

THE INFLUENCE OF EXTRUSION PROCESSING AND FORMULATION  
ON FORM-STABLE PHASE CHANGE MATERIAL

By

GREGORY DALE ESTEP

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of  
GREGORY DALE ESTEP find it satisfactory and recommend that it be  
accepted.

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Donald A. Bender, PhD., Co-Chair

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Long Jiang, PhD., Co-Chair

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Karl Englund, PhD.

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# THE INFLUENCE OF EXTRUSION PROCESSING AND FORMULATION ON FORM-STABLE PHASE CHANGE MATERIALS

Abstract

By Gregory Dale Estep, M.S.  
Washington State University  
August 2010

Co-Chairs: Donald A. Bender and Long Jiang

There is a need in light-frame wood construction to develop mechanisms for thermal storage to lower energy demand and/or shift peak energy consumption to off-peak energy consumption times. Phase change materials (PCM) have the ability to store significant latent thermal energy with minimal volume and mass requirements. One technical challenge is to contain the PCM during the liquid phase. *Form stable* PCMs have been suggested as one solution. In form stable PCMs, the PCM is blended with a polymer, of a higher melting point, that adds structural stability to the blend and encapsulates the PCM melt to prevent leakage.

The objective of this study is to determine the effect of processing method on the morphology and thermomechanical properties of three formulations of HDPE/paraffin blend. Form stable phase change materials consisting of 75/25, 60/40, and 50/50 blends of paraffin (octadecane)/high density polyethylene (HDPE) were produced at three different extrusion processing speeds and tested for leakage, thermal conductivity, latent heat storage capacity, storage modulus and dispersion. Paraffin with a melt temperature of 28°C was chosen as the PCM with HDPE as the containment polymer with higher melt temperature of 130°C.

Thermal conductivity, measured by a KD2-Pro, of the blends increased (.330, .336, .358 W/mK at 100 rpm) with increasing amounts (25, 40, 50% respectively) of HDPE (the more thermally conductive material), attributing to good dispersion between the two materials. As characterized by DSC, latent heat storage capacity of the blends within the desirable range (25°C to 35°C) increased (98, 116, 153 J/g) with increasing amounts (50, 60, 75% respectively) of paraffin. Leakage of paraffin was measured by placing form stable PCM samples in solvent baths, recognizing that *in situ* leakage in building applications would be much less. Samples that were submerged for 10 hours showed percentage of total paraffin losses to be 38%, 36% and 28% for the formulations of 75/25, 60/40 and 50/50 paraffin/HDPE, respectively. While the morphology of the blend does allow pathways for some paraffin movement in a solvent bath, the practical amounts of leakage that might occur in a building product application have yet to be determined.

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## 1. INTRODUCTION

A typical residential home in the United States (US) uses about 56% of total energy consumed for heating and cooling (DOE). In order to lower energy demand and/or shift peak energy consumption to off peak energy consumption times, different technologies are being studied for the storage of thermal energy in the walls, floors and ceilings of light frame construction buildings.

Light-frame wood construction is common for residential buildings in the US. These building envelope assemblies can achieve relatively high R-values, or resistance to heat flow, but they lack thermal mass due to the lightweight nature of the system. The next logical step is to not only slow the heat transfer, but store the thermal energy in the wall itself for later use. By storing the thermal energy, the temperature fluctuations in the interior of a dwelling can be decreased. Studies have shown favorable results of limiting this heat exchange by the use of phase change materials (PCM) in walls, floors and roofs (Zhang et al., 2006 ; Zhou et al., 2007 ; Medina et al., 2008 ; Kosny et al. ORNL). Furthermore, by using an energy storage material such as a PCM, the thermal energy that is consumed will later be released, further stabilizing the temperature of the area it encompasses.

