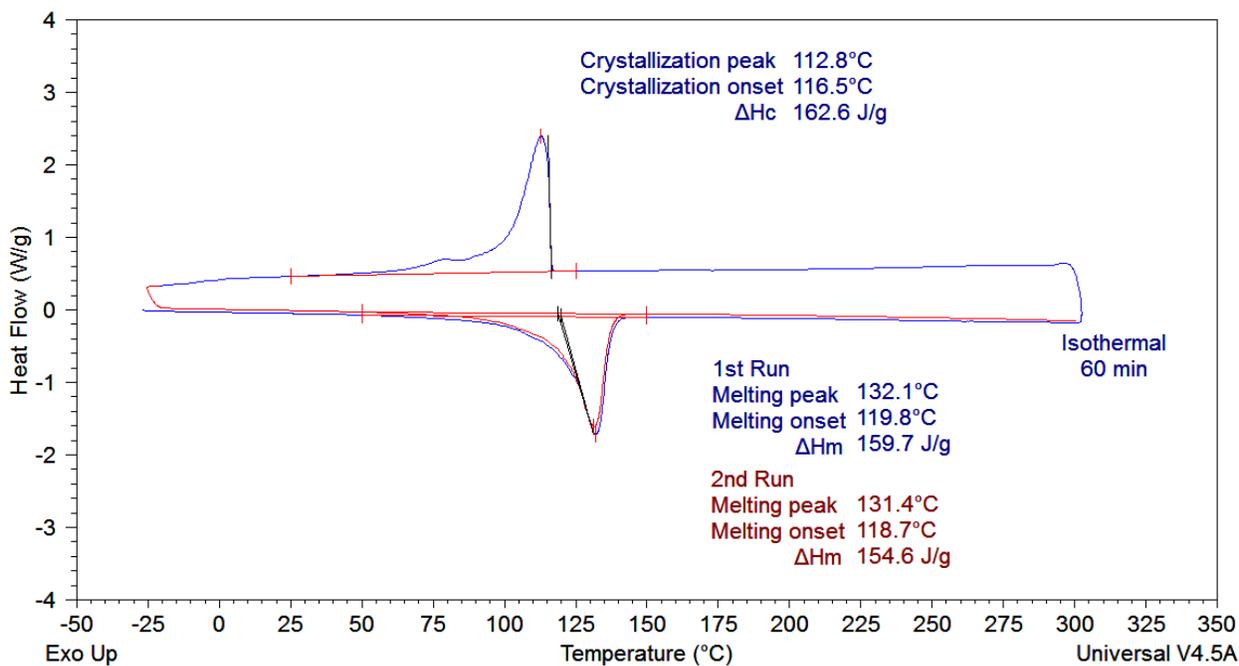


Figure 4-4: DSC results for the RPs (purge gas: nitrogen)

Since the thermal history, specifically cooling rate that can affect the crystallinity and thus heat of fusion, is unknown, the heat of fusion during the second run, after controlled cooling subsequent to the first ramp, is compared in Table 4-1. The heat of fusion for VXHDPE is higher than the other samples suggesting that the amorphous content is greater in the rest.

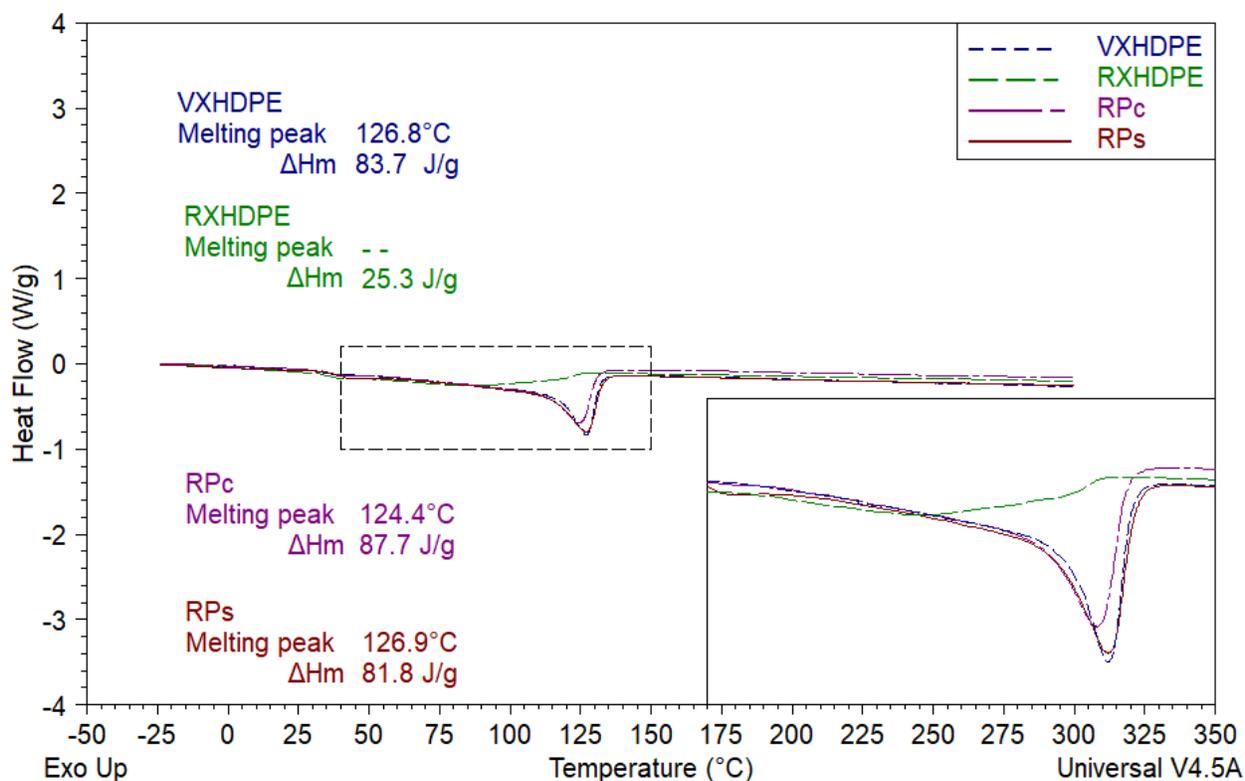
The heat of fusion of reported in the literature [33, 34] for 100% crystalline polyethylene is in the range of 286 – 293 J/g. Using 293 J/g, the % crystallinity in VXHDPE is 66.1. The % crystallinity in RXHDPE, RPc, and RPs are 62.9, 63.3, and 54.6 respectively. Since the cooling rate is the same, the decrease in % crystallinity and increase in % amorphous region in these materials when compared to VXHDPE, is due to crosslinking. The pulverized RXHDPE is a mixture of RPc and RPs; the similar crystallinity for RXHDPE and RPc suggests that the amount of RPs in RXHDPE is minimal; in other words, a very thin surface layer of the rotomolded part crosslinks to a higher extent than the rest of the part. Also, the small difference in the heat of fusion (4.8%) between RXHDPE and VXHDPE suggests that the amount of crosslinking in RXHDPE is low.

Since the surface of the rotomolded part is in contact with air (rather than nitrogen used in the DSC tests discussed above), the above samples were held at 220°C for 60 min in a convection oven. The temperature is recommended for rotomolding of the Paxon™ 7000 series VXHDPE. The VXHDPE and RXHDPE powder were spread on a plate such that the powder particles did not touch each other, RPc and RPs were in the form of thin slices.

After the isothermal treatment in contact with air, the samples were tested in the DSC, using nitrogen as the purge gas. Figure 4-5 shows the comparison of the results for the four materials.

Table 4-1: Summary of DSC results

	VXHDPE	RXHDPE	RPc	RPs
<b>1st Run</b>				
Melting peak (°C)	131 (±0.1)	128 (±0.1)	131 (±0.5)	131 (±1.0)
Melting onset (°C)	123 (±0.3)	119 (±0.3)	120 (±0.6)	113 (±7.2)
$\Delta H_m$ (J/g)	194 (±3.7)	164 (±1.6)	181 (±2.3)	168 (±8.5)
<b>Crystallization Run</b>				
Crystallization peak (°C)	114 (±0.4)	112 (±3.0)	112 (±0.1)	110 (±2.3)
Crystallization onset (°C)	116 (±0.3)	115 (±0.3)	115 (±0.1)	116 (±0.5)
$\Delta H_c$ (J/g)	197 (±3.4)	188 (±0.2)	187 (±3.4)	167 (±3.9)
<b>2nd Run</b>				
Melting peak (°C)	130 (±0.4)	130 (±0.5)	130 (±1.1)	130 (±1.4)
Melting onset (°C)	121 (±0.9)	117 (±2.6)	118 (±1.1)	113 (±5.7)
$\Delta H_m$ (J/g)	194 (±3.1)	184 (±0.2)	186 (±1.0)	160 (±5.3)



The  $\Delta H_m$  decreased for all materials after the isothermal hold in the presence of air. VXHDPE, RPc and RPs exhibited a  $\Delta H_m$  of 83.7, 87.7, and 81.8 J/g, which corresponds to 28.6%, 30%, and 27.9% crystallinity, respectively. RXHDPE did not show a clear melting with the  $\Delta H_m$  of 25.3 J/g and a crystallinity of 8.6%. This result confirms that the exposure to air at high temperatures is required for significant crosslinking. The results also suggest that the pulverized RXHDPE powder crosslinks more than the other three. This will be discussed further in subsequent paragraphs.

Crosslinking kinetics of VXHDPE and RXHDPE was studied using the DSC with air as the purge gas. Results for 3 different ramp rates (5°C/min, 10°C/min and 20°C/min) are compared in Figure 4-6. All exhibited exothermic peak corresponding to crosslinking. This was not observed during testing the sample under nitrogen, as shown in Figures 4-1 and 4-2, confirming the need for the presence of air for crosslinking of XHDPE. The onset temperature for crosslinking increased with increase in temperature and the ramp tests were terminated at 300 °C to prevent degradation of the material. No weight loss was observed after the test.

Based on the crosslinking onset temperature at 5°C/min, four isothermal test temperatures (185°C, 195°C, 205°C and 220°C) were chosen and the VXHDPE and the RXHDPE were tested at these temperatures for 2 hours using air as the purge gas. The results for the VXHDPE are compared in Figure 4-7. The crosslinking reaction was autocatalytic.

The  $\Delta H_x$  increased from 330 J/g at 185°C to 354 ( $\pm 26$ ) J/g at 220 °C. This increase is believed to be due to (a) increase in crosslinking reaction with temperature and (b) increase in level of oxidation with temperature (to be discussed in the next section).