There are three ways to store thermal energy: reversible chemical reactions, sensible heat and latent heat. Of these three, latent heat is best suited for increasing a building's thermal efficiencies due to its ability to capture and release large amounts of energy per unit mass of a material during its phase change. Latent heat of fusion is the amount of energy needed to fully

change the phase of a material from a solid to a liquid. The higher the latent heat of fusion is, the more energy the PCM can absorb and contain. As thermal energy is introduced to a PCM, it starts to absorb the energy and begins to melt. During this phase transition, the temperature of the material remains nearly constant until the phase transformation is complete. As the ambient temperature surrounding the material drops below the phase transition zone, the material begins to solidify and therefore releasing the stored thermal energy at a nearly constant temperature until the phase change is complete. In other words, the PCM functions as a *thermal battery*. A major obstacle in using PCM as latent heat energy storage system is containment while in liquid form.

Various types of encapsulation methods have been studied for containing PCMs in their molten forms; however, there are some disadvantages when compared to a form stable PCM blend. The absorption of paraffin was early introduced as an effective way to incorporate up to 24-wt % of the PCM into gypsum wallboard, thereby increasing its thermal mass (Feldman et al., 1995). This however lowered the gypsum's function to retard flames and increased the heat released during a fire and therefore did not meet all the requirements set by the National Building Code (Banu et al., 1998). Macro encapsulation is the containment of a PCM in a sphere (75mm in diameter) and has been shown as a viable solution to increasing the thermal mass of a concrete slab (Farid & Kong 2002), but could suffer rupture if placed in an area prone to drilling, nailing or cutting.

Micro encapsulation is yet another method being studied to contain PCMs in the melt phase. Micro encapsulation of PCM can be achieved by the addition of formaldehyde based

thermosetting resins at high (2000 rpm) mixing rates (Zhang et al. 2004). A capsule is formed around the PCM and cured as the temperature of the solution is decreased. Some of the great advantages of micro-encapsulation is their size (0.2 – 5.6 micro meters); therefore, they do not have to be protected from damage while in use (puncture from nails or screws, etc.) and also that they can be directly incorporated, with little change, to the production process of some materials such as gypsum board. However, some disadvantages of this material are the cost, decrease in thermal conductivity, and durability of the encapsulating material. PCMs such as paraffin have been shown to dimple the encapsulating, formaldehyde based, spheres due to the difference in volumetric expansion and contraction between the PCM and the encapsulating material (Zhang et al. 2004).

Recently, copolymer blends containing polyethylene glycol (PEG) as the phase change material have been suggested as a solution for containing thermal energy through a solid-solid phase change (Meng & Hu 2008, Xi et al. 2008, Hu et al. 2006, Su & Liu 2006). These copolymers utilize a phase change that occurs from the crystalline structure to the amorphous structure of the polymer to absorb thermal energy and therefore do not have the issue of containing the PCM while in molten state. An early study suggested low entropy of this type of material (27 J/g Hu et al 2006), however more recent research indicates entropy achievements as high as 120 J/g (Meng and Hu 2008).

Form-stable PCMs utilize a polymeric matrix to inhibit to the loss of the phase change material, while providing structural stability. In these blends, the PCM is evenly dispersed through a polymeric (or other type) matrix material. The matrix, with its higher melt

temperature, acts as the supporting material that prevents leakage of the PCM while in its liquid state. Immiscibility between the two materials allows the formation of PCM pockets, therefore containing the material while above its melting point. Furthermore, the small size (5-50 microns) of the paraffin pockets encapsulated in this material will minimize leakage of the PCM in the event of piercing or cutting of the blends (Lee & Choi 1998).

PCMs being studied for latent heat storage vary between organic, inorganic and eutectics (Tyagi & Buddhi, 2007). A common selection of organic phase change material is paraffin. Unlike salt hydrates, paraffin does not have the problem of incongruent melting, therefore retaining its heat storage capacity after many phase change cycles (Hasenohrl 2009). Paraffin also is well known for its high heat of fusion (189 kJ/kg) when compared with other organic PCMs (140-200 kJ/kg) in the same melting range of 19 to 29 degrees C (Pasupathy et al. 2008).

High density polyethylene (HDPE) is a low cost (\$0.75-0.76 per pound; Plastics News Feb. 2010), highly available polymer used (16.5 million metric tons in 2008; American Chemistry Council) and recycled (417 thousand metric tons in 2007; Miller 2007) widely throughout the US. This polymer is chemically inert and has a relatively low melting point (~130 C) as compared to similar thermoplastic polymers such as polypropylene(~176 C) or polystyrene (~240 C) (Gerdeen et al. 2006 ).