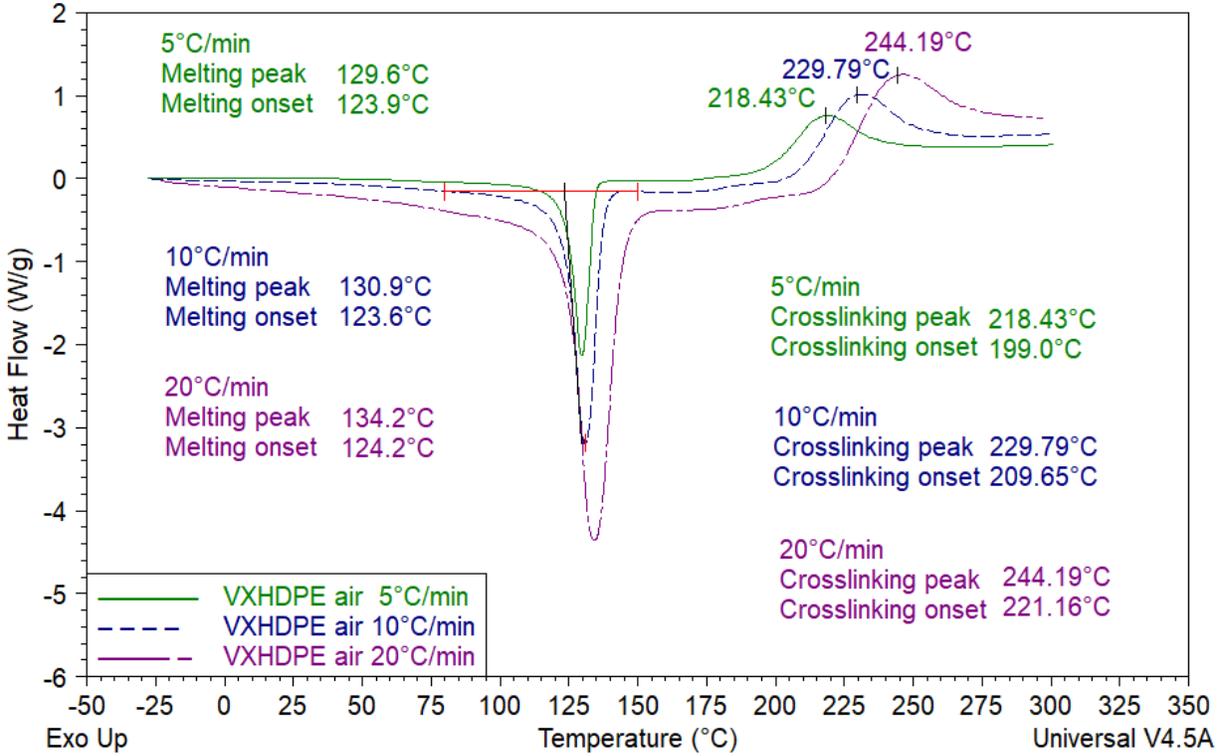


Figure 4-6: DSC results of VXHDPE comparing three different ramp rates

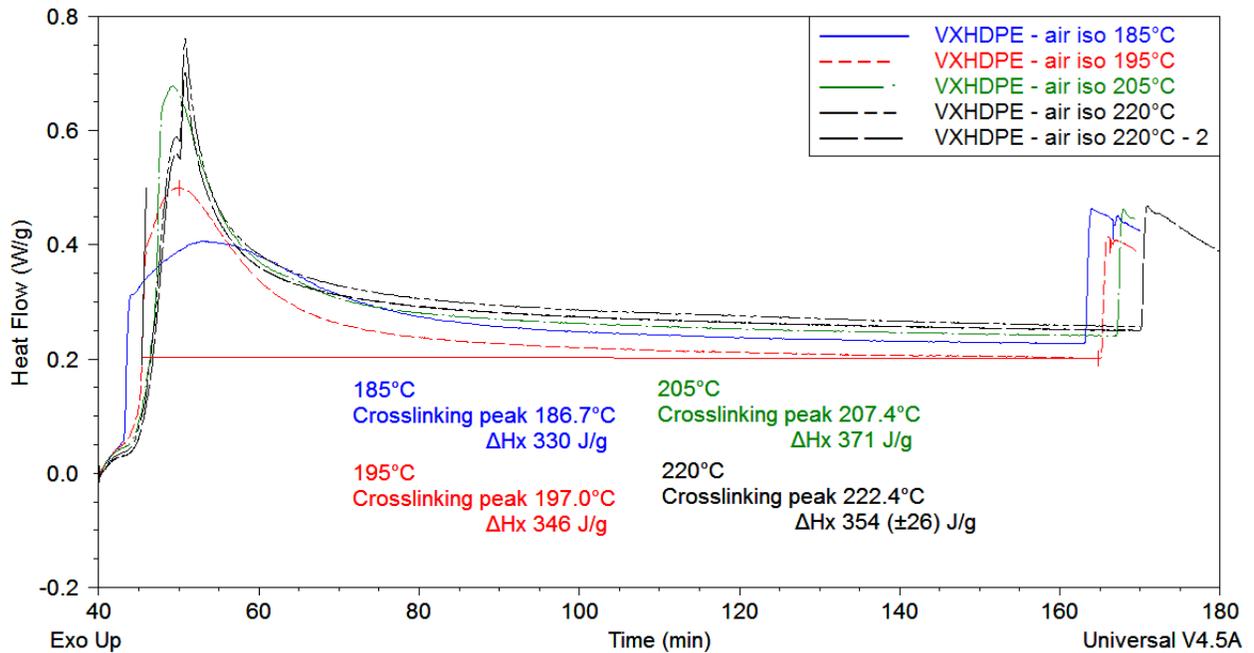


Figure 4-7: Isothermal DSC results of VXHDPE at four temperatures (experiment was repeated twice for 220°C).

The heat of fusion ( $\Delta H_m$ ), measured during subsequent ramp tests, decreased with increase in  $\Delta H_x$  as shown in Figure 4-8. However, the decrease in  $\Delta H_m$  at 220°C was only 20%, suggesting that the VXHDPE was not completely crosslinked even in the presence of air.

However, the heat of reaction for crosslinking of RXHDPE at these isothermal temperatures are almost 10 times higher, as shown in Figure 4-9. The values for  $\Delta H_x$  ranged from 1202 J/g at 185 °C to 4121 ( $\pm 2.5$ ) J/g at 220°C. The samples' weight was measured before and after the experiment and no weight loss was detected using a balance with a resolution of 1mg. This increase is believed to be due to (a) increase in crosslinking reaction with temperature and (b) increase in level of oxidation with temperature (to be discussed in the next section).

The second ramp test, after isothermal testing, yielded a very low value for  $\Delta H_m$ . Comparing the two extreme temperatures, the isothermal crosslinking at 185°C yielded a  $\Delta H_m$  of 57.4 J/g while that at 220°C yielded about 14.1 J/g. Due to the lack of clear melting peaks, the above values are likely to be not the true value. Due to the low magnitude of these values, it can be concluded that the RXHDPE is crosslinked to near completion.

The difference in the crosslinking behavior is due to difference in changes to the morphology of the pulverized powders during heating to the isothermal crosslinking temperatures. The pulverized VXHDPE powders melt and fuse together into a thin film with a glossy surface as shown in Figure 4-10 (a). Hence, only the top surface of the film is exposed to air and crosslinking. However, the pulverized RXHDPE powders do not fuse after melting, as shown in Figure 4-10 (b). Due to exposure of more surface area to air, higher amount of crosslinking is achieved in RXHDPE. In order to confirm this, the thin film of VXHDPE in Figure 4-10 (a) was cut to small pieces as shown in Figure 4-10 (c) and subjected to a second isothermal crosslinking reaction at 220°C. The heat of reaction increased substantially as shown in Figure 4-11.

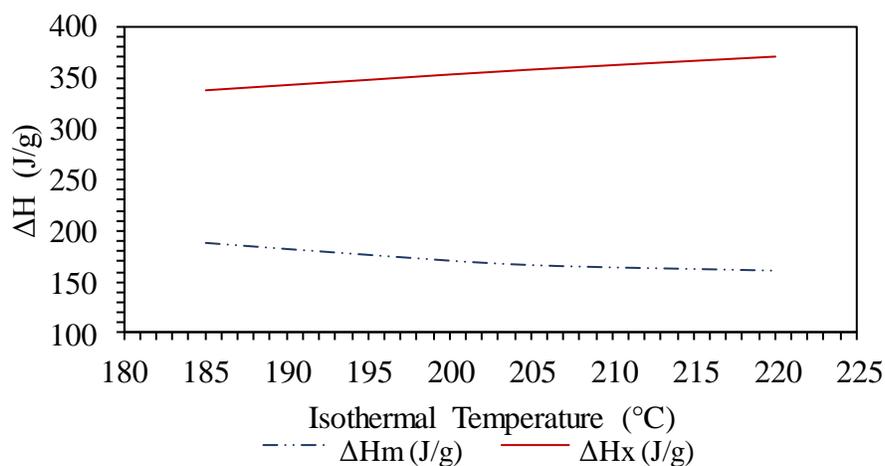


Figure 4-8: Comparison of heat of reaction and melting for VXHDPE after isothermal testing at various temperatures

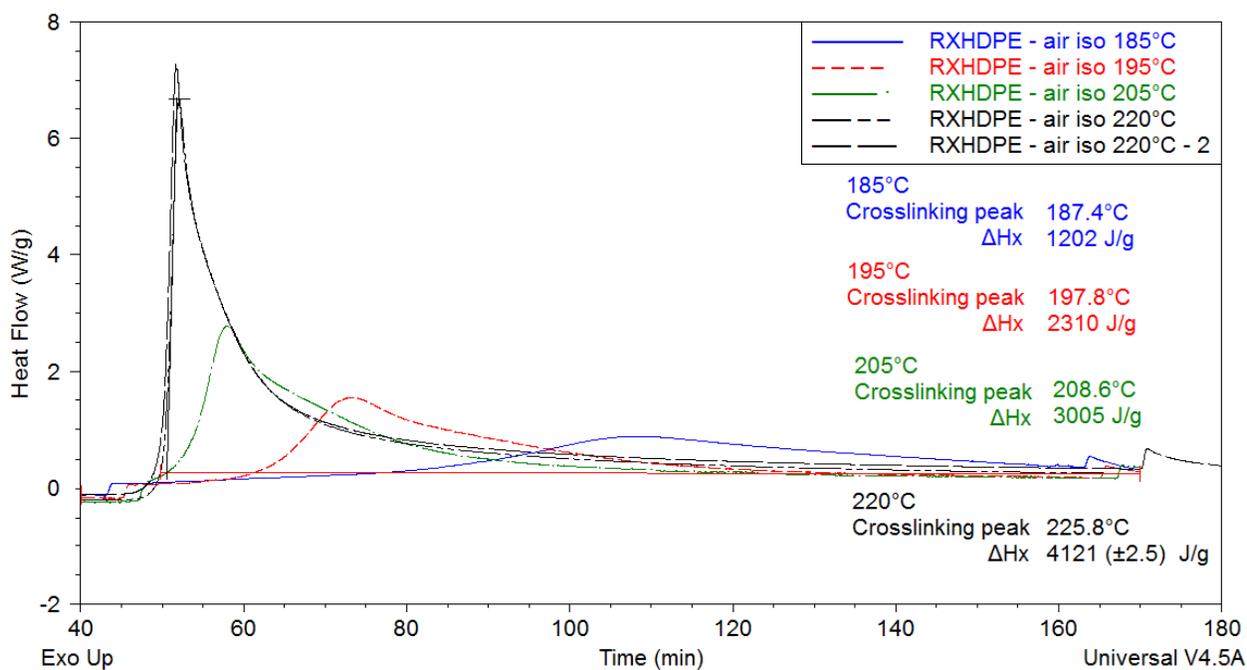


Figure 4-9: Isothermal DSC results for RXHDPE at four temperatures (experiment was repeated twice for 220°C).