In form stable PCMs some latent heat storage capacity, in the applicable temperature range, is sacrificed by the amount of supporting material in the blend. In form stable phase change materials, formulations containing the supporting material styrene maleic anhydride copolymer

(SMA) and as much as 85% of a PCM (fatty acids such as stearic acid (SA), palmitic acid (PA), myristic acid (MA), and Lauric acid (LA)) have been achieved with no reported leakage when the blend was heated above the melting point of the PCM (Sari et al. 2008). Additional leakage tests or repeat freeze thaw cycles were not mentioned as further testing to confirm the blends' ability to contain the PCM during service life applications.

In addition to the amount of PCM in a blend, several other parameters should be known to fully capitalize on the value of form stable phase change materials. One key attribute is to contain the PCM during the phase changes. There is a dearth of technical literature on leakage characteristics of form stable PCMs. One study measured weight loss of paraffin in a HDPE/paraffin blend by cyclical heating (Lee & Choi 1998) The sample's weight loss was estimated after wiping the surface of the sample, following each cycle. After the fifth cycle, weights' of the samples using h-HDPE leveled with increasing cycles, indicating the remaining paraffin was trapped inside. Another way to predict the leakage of a PCM blend is through Optical Microscopy (OM) or Scanning Electron Microscopy (SEM). By OM or SEM, PCM dispersion can be qualified and investigated for encapsulation (Sari 2004 ; Cai et al. 2008 ; Lee & Choi 1998 ; Cai et al. 2007 ; Inaba & Tu 1997). Interconnection of these materials in the blend is difficult to characterize through microscopy alone.

Other important characteristics to test include thermal conductivity and latent heat of fusion. High thermal conductivity allows the thermal energy to flow quickly through the blend, reaching the PCM. However, it is important that the PCM's thermal conductivity is high enough to allow the material to completely change phase and utilize its full thermal energy storage capacity before

allowing additional thermal energy to pass through the polymeric matrix that surrounds it. Therefore, the addition of materials with high thermal conductivity, such as expanded graphite, have been studied with good results (Xiao, Feng & Gong 2002 ; Fang & Zhang 2006 ; Zhang et al. 2006 ; Karaipekli, Sari & Kaygusuz 2007).

Little specific information appears in the technical literature with respect to processing methods of form stable PCMs. Research is needed on processing methods to encourage commercialization of PCMs.



### *1.1 Objective statement*

Blends of paraffin and HDPE have shown good promise as form stable phase change materials (Inaba and Tu, 1997; Lee and Choi, 1998; Sari 2004; Zhang et al., 2006; Cai et al. 2008). However, it is unclear how different processing methods will affect attributes such as: dispersion of the paraffin in an HDPE matrix, containment of the paraffin, thermal conductivity and mechanical properties (in the paraffin melt phase). As form-stable phase change materials move towards commercialization, high-throughput processing methods and subsequent thermal molding methods need to be explored.

The objective of this study is to determine the effect of processing method on the morphology and thermomechanical properties of three formulations of HDPE/paraffin blends.

Processing methods to be investigated include:

- Parallel co-rotating twin screw extrusion at three screw speeds with a base temperature profile<sup>1</sup>

Formulations

- 25% HDPE (Bamberger HP54-60) 75% paraffin (Octadecane, melting point 28.2 C)
- 40% HDPE (Bamberger HP54-60) 60% paraffin (Octadecane, melting point 28.2 C)
- 50% HDPE (Bamberger HP54-60) 50% paraffin (Octadecane, melting point 28.2 C)

Thermomechanical properties

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<sup>1</sup> Vacuum was applied during the extrusion of the formulation containing 75% paraffin and 25% HDPE

- thermal conductivity, melt temperature, heat of fusion
- storage moduli before and after paraffin melt

Morphology and paraffin containment will be studied by

- SEM and OM (reflective) imaging
- Paraffin loss from fresh-cut surfaces
- HDPE network characteristics determined by solvent extraction of the paraffin

## 2. MATERIALS AND METHODS

### 2.1 *Materials and processing parameters*

Three formulations of paraffin/HDPE were investigated over three extrusion speeds. The PCM selected to be used was technical grade Octadecane (paraffin) with an average melting point of 28° C. This melting point was judged to be reasonable for use in an interior building envelope. The polymer added to contain the PCM was high-density polyethylene (HDPE), Inoes HP54-60 with a 0.5 melt flow index (MFI). HDPE was chosen due to its widespread availability both as virgin and recycled material, acceptable melting point, low cost and structural integrity. The paraffin was purchased from Roper Thermals and the HDPE was purchased from Bamberger Polymers.

Specific formulations of the form stable PCM and HDPE blends included:

- 75% Paraffin – 25% HPDE
- 60% Paraffin – 40% HDPE
- 50% Paraffin – 50% HDPE

Ideally, the highest possible percentage of paraffin PCM would be preferable; however, previous research (Sari 2004, Inaba 1997, Xiao 2002, Zhang 2006) indicated an upper limit of approximately 75-80%.

Each formulation was processed at the three different extrusion speeds as follows:

- 80 rpm (vacuum assisted)

- 100 rpm
- 150 rpm

The HDPE (in powder form) and the paraffin (in liquid form) were premixed by weight percentage (%) in preparation for extrusion. During extrusion of each formulation batch, the remaining premixed slurry of HDPE and paraffin was continuously stirred prior to entering the extruder to ensure good dispersion. Extrusion was performed with a Leistritz (ZSE-18HP) – parallel, co-rotating, twin-screw extruder. The temperature profile of the seven heating zones from the intake of the barrel to the output were set at 140/165/170/170/170/170/170°C, respectively to initiate then complete the melting of the HDPE (130°C). A prescriptive method for processing these blends is located in the Appendix. This temperature profile was used in all formulations and production speeds of this study. Upon extruding the samples, the melt was collected in a casting die and allowed to cool naturally at room temperature until the samples solidified.

Due to the relatively low viscosity of the paraffin/HDPE blend in the formulation containing 75% paraffin, a vacuum was applied to the vent of the extruder to remove air voids in the mixture that would have been otherwise passed through the machine and into the final product samples.

## *2.2 Testing and Evaluation*

Samples from each of the 9 combinations of formulations and processing speeds were observed through the use of a Field Emission Scanning Electron Microscopy (FE SEM, Quanta

200F) at magnifications of 500x, 1000x, and 2000x for each sample. The samples were produced via a microtome and then submerged in a chloroform bath for approximately 90 seconds to remove paraffin from the surface of the samples to reveal the HDPE structure. According to the Merck Index (Mereck 2001), chloroform is a suitable solvent for the paraffin. Research by Lyu et al. (2000) confirmed that chloroform did not dissolve HDPE at room temperature.

Thermal conductivity was measured using a KD2 PRO Thermal Properties Analyzer developed by Decagon. This device utilizes a transient line heat source method and has an accuracy of 10% when testing thermal conductivity. Three samples from each combination of formulation and processing speed were placed in a conditioning room at a constant temperature of 20° C (+/- 2° C) then predrilled to accommodate the length and diameter of the testing probe. The testing probe was inserted into the samples and allowed to equilibrate to the samples temperature before taking readings. Readings, obtained as watts per meter Kelvin (w/Mk) were taken 20 minutes apart (5 minutes longer than the manufacturers' recommended minimum lag time) to ensure thermal gradients had dissipated from the previous test. The probe was lightly coated in Arc Silver, highly conductive thermal grease, to ensure maximum contact between the probe and the test samples.

Three samples (approximately 17.8mm x 11mm x 2.5mm) were cut for each of the 9 combinations of formulation and processing speeds. Dynamic mechanical properties of the samples were then obtained using a TA Q-800 dynamic mechanical analysis (DMA) machine. The reason for this test is to follow the storage modulus change of the blends during the solid and liquid phases of the PCM, within the range of temperatures anticipated for wall envelope

applications. Strain was kept constant at 0.05% (within the linear viscoelastic region of the samples) through the oscillatory force of a single cantilever jig head while temperature was increased at 2°C/min, from -10° C to +40° C. Measurements of storage modulus were taken throughout this temperature range and compared to the other samples.