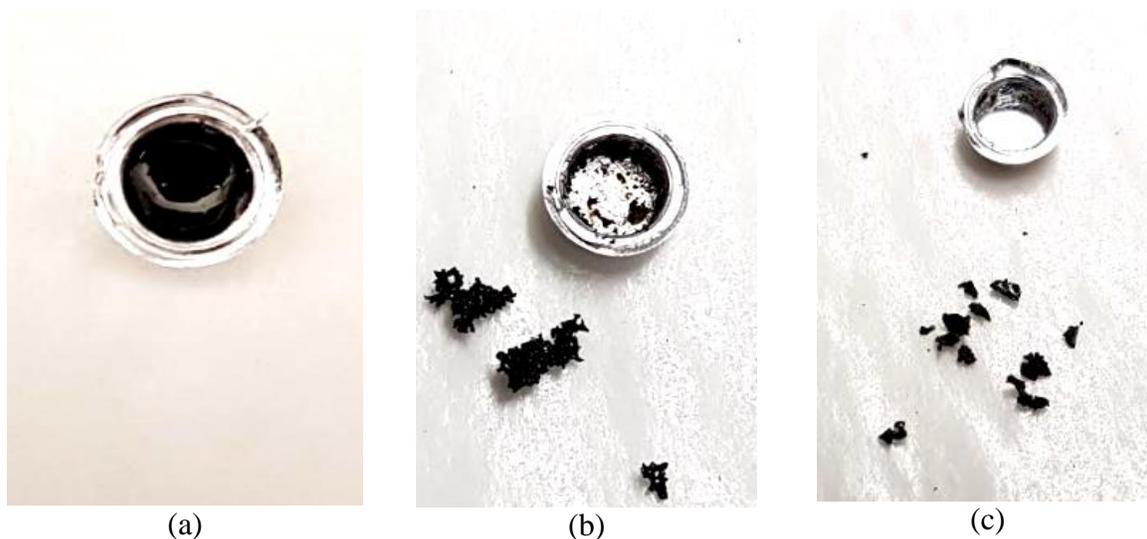


Figure 4-10: (a) VXHDPE after 1<sup>st</sup> isothermal, (b) RXHDPE after isothermal, (c) VXHDPE after 2<sup>nd</sup> isothermal (sample “a” was cut into slices to perform “c”)

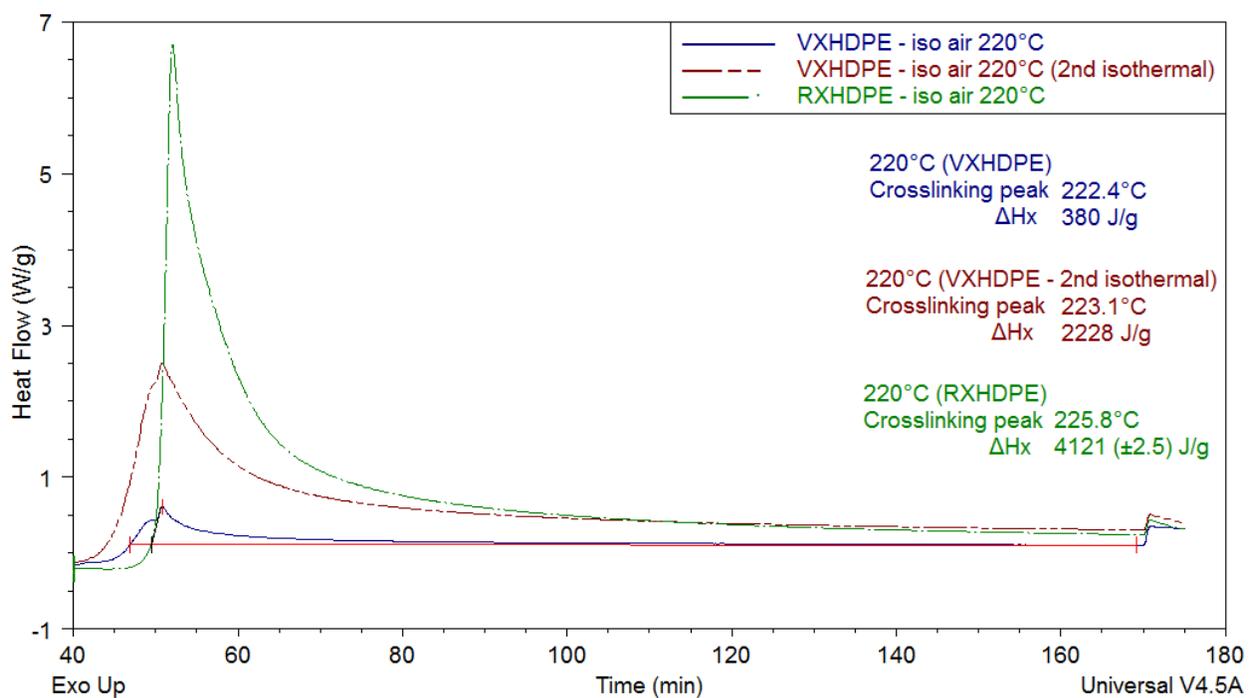


Figure 4-11: Isothermal DSC results for RXHDPE, VXHDPE and sliced VXHDPE (after first isothermal)

The  $\Delta H_x$  for VXHDPE at 220°C was still lower than that for RXHDPE at 220°C and this is thought to be due to the difference in the powder size. This is corroborated by  $\Delta H_m$  measured during subsequent DSC ramp test as shown in Figure 4-12. The  $\Delta H_m$  after the second isothermal was lower than the  $\Delta H_m$  after the first isothermal.

The above results can be used to interpret the difference in the melting behavior of RPC and RPs discussed before. During rotomolding, the VXHDPE turns into a dense part. The interior surface of the part (RPs) would be in contact with air while the material below the surface (RPC) across its thickness will not be in contact with air. This would have resulted in relatively higher crosslinking and lower  $\Delta H_m$  during the DSC test in RPs when compared to RPC.

#### ***4.2.2 Thermogravimetric Analysis (TGA) results***

The results from TGA ramp tests at 10°C/min in nitrogen, shown in Figure 4-13, indicate that both the VXHDPE and RXHDPE degrade similarly.

The decomposition initiation and completion temperatures as well as the weight loss, under nitrogen atmosphere, are similar for both materials. These temperatures are much higher than the temperatures used in rotomolding of VXHDPE.

The TGA results for VXHDPE and RXHDPE, obtained during ramp testing at 10°C/min under the flow of air, are compared in Figure 4-14. The degradation onset temperatures in air for both materials were lower than the degradation onset temperatures in nitrogen. The VXHDPE exhibited a weight loss of 8.5% from 220°C to 384°C. Beyond this temperature, the degradation accelerated.

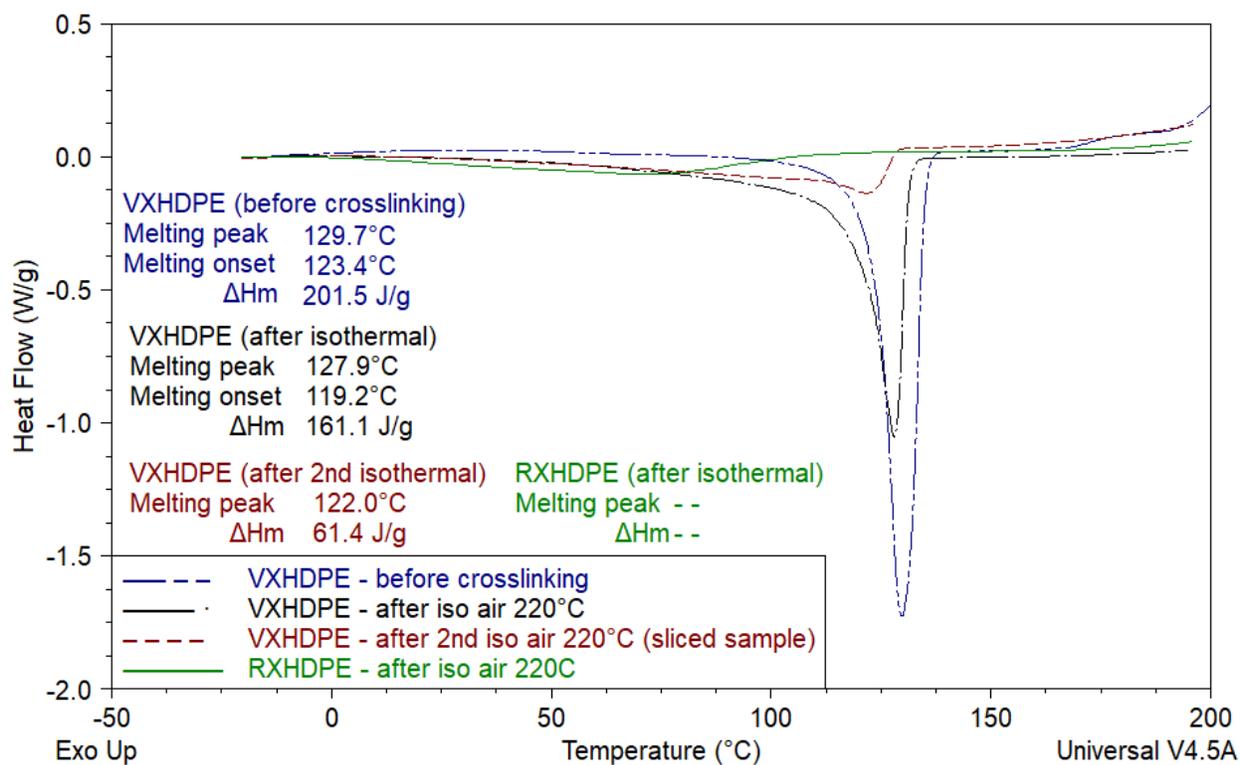


Figure 4-12: DSC results comparing the melting of RXHDPE, VXHDPE and VXHDPE (after second isothermal) of sample cut into slices.

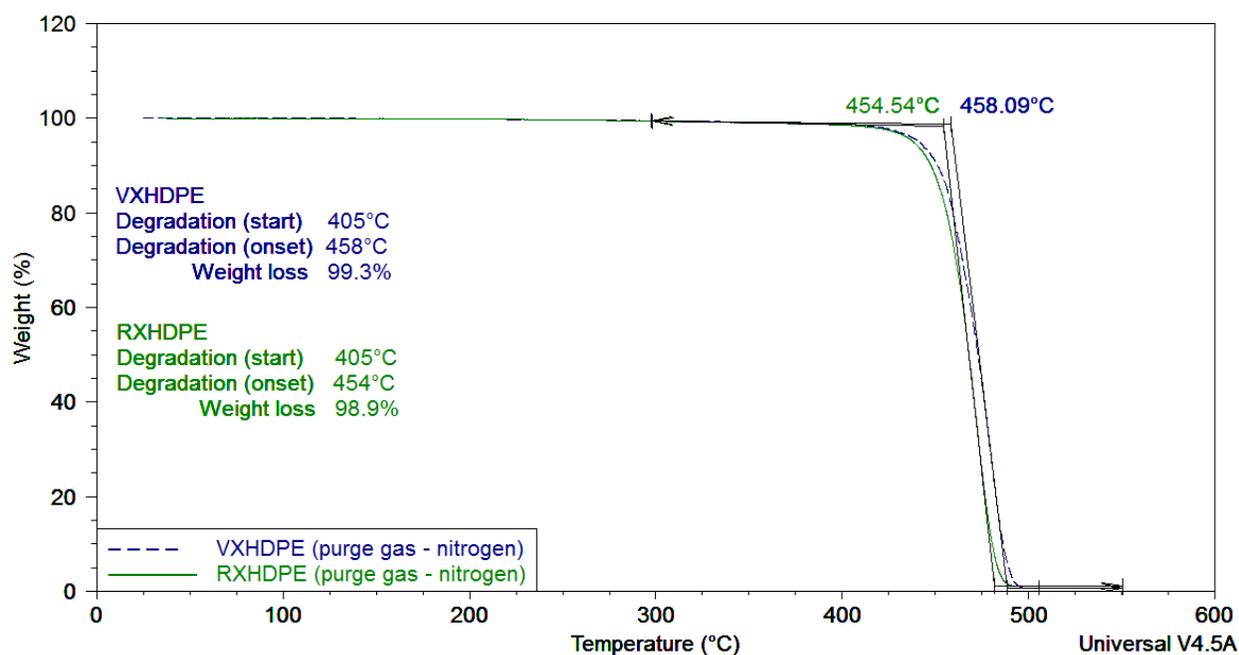


Figure 4-13: TGA results comparing VXHDPE and RXHDPE (purge gas – nitrogen)

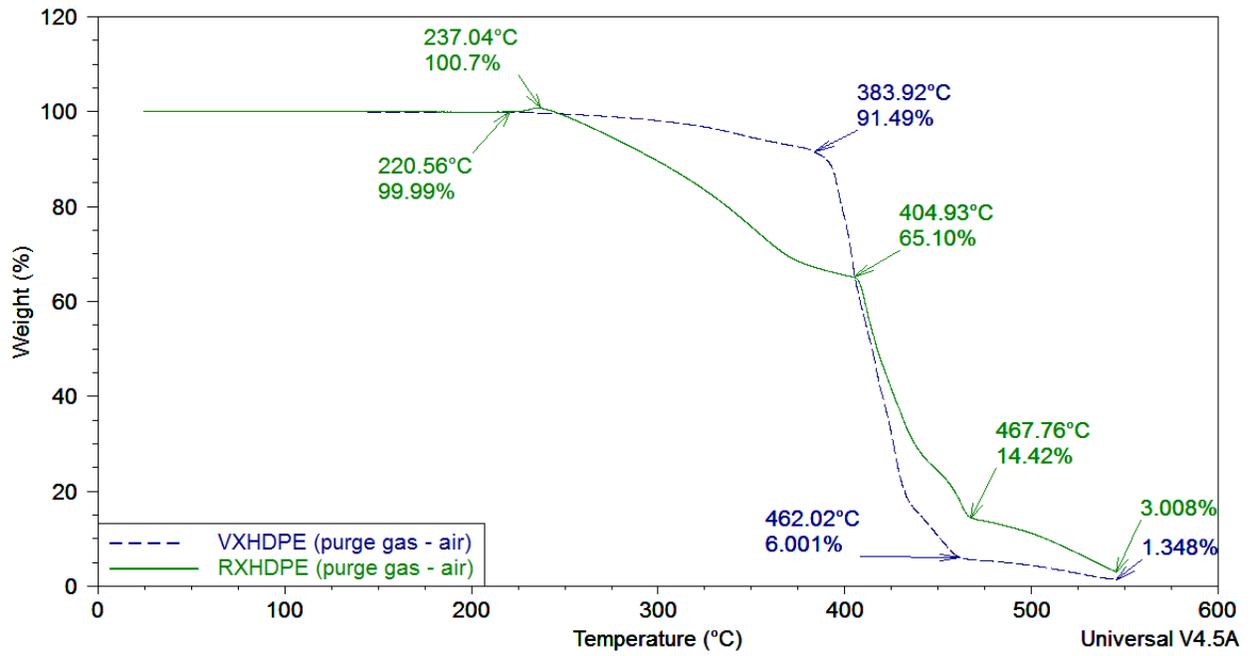


Figure 4-14: TGA results comparing VXHDPE and RXHDPE (purge gas – air)

The RXHDPE exhibited an increase in weight by 0.8% from 220°C to 237°C. This has been observed in non-crosslinkable HDPE also and has been explained to be due to oxidation [35]. Subsequently, the mass of the sample decreased in three steps. The mass loss was 35% between 237°C and 404°C, 51% between 404°C and 468°C and 14% beyond 468 °C. Based on these results, testing and manufacturing in air was limited to 250°C to avoid degradation of the material.

Subsequently, the level of degradation during isothermal DSC crosslinking kinetics testing, was investigated using isothermal TGA tests in air. The temperatures chosen for isothermal tests were 185°C, 195°C, 205°C and 225°C, with a hold time of 3 hours. As the weight loss of VXHDPE was very low, just one isothermal testing at 225°C was completed. Figure 4-15 compares result from the isothermal TGA testing.

After 3 hours at 225°C the VXHDPE had a very small weight loss of just 2.5% without any weight gain at the start. In contrast, the RXHDPE exhibited a weight gain at the start. While the rate of weight gain decreased, the maximum weight gain increased with decrease in isothermal test temperature. The net change in weight by the end of the isothermal hold period is due to weight gain due to polymer oxidation, crosslinking and weight loss due to degradation. The RXHDPE exhibited a much higher weight loss of 20% at 225°C, with a weight increase peak followed by weight loss. The weight gain indicates a possible crosslinking process. Similar trend was observed at for 205°C but with a lower weight loss of 7%. For 185°C, the weight gain peak reached 2.4%, which for that sample represents an increase by 0.29 mg. Considering the results, the only result which shows high degradation was the experiment performed at 225°C. Thus, this temperature was avoided for DSC isothermal experiments performed under air exposure.

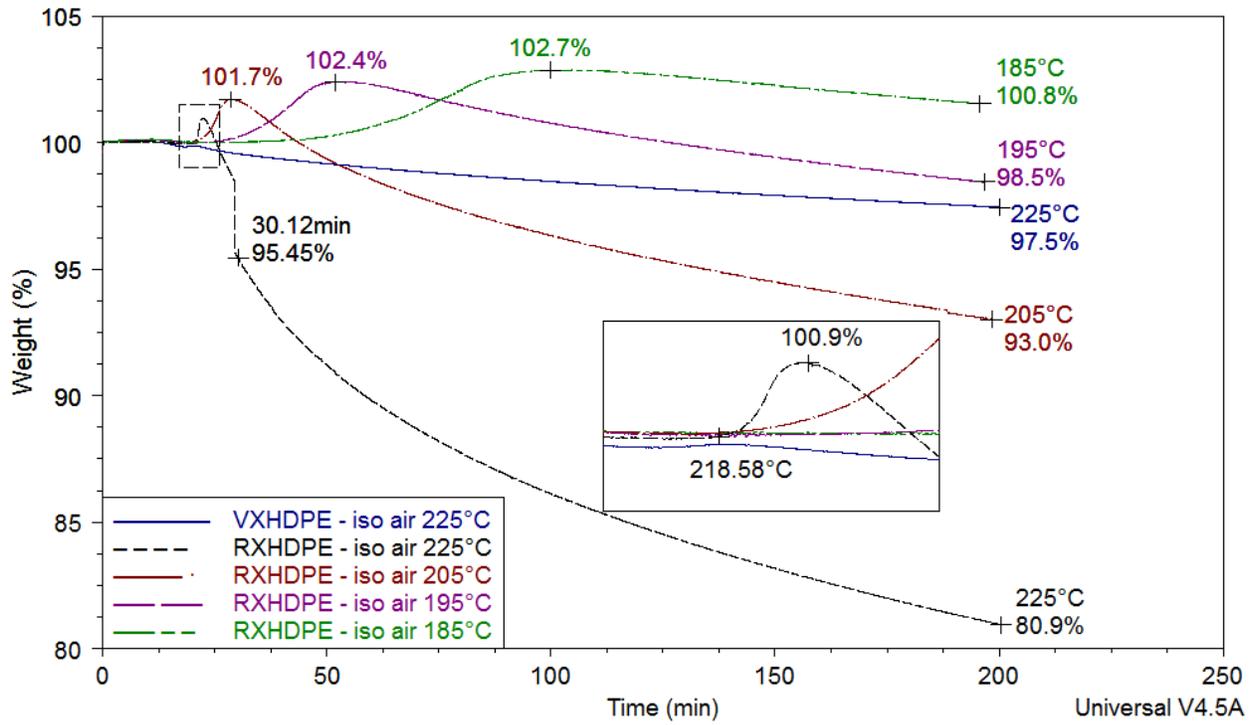


Figure 4-15: Isothermal TGA results for VXHDPE and RXHDPE

### ***4.2.3 Consolidation test results***

Consolidation of the pulverized powder was studied using the rheometer, as per the procedure discussed in Chapter 3, to select the optimal manufacturing conditions for compression molding of test specimens.

The reduction in thickness of the VXHDPE during ramping at 5°C/min to 250°C is plotted in Figure 4-16 for various applied stresses. Sudden decrease in thickness occurred at 129°C for 0.008 MPa, considering the temperature at the center of the transition line, which is due to melting and flow. At 0.008 and 0.040 MPa, the stress was not enough to force the molten polymer through the clearance (0.02 mm) between the top and bottom halves of the mold. Hence, the consolidation reached a plateau beyond the melting temperature.