Melting point and latent heat of fusion were then measured using a Mettler DSC822° differential scanning calorimeter (DSC). Three samples between 5 and 10 micrograms were obtained from each of the 9 combinations of formulations and processing speeds and crimp sealed in 40 µl aluminum crucibles. The testing profile used, initially cooled the sample to 0°C and remained isothermal for 1 minute. The sample was then heated at a rate of 20° C per minute to 150° C and remained isothermal for 2 minutes. The sample was then cooled at a rate of 20° C per minute to 0° C and remained isothermal for 2 minutes. The sample was once again heated at a rate of 20° C per minute to 150° C. Upon reaching this temperature, the sample was cooled to room temperature and removed.

The samples were heated twice from 0° C to 150° C. The initial heating was performed to allow the blend to melt and completely cover the bottom of the testing containers and to remove thermal history. This allowed sharper entropy peaks to be observed during the second heating due to a more uniform heating of the sample.

Leakage tests were devised to investigate the degree of interconnectivity of the paraffin and HDPE phases in the blend. The tests were designed to subject the samples to a harsher environment than they would normally be subjected to during *in situ* applications. Rectangular

cubes were cut by razor blade, measured (approximately 12mm x 8mm x 8mm) and weighed for each of the 9 combinations of formulations and processing speeds and submerged in a chloroform bath. Samples were held under the surface of the chloroform by stainless steel mesh. Then they were removed at 2, 4, 6, 8, and 10 hours, respectively. The samples were allowed to dry under a fume hood for 72 hours before being weighed to allow the chloroform time to evaporate from the cavities of the samples. The 72 hr time period was judged to be sufficient by repeated measurements until the sample weights stabilized. Percent loss of the paraffin, as normalized by formulation, was calculated using the following formula:

$$L = (W_s - W_e) / (W_s * F_p)$$

Where:

L = Percent paraffin leakage of the blend

$W_s$  = starting weight of sample

$W_e$  = ending weight of sample

$F_p$  = percent of paraffin in formulation

### 3. RESULTS AND DISCUSSION

#### *3.1 Observations during extrusion*

Extrusion of the two formulations containing 40% and 50% HDPE resulted in blends that appeared to be homogeneous and air void free by visual inspection. The formulation containing 25% HDPE however showed visible, well-dispersed air voids in the material as it exited the extruder. A vacuum was attached on the vent of the extruder to draw the air voids from the blend in the extruder barrel. The applied vacuum appeared to solve the air void problem as judged by visual inspection. These air voids, if left in the blend, would decrease the density of the material and therefore lower the thermal conductivity and thermal storage capacity of the blend.

Viscosities of the different formulations rose with an increased amount of HDPE in the blends. This was evident by the increase in torque applied by the extruder, relative to the increase in HDPE content, to process the blends. Those of a higher viscosity could have an advantage in commercialized manufacturing processes such as sheet or panel extrusion, where the additional melt strength could be beneficial to maintaining the product shape until the material solidifies.

#### *3.2 Morphology analysis of the PCM/HDPE blend*

**Fig. 1** shows representative SEM micrographs for formulations containing 50, 60, and 75% paraffin respectively processed at 150 rpm. The formulation containing 75% paraffin has a slightly rougher surface of HDPE, attributing to the homogeneously distributed paraffin throughout the blend. As the percentage of paraffin decreases, the HDPE surface on the micrographs becomes smoother, indicating a lesser degree of paraffin dispersion. The



micrographs of these formulations are similar to those found by other researchers (Zhang et al. 2006); however, neither the formulations nor materials were fully described in their article. **Fig. 2, 3 and 4** show SEM micrographs for the three formulations prepared using 80, 100, and 150 rpm speeds, respectively. There is no visual evidence of a relationship between the blend morphology and the processing speed based on these micrographs.

It is difficult to determine the microstructures, i.e. co-continuous or matrix-inclusion, of the PCM/HDPE blends solely based on the obtained micrographs. However, we believe that the blends form a co-continuous phase structure, meaning both materials form interconnected pathways with each other throughout the blend, during extrusion. This will be further discussed in later parts of this paper.