However, at stresses higher than 0.040 MPa, squeeze flow in the clearance occurred, resulting in further decrease in thickness beyond 130°C and lip formation. This cannot be construed as consolidation. The lip formation stopped at 170°C followed by thermal expansion of the material. No other thickness change was observed during heating and cooling, but the crystallization point at 118°C.

The increase in the slope of the curve below the melting temperature is believed to be due to increase in the packing of powders due to applied stress and increase in the volume of the mold cavity due to thermal expansion of the mold material.

The density of the consolidated VXHDPE samples, which would not be affected by squeeze flow, is provided in Table 4.2 and plotted in Figure 4.17 as a function of stress. The density increased non-linearly with stress towards a plateau value. All stresses yielded samples that looked dense, as shown in Figure 4-18 where the lip formation is more evident with the stress increase.

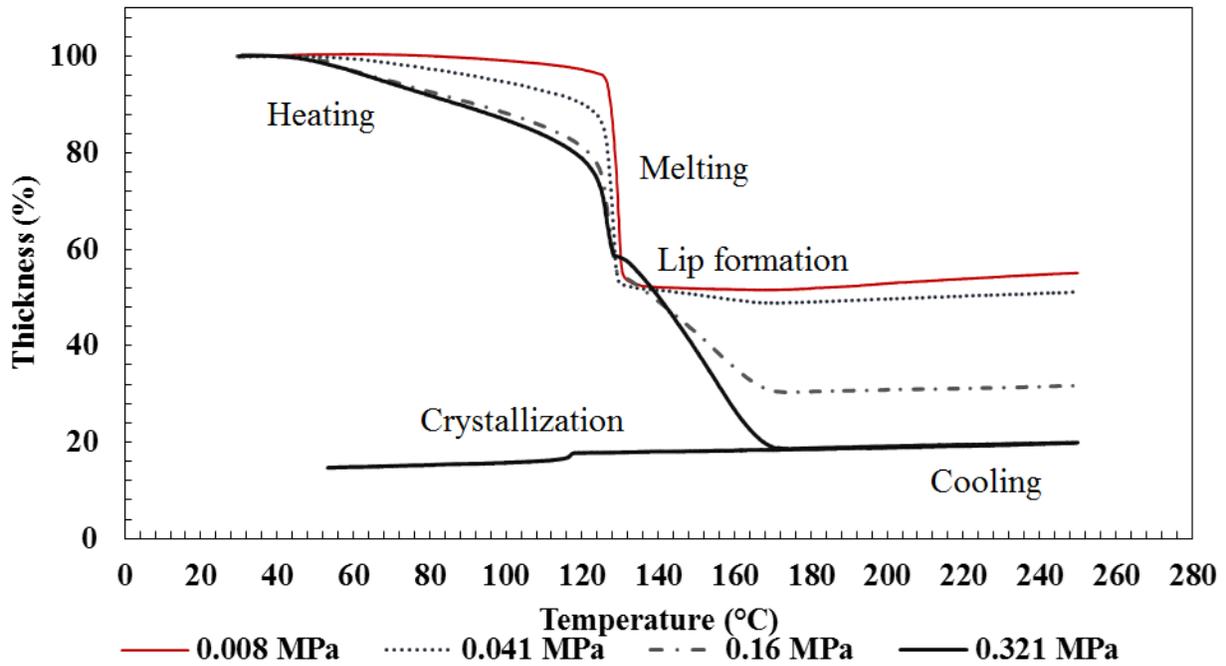


Figure 4-16: Consolidation behavior of VXHDPE powders during ramping under various applied stresses. Full graph is presented for 0.32 MPa with cooling process

Table 4-2: Comparison of densities of VXHDPE specimens consolidated during rheometer tests

Specimen	Stress (Mpa)	Ramp rate (°C/min)	Temperature (°C)	Density (g/cm <sup>3</sup> )
VXHDPE-200	<b>0.008</b>	5	250	0.932 (±0.005)
VXHDPE-201	<b>0.040</b>	5	250	0.944 (±0.004)
VXHDPE 202	<b>0.160</b>	5	250	0.947 (±0.002)
VXHDPE-203	<b>0.321</b>	5	250	0.952 (±0.004)

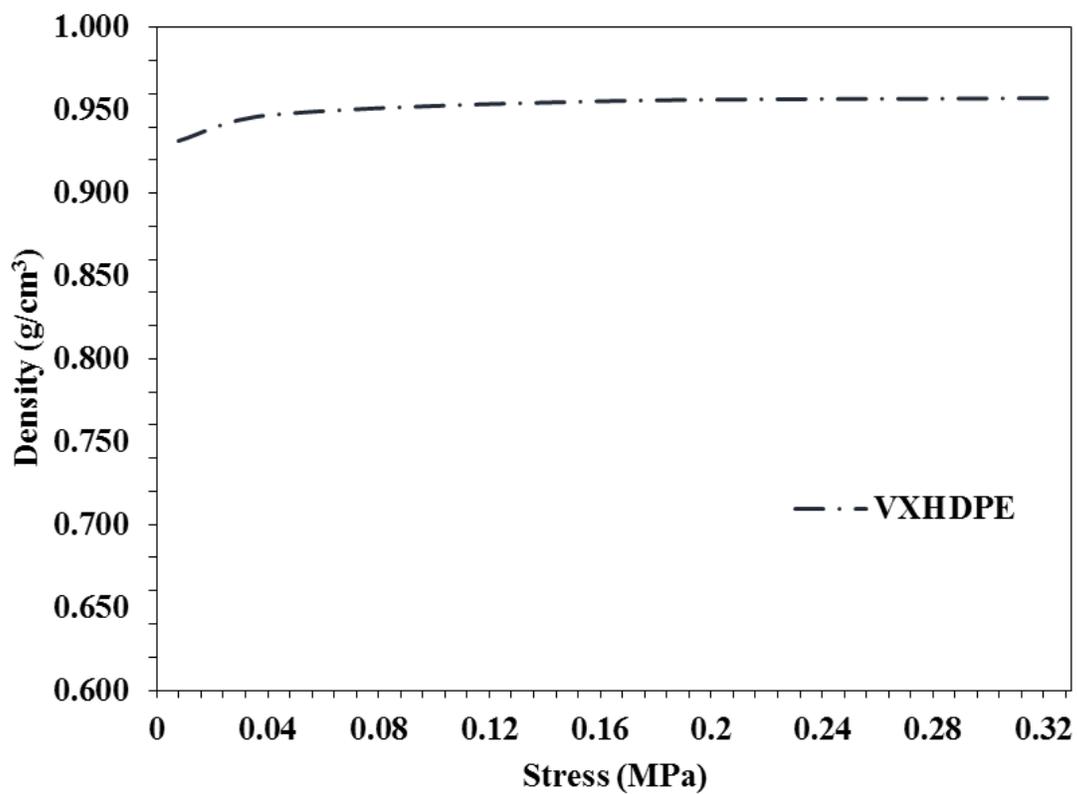


Figure 4-17: Stress effect on the final density of VXHDPE

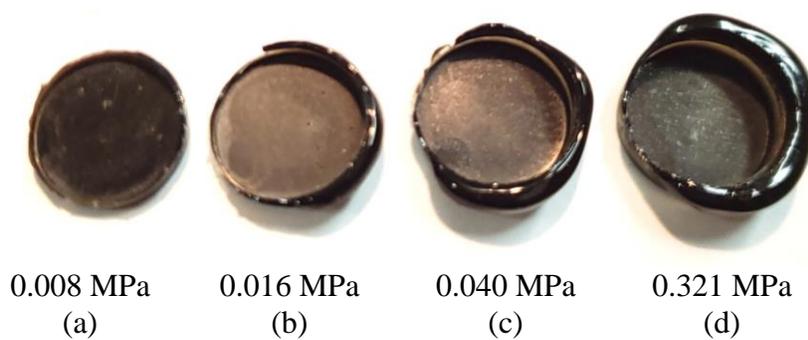


Figure 4-18: Images of VXHDPE consolidated sample prepared at various stresses during ramping from 30°C to 250°C.

The reduction in thickness of the RXHDPE during ramping at 5°C/min to 250°C is plotted in Figure 4-19 for various applied stresses. The consolidation behavior is slightly different from that of VXHDPE. Sudden decrease in thickness, corresponding to consolidation, occurred at 127°C for 0.008 MPa, which is comparable to the melting peak. However, this consolidation temperature decreased when the stress was increased to 0.321MPa. This is believed to be due to higher viscosity of RXHDPE, which is corroborated by the physical state of the samples shown in Figure 4-20.

Under no stress, the powder meld only at the point of contact resulting in a foam (See Figure 4-20 (a)). With increase in stress, flow of the melt increases displacing the voids and increasing the consolidation of the specimens as shown in Figure 4-20. This is reflected in the measured densities tabulated in Table 4-3 and plotted in Figure 4-21.

The magnitude of melt flow is a function of viscosity and applied stress. At lower stresses such as 0.008 MPa, the RXHDPE viscosity at the melting temperature was not enough to cause a complete melt flow and consolidation. With increase in applied stress, the melt flow increased even at higher viscosities (i.e. lower temperatures).

Hence, the decrease in consolidation temperature with increase in stress is due to this combined effect of stress and viscosity on the melt flow. In contrast, the melt flow in VXHDPE was substantial at the melting temperature at all stresses resulting in well consolidated samples at all stresses. No squeeze flow was observed in the RXHDPE due to its higher viscosity.

A secondary consolidation was observed in the temperature range of 200 to 230 °C at 0.008 and 0.040 MPa. During DSC ramp testing under air, exothermic crosslinking was observed in this temperature range. Thus, temperatures above 230°C are indicated for compression molding to include this possible secondary consolidation.

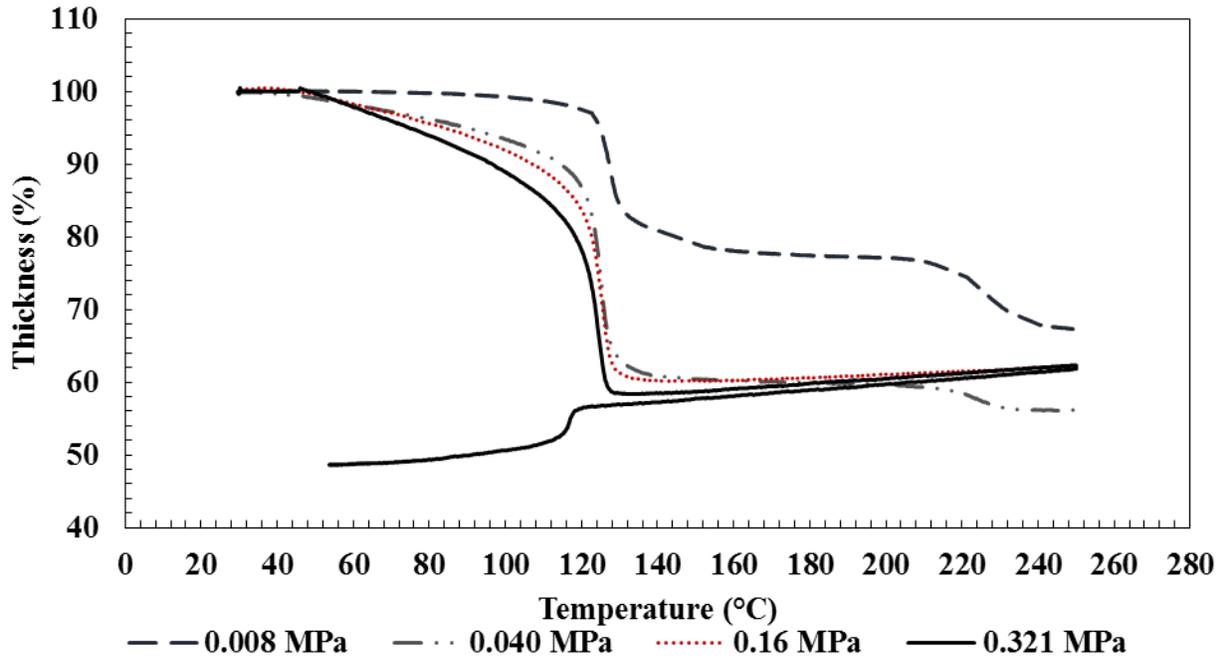


Figure 4-19: Consolidation behavior of RXHDPE powders during Rheometer test

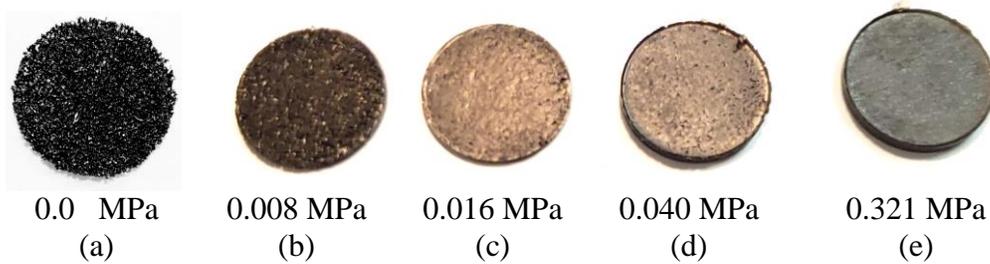


Figure 4-20: Images of RXHDPE consolidated sample prepared at various stresses during ramping from 30°C to 250°C

Table 4-3: Density comparison of RXHDPE specimens consolidated during rheometer tests

Specimen	Stress (MPa)	Ramp rate (°C/min)	Temperature (°C)	Density (g/cm <sup>3</sup> )
RXHDPE-300	<b>0.008</b>	5	250	0.710 (±0.009)
RXHDPE-301	<b>0.040</b>	5	250	0.837 (±0.007)
RXHDPE-302	<b>0.160</b>	5	250	0.917 (±0.020)
RXHDPE-303	<b>0.321</b>	5	250	0.952 (±0.003)

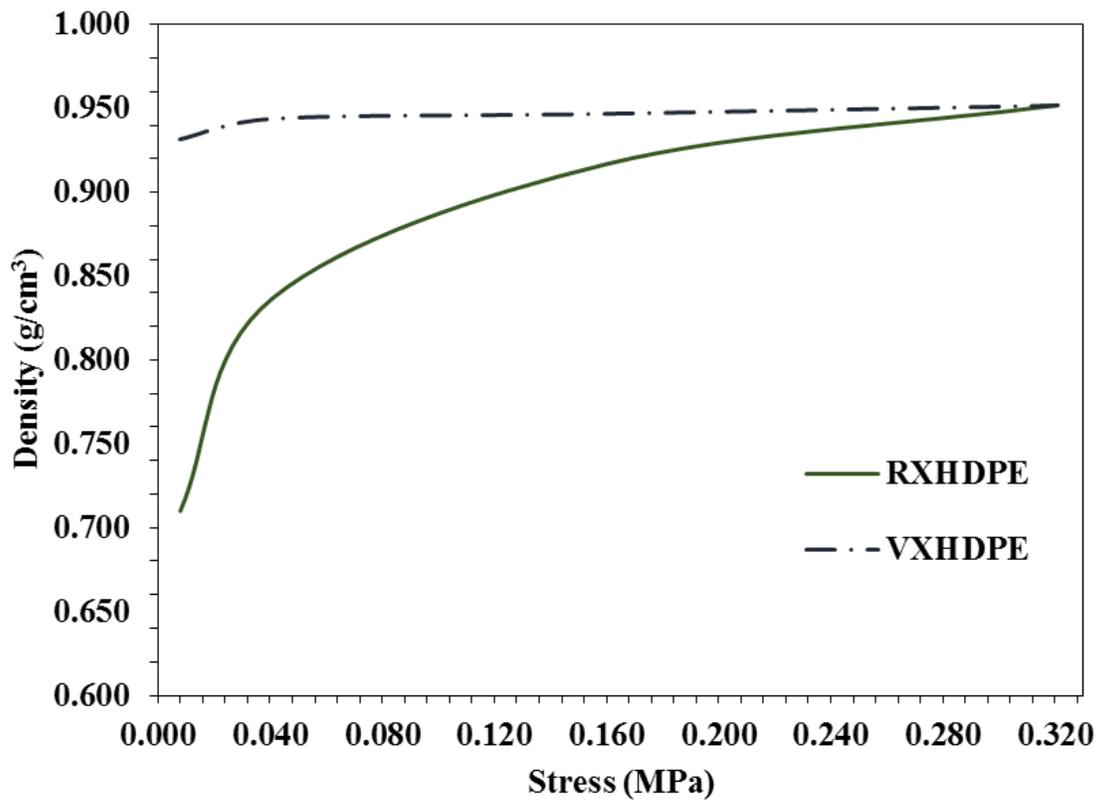


Figure 4-21: Stress effect on the final density of RXHDPE

Hence, the secondary consolidation is believed to be due to this crosslink-induced shrinkage. At higher stresses, the specimens consolidate well before reaching this temperature range. Lack of access to air precludes any crosslinking and hence, no secondary consolidation is observed at stresses  $> 0.040$  MPa.

The increase in the slope of the curve below the melting temperature is believed to be due to increase in the packing of powders due to applied stress and increase in the volume of the mold cavity due to thermal expansion of the mold material. At any given stress, the density of RXHDPE was lower than that for VXHDPE, which is believed to be due to limited flow caused by higher viscosity of the former.

Rheometer results indicates that the highest density achievable through compression molding is  $0.95 \text{ g/cm}^3$ , which was the case for the samples VXHDPE-203 and RXHDPE-303. This result confirms that compression molding can result in RXHDPE plates with density comparable to that for the compression molded VXHDPE plates. Additional tests were done to investigate the effect of molding temperature, ramping rate and isothermal to mold temperature. The results are tabulated in Table 4-4 for RXHDPE. Under the maximum stress of  $0.321$  MPa, the density of the consolidated specimen increased when the final temperature was increased from  $140^\circ\text{C}$  to  $250^\circ\text{C}$ . This is believed to be due to increase in the amount of melt flow with increase in temperature, resulting in increase of the elimination of void content and increase in density. Finally, isothermal experiments performed at  $250^\circ\text{C}$  resulted in sample sticking to the mold, which could be caused by limitations of the mold release coat applied.

#### ***4.2.4 Compression molding***

Based on the rheometer test results,  $230^\circ\text{C}$  was used as the compression molding temperature to avoid damage to the mold caused by RXHDPE sticking to the mold. Also, the compression mold was manufactured with a clearance of  $0.2$  mm (ten times that used in rheometer tests). Images of compression molded plates are shown in Figure 4-22.

Table 4-4: Comparison of densities of RXHDPE specimens consolidated during rheometer tests as a function of temperature and ramp rate

Specimen	Stress (MPa)	Ramp rate (°C/min)	Temperature (°C)	Density (g/cm <sup>3</sup> )
RXHDPE-303	0.321	5	<b>250</b>	0.952 (±0.003)
RXHDPE-304	0.321	5	<b>200</b>	0.943 (±0.005)
RXHDPE-305	0.321	5	<b>140</b>	0.919 (±0.013)
RXHDPE-306	0.321	<b>1</b>	250	0.936 (±0.003)
RXHDPE-303	0.321	<b>5</b>	250	0.952 (±0.003)
RXHDPE-307	0.321	<b>10</b>	250	0.938 (±0.002)



Figure 4-22: Compression molding specimens. (a) RXHDPE sample with voids in the center caused by lack of lateral stress; While lip due to squeeze flow is observed in (c), it has been removed in (a) and (b).

The density of plates compression molded under various stresses is tabulated in Table 4-5. The density of VXHDPE and RXHDPE plates, molded under 0.321 MPa, are lower than that achieved during rheometer tests. This is due to the difference in the clearances used in the two molds. The melt tends to flow laterally under the applied stress and is constrained by the walls of the lower mold. Clearance between the walls of the two mold halves allows the melt to get squeezed out. The amount of squeeze flow depends on the clearance. Constraint to this squeeze flow results in compressive forces along the lateral direction. Lower clearance results in higher lateral stress than the larger clearance. This is believed to be the reason for the lower density in compression molded plates when compared to specimens consolidated in the rheometer. Also, due to higher viscosity and lower melt flow, the magnitude of constraint is likely to be lower in RXHDPE resulting in lower density as compared to VXHDPE at 0.321 MPa.

Increasing the molding stress beyond 0.321 MPa to 4.8 MPa increases the density of RXHDPE; however, it does not reach the value achievable at 0.321 MPa using the rheometer. Further reduction in the clearance used in the compression mold is required. Lowering the molding temperature to 145°C lowers the density, confirming the trend observed in rheometer tests.

### **4.3 Mechanical properties**

From each plate, 5 tensile samples were prepared following the ASTM D638. The tensile test was performed at 50mm/min which is the same speed rate identified in the data sheet supplied by the material supplier. Tensile test results for various specimens are compared in Figure 4-23 and properties determined from this figure are tabulated in Table 4-6.

Table 4-5: Density of compression molded plates.