### *3.3 Thermal Conductivity*

In this study, paraffin was used as the PCM with no additives to increase its thermal conductivity (0.325 W/mK, measured by the KD2-Pro). Researchers (Xiao et al. 2002, Zhang et al. 2006) explored adding expanded graphite or carbon fiber to increase the thermal conductivity of paraffin. The purpose of having a higher thermal conductivity is to ensure the full efficiency of the PCM in the blend. When thermal energy is traveling through the PCM blend, it is important that all of the PCM has undergone complete phase change before the thermal energy continues to pass through the material. If the thermal conductivity of the supporting material is higher than that of the PCM, thermal energy will continue through the supporting material before fully charging the PCM.

**Fig 5.** illustrates the average measured conductivity values for each formulation to the values calculated based on a rule of mixtures equation:

$$k = \Phi_p * k_p + \Phi_h * k_h$$

Where:

$k$  = thermal conductivity of the material blend

$\Phi_p$  = weight percentage of paraffin

$k_p$  = thermal conductivity of the paraffin

$\Phi_h$  = weight percentage of HDPE

$k_h$  = thermal conductivity of HDPE

The experimental and calculated values are in good agreement, indicating a nearly homogeneous mixture in all tested samples. **Fig 6.** shows thermal conductivity results for neat HDPE, neat paraffin and for each of the three formulations at three different extrusion speeds. Results qualitatively indicate a slight increase in thermal conductivity with higher screw speed. This may be due to better dispersion of the HDPE phase, the more thermally conductive component in the blend, at higher processing speeds. Analysis of variance was performed through the statistical software Minitab and concluded that processing speed with a probability value ('p' value) of 0.025 did have an effect on the thermal conductivities of the formulations at a significance level of 5 percent. Although small variations were found in thermal conductivity results between processing speeds within a formulation, these differences are of little practical

importance. Furthermore, it was the formulations themselves that had a significant effect on the thermal conductivities of the materials with a ‘p’ value of less than 0.001 (**Appendix**). Formulations increased in thermal conductivity with increasing amounts of HDPE, the more thermally conductive material.

### *3.4 Evaluation of Mechanical Properties by DMA*

One key attribute of a form-stable PCM is its ability to maintain form while the PCM is in liquid state. In this study HDPE is used as the supporting material to maintain the structural integrity of the PCM. **Fig. 7** compares the average storage modulus of neat HDPE and the three formulations. The three formulations show substantially lower modulus than does neat HDPE because of their inclusion of low-modulus paraffin. Between the three formulations, the modulus differences appear to be small over the whole temperature range. The modulus differences between neat HDPE and the formulations increases with increasing temperature due to the softening and melting of the paraffin in the formulations. The formulation samples maintain their some structural integrity after the melting of paraffin at 28°C, which indicates that HDPE phase forms an interconnected structure capable of withstanding load when the paraffin phase is in molten state.

Extrusion speed was also found to affect the storage modulus. Results in **Fig. 8, 9** and **10**, indicate the storage modulus of different formulation blends vary with respect to screw speed. Further studies are needed to determine a reasonable trend associated with storage modulus and processing speed. However, the differences found should not affect the practical use of this

material as it is not designed for structural support application but rather, only needs to support its own weight and form.

### 3.5 *Evaluation of Thermal Properties by DSC*

A typical DSC curve for the paraffin/ HDPE blend can be seen in **Fig. 11**. The first peak indicates the phase change of the paraffin while the second peak is the crystalline melt of the HDPE. In this figure, melting temperature is denoted by an 'x' at the peak of the thermograms. Heat of fusion was determined by first normalizing the data to the sample weight. Then the area enclosed by the curve, indicated by the straight line above the curve, was integrated. Beginning transition temperature (Onset) and ending transition temperature (Endset) are labeled for the paraffin and the HDPE on the thermogram. These are the beginnings and ends (from left to right) of the lines used to calculate the heat of fusion. Thermal storage capacity of the blend is equal to the heat of fusion of the paraffin phase in the blend.