Specimen	Stress (MPa)	Ramp rate (°C/min)	Temperature (°C)	Density (g/cm <sup>3</sup> )
VXHDPE-400	0.321	10	230	0.935 (±0.002)
RXHDPE-500	0.321	10	230	0.850 (±0.075)
RXHDPE-501	1.6	10	230	0.933 (±0.005)
RXHDPE-502	4.8	10	230	0.940 (±0.004)
RXHDPE-503	4.8	10	145	0.934 (±0.001)

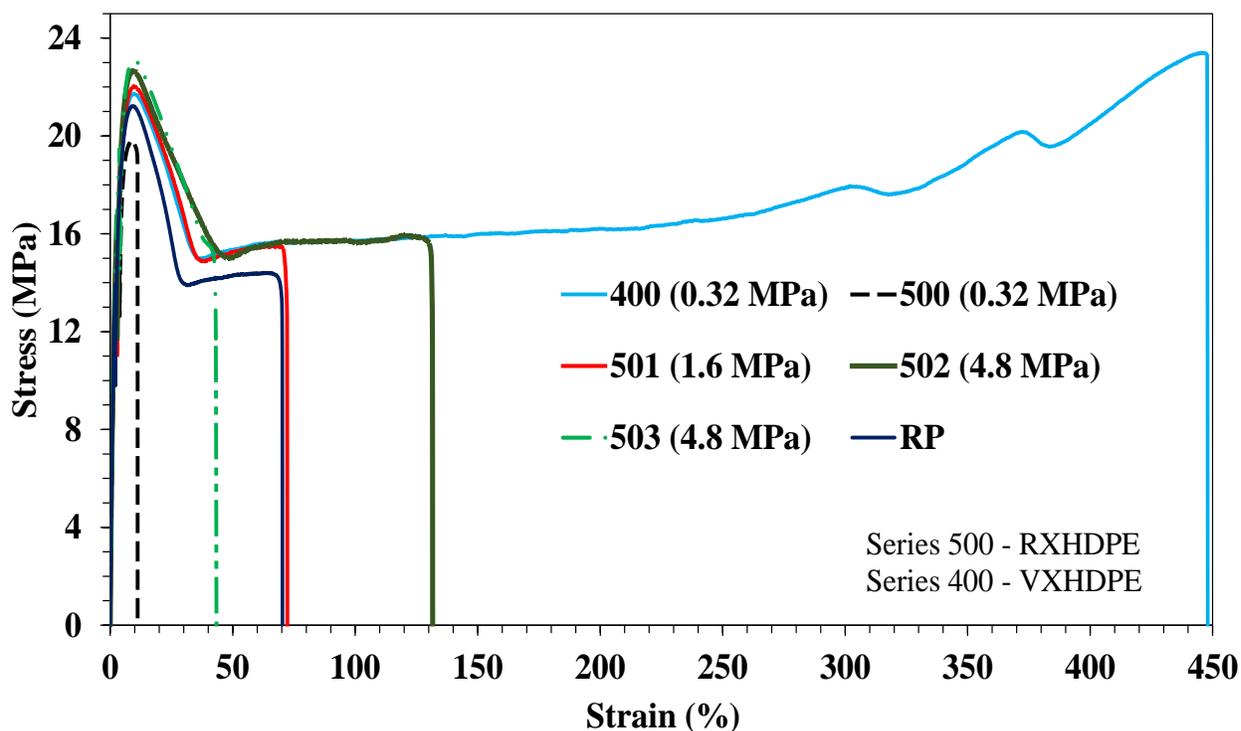


Figure 4-23 Tensile test results for both virgin and recycled XHDPE

Table 4-6: Mechanical properties of the compression molding samples

Specimen	Elastic Modulus - 1% secant (MPa)	Tensile Strength at Yield (MPa)	Elongation at Break (%)	Strength at Failure (MPa)
VXHDPE-400	900 (±36)	21.5 (±0.3)	318.1 (±124.7)	18.2 (±4.1)
RXHDPE-500	787 (±198)	13.3 (±2.8)	6.7 (±2.8)	10.6 (±3.7)
RXHDPE-501	890 (±14)	21.9 (±0.2)	61.1 (±10.8)	11.2 (±2.7)
RXHDPE-502	929 (±32)	22.4 (±0.2)	113.3 (±35.2)	14.8 (±2.8)
RXHDPE-503	974 (±48)	23.1 (±0.2)	38.8 (±3.6)	13.7 (±1.4)
RP	1131 (±17)	21.5 (±0.2)	68.1 (±19.2)	8.3 (±4.4)
Paxon <sup>TM</sup> 7000	-	19	390	-

Properties of VXHDPE are comparable to those of Paxon<sup>TM</sup> 7000 provided in the data sheet. Observed difference could be due to difference in the manufacturing process – compression molding versus rotomolding. In rotomolding, no stress is used. The scatter in the strain to failure suggests that there may be microvoids within the plate acting as stress-concentrators. Refinement in mold design, enhancing the lateral stress, is suggested to increase the density and to reduce the scatter.

The modulus and yield strength of RXHDPE-500 are lower than those for VXHDPE-400 although both were molded under same stress of 0.321 MPa. This is due to the presence of voids indicated in the Figure 4-22 (a) which caused the lower density of RXHDPE-500. When the molding stress was increased to 1.6 MPa resulted in RXHDPE-501 with density, modulus and yield strength comparable to those of VXHDPE-400. Increasing the molding stress further to 4.8 MPa resulted in density, modulus, and yield strength of RXHDPE-502 higher than those of RXHDPE-501 and VXHDPE-400.

Molding at a lower temperature of 145 °C resulted in lower density in RXHDPE-503 when compared to the density of RXHDPE-502 molded at 230 °C. Despite the lower density, the modulus and yield strength were higher. Lower density suggests more entrapped air in RXHDPE-503, which could have resulted in more crosslinking of material surrounding these voids, resulting in a higher modulus and yield strength when compared to RXHDPE-502. Further study is required to elucidate this.

Tensile strength and failure strain of all RXHDPE samples were lower than those of VXHDPE. These properties of RXHDPE were improved when molding stress was increased from 0.321 to 4.8 MPa. This is due to decrease in void content (i.e. increase in density) due to increase in molding stress.

Yet, these properties of RXHDPE-501 were inferior to those of VXHDPE-400 with similar density. It is possible that the size, shape and distribution of voids in RXHDPE are different than those in VXHDPE due to difference in viscosity and flow. This difference is believed to be the reason for the observed difference.

Thus, to elucidate this, a microscopy analysis was performed with three samples of VXHDPE-400 and RXHDPE-502. Films with thickness of 0.1mm were cut to observe the presence of voids. Figure 4-24 compares micrographs from various samples. Virgin samples shows round voids in few locations while the recycled samples presents higher number of voids with a star shape. The void shape in the recycled sample indicates that the powder is not fully flowing in some locations during the consolidation process.

In summary, these results suggest that RXHDPE can be successfully recycled through compression molding. However, RXHDPE would require a higher molding stress than VXHDPE to achieve a similar density. While both materials with similar density have comparable modulus and yield strength, the tensile strength and failure strain of RXHDPE were inferior to those of VXHDPE. This is believed to be due to difference in size, shape, and distribution of voids. Increasing the lateral stress through reduction in the clearance between the walls of the top and bottom mold halves will likely improve the density, narrow the difference between the two materials, and improve the failure strain and stress.

Finally, RXHDPE-502 shows elastic modulus 17.9% lower than the RP sample, but tensile strength and elongation to break 4.2% and 66.4%, respectively, higher than RP. This indicates that the recycled material has properties very similar to the rotomolding part and confirms the effectiveness of the recycling process.

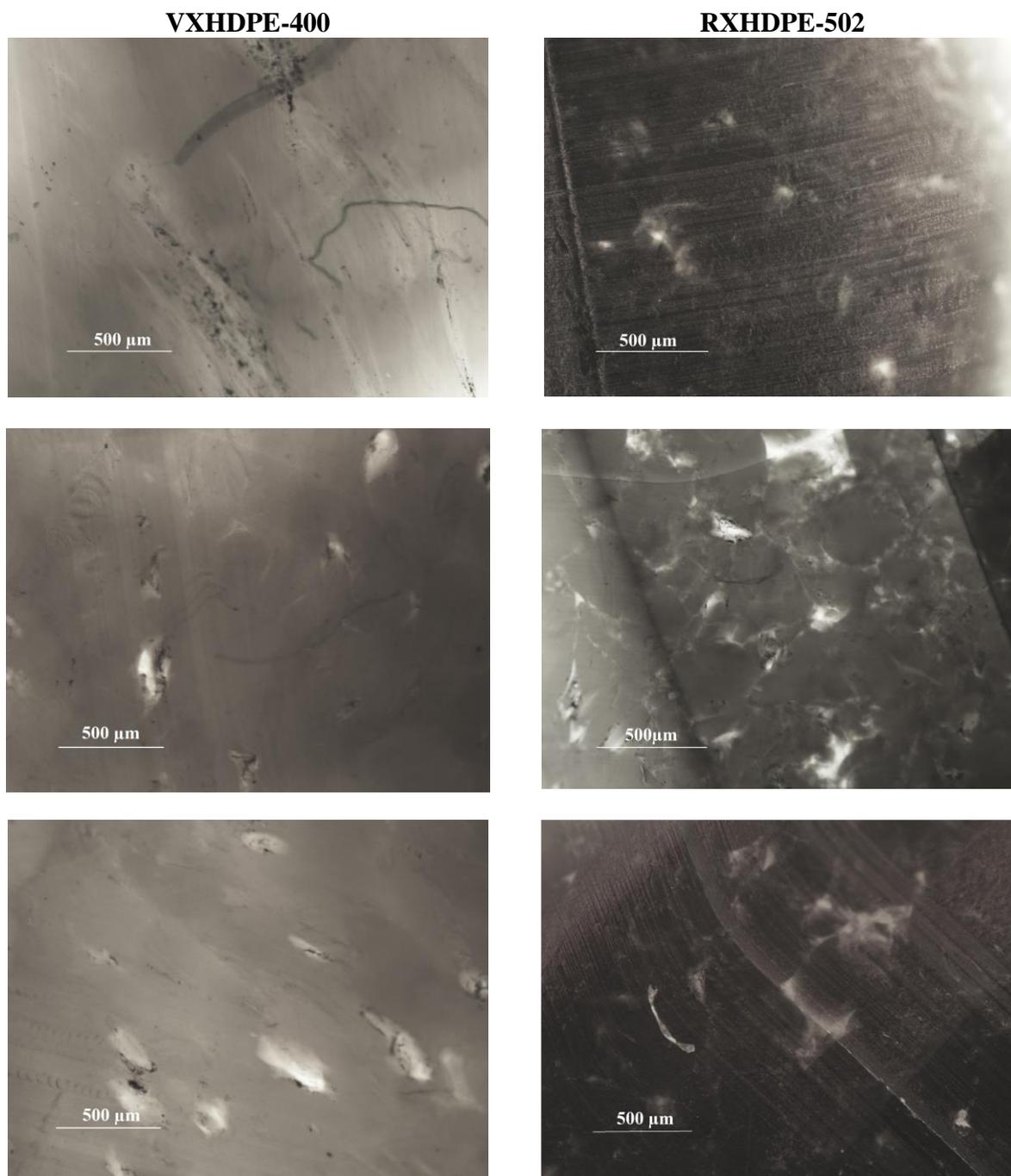


Figure 4-24: Images of VXHDPE and RXHDPE using the microscope Nikon LV100 at 3 different locations.

## CHAPTER 5. CONCLUSIONS

The goal of this thesis was to develop a process to recycle crosslinked HDPE waste, generated during rotomolding process and after use. This goal and the four objectives, proposed to realize this goal, have been successfully realized through the development of a compression molding process to recycle this material. The thermal properties of VXHDPE and RXHDPE were investigated using DSC and TGA. Based on the thermal properties results, test conditions were chosen to study the consolidation behavior using a Rheometer. Based on these results, compression molding conditions were chosen to manufacture tensile specimens using both VXHDPE and RXHDPE. Both materials exhibited similar tensile properties with the exception of failure strain and stress, which was less for the recycled material. Improvement in mold design required to improve the failure strain and stress has been identified. This Chapter presents a summary of findings from the tasks completed during this thesis, conclusion based on these findings, and recommendations for future work.

### 5.1 Summary of results

Findings based on the tasks completed during this thesis are as follows:

- The crosslinking of VXHDPE during rotomolding varies across the thickness of the part – maximum at the surface (i.e. air side), which decreases towards the surface in contact with the tool. This is due to the role played by the air in crosslinking, despite the use of thermally activated peroxide initiator in the material.

- The pulverized RXHDPE powder, consisting of crosslinked and non-crosslinked material, could be melted and thus recycled. The heat of fusion of RXHDPE was lower than that of VXHDPE by ~6% suggesting that the crosslinked amount was minimal.
- Consolidation studies using rheometer indicated that both RXHDPE and VXHDPE could be compression molded to a density of 0.95 – 0.958 g/cm<sup>3</sup>. However, higher consolidation stress is required for RXHDPE when compared to VXHDPE to realize the same density. Higher consolidation temperature resulted in higher density and optimal temperature was found to be 250°C. The optimal ramp rate of 5°C/min, which resulted in the highest density, was lower than achievable in the hydraulic press used in compression molding.
- Density achieved using compression molding in the hydraulic press was lower than that achieved during consolidation studies using the rheometer. This is due to higher clearance between walls of the top and bottom halves of the mold used in compression molding. Higher clearance led to squeeze flow of the melt, which is believed to have resulted in lower lateral compaction stress and hence, lower density.
- Modulus and yield strength of compression molded RXHDPE were comparable to those of compression molded VXHDPE with comparable density. However, the failure strain and stress (i.e. tensile strength) were lower.

## 5.2 Conclusions

Based on the summary of results, the following can be concluded.

- RXHDPE can be successfully recycled through compression molding. However, RXHDPE would require a higher molding stress than VXHDPE to achieve a similar density.
- While both materials with similar density have comparable modulus and yield strength, the tensile strength and failure strain of RXHDPE were inferior to those of VXHDPE. This is believed to be due to difference in size, shape, and distribution of voids.
- Increasing the lateral stress through reduction in the clearance between the walls of the top and bottom mold halves will likely improve the density, narrow the difference between the two materials, and improve the failure strain and stress.

## 5.3 Contribution to knowledge creation

According to the best knowledge of the author, the following contributions are the first in this area:

- a) A thorough comparative thermal analysis of both virgin and recycled HDPE to show that the latter is recyclable, due to limited crosslinking during rotomolding process as a result of the role played by air in crosslinking.
- b) Development of a process to recycle partially crosslinked high density polyethylene waste, which includes pulverization of the rotomolded part and high stress compression molding of the pulverized powder.

#### **5.4 Recommendations for future work**

(a) It is recommended to study the effect of clearance in the mold on lateral stress to optimize the mold design and thus the density and properties of the recycled material.

(b) An important step is to explore compression molding process at temperatures above 250°C using release agents recommended for higher temperatures.

(c) Decreasing the powder size could improve the consolidation process requiring lower stress to obtain a dense product.

(d) This work also resulted in the development of a process to recycle RXHDPE into foams instead of solid products. This is a novel invention to manufacture foams without foaming agents. This will be pursued by the author of this thesis for his Ph.D. Preliminary findings of the tasks completed during this thesis are highlighted below.

(i) Under no stress, the pulverized RXHDPE particles meld at the surface, at temperatures higher than the melting temperature of the VXHDPE, to result in open cell foams as shown in Figure 5-1.

(ii) Foams exhibit a shiny appearance under good exposure to air, which results in better properties, as shown in Figure 5-2.

(iii) The foam density depends on the process temperature and time as shown in Figure 5-3.

(iv) Thickness of the free-form foam appears to influence the density of the foam, believed to be due to (ii). In case of foam formed in a mold to achieve a certain shape, the lateral constraint stress to thermal expansion of the powder results in consolidation of powders and variation of density across the thickness of the foam.

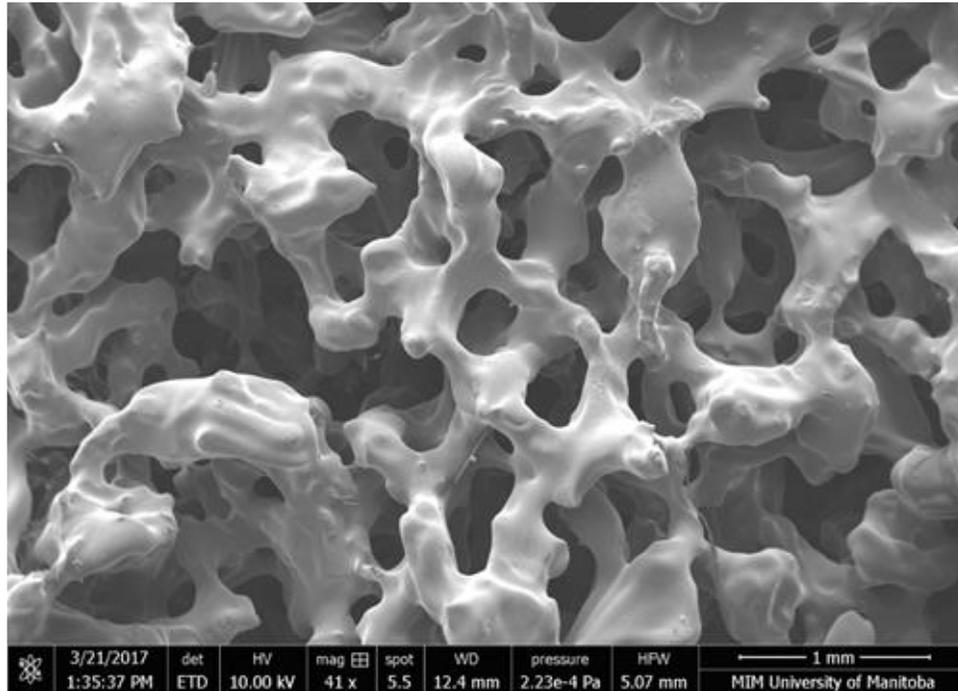


Figure 5-1: SEM image of the foam

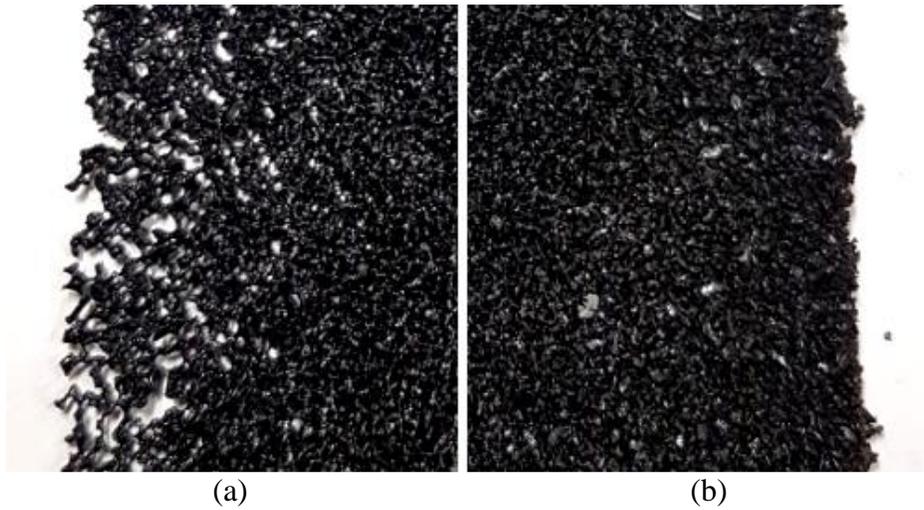


Figure 5-2: Foam appearance in function of air exposure, where (a) powder fully exposed to the air and (b) powder covered with plate

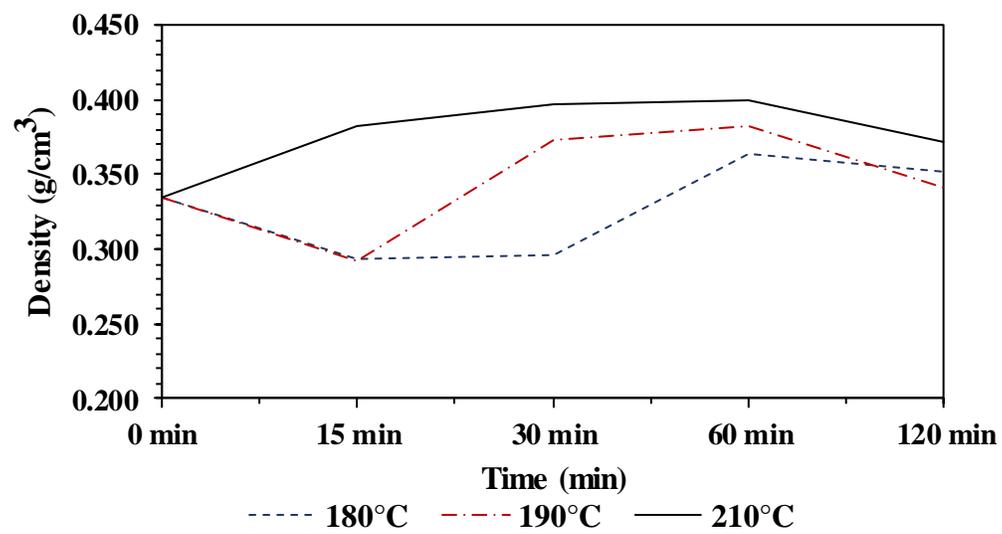


Figure 5-3: Foam density as a function of time and temperature

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## APPENDIX I

This section presents the design of the mold (top plate) used for compression molding.

The mold was prepared with imperial units.