As shown in **Fig. 12**, processing speeds seem to have a small effect on the thermal energy storage capacities of the blends particularly at 80 rpm. These fluctuations could indicate larger, localized pockets of paraffin by result of lower dispersion when compared to those of higher processing speeds. Energy storage capacities, however, were influenced greatly by the weight percentage of paraffin in the blend. Analysis of variance was performed through the statistical software Minitab and concluded that processing speed with a probability value ('p' value) of 0.027 did have an effect on the thermal storage capacities of the formulations at a significance level of 5 percent. Furthermore, it was supported that the formulations themselves had a significant effect on the thermal storage capacities of the materials with a 'p' value of less than

0.001 (**Appendix**). By increasing the weight percentage of PCM in the blend, the PCM/HDPE blend consequently increases in its thermal energy storage capacity.

In **Fig. 13**, the DSC curve shows that the melting point of HDPE shifts to lower temperatures with increasing paraffin content, indicating a certain degree of miscibility between the paraffin and HDPE during extrusion. Krupa et al (2007) observed similar phenomenon in paraffin/low density polyethylene (LDPE) blends. The miscibility between paraffin and HDPE is an important finding because it significantly influences the phase structures of paraffin/HDPE blends. The shift in melting point could be due to the paraffin acting as a plasticizer of the HDPE. This indicates a great affinity between the two materials and facilitates a co-continuous structure even at 75 weight percentage of paraffin, allowing form stability of the blend.

### *3.6 Evaluation of Morphology by Solvent Extraction*

To be a viable thermal energy storage material, the PCM in the paraffin/HDPE blend should not leak during its liquid phase. Several studies (Sari et al. 2008, Sari 2004, Inaba et al. 1997, Alkan et al. 2008) of form stable PCMs have indicated little or no loss of the PCM when exposed to temperatures above the melting point of the PCM, but there are no published results of PCM leakage amounts or confirmation of interconnectivity for extruded form stable PCM. Therefore, this test was designed to determine the encapsulation of the paraffin in the PCM/HDPE blend by subjecting it to a known paraffin solvent (i.e. chloroform) that does not dissolve HDPE under the testing conditions. The solvent bath is a much more stringent test of leakage that would be expected in field conditions. However, it is necessary to determine the

interconnectivity of the paraffin phase to establish if the PCM could eventually seep from the material in long-term usage through interconnected passages.

**Fig. 14, 15 and 16** compare percentage leakage of the paraffin after different immersion times for the three formulations prepared using three processing speeds. It appears that the samples prepared at 80 rpm show the highest leakage, and the leakage differences between the samples prepared at 100 and 150 rpm are small. Analysis of variance was performed on samples with submerge times of 10 hours through the statistical software Minitab, and concluded that processing speed with a probability value ('p' value) of 0.005 did have an effect on the paraffin leakage at a significance level of 5 percent. The lowest processing speed, 80 rpms, caused the highest leakage in all formulations. This may be due to coarser paraffin dispersion throughout the blend at low processing speed (i.e. larger interconnected paraffin channels), which allows for easier chloroform extraction.

**Fig. 17** compares paraffin leakage across the three formulations. Tests were performed for up to 386 hours of submersion of the samples in the chloroform bath. Results show an increasing amount of leakage with time throughout all formulations. Initial weight loss can be explained from solvent extraction of surface paraffin and the shallow connections that are tied to the surface. This, as seen from the FE SEM pictures can occur within only a couple of minutes. Paraffin leakage is also found to increase with increasing paraffin content. Statistical analysis proved that paraffin content had a significant effect on the leakage of the samples with a 'p' value of less than 0.001 (**Appendix**).

Majority loss of the paraffin throughout all formulations, with respect to time, suggests little paraffin encapsulation throughout the blend. These open pathways could prevent the material blend from achieving leak free performance in long-term applications. Extrusion is an efficient and economical method to produce PCM blends in large scale. However, to reduce or stop the leakage of PCM from the blend, further research on extrusion process and/or formulation of the blend is needed to achieve leakage free microstructures such as a completely encapsulated PCM phase.

Both DMA and leakage tests indicate that HDPE and paraffin form co-continuous structure in the blends despite the large viscosity disparity between the two phases and high paraffin contents. DSC results show a shift in the HDPE melting point, an indication of miscibility between paraffin and HDPE in their molten state. During the cooling phase, HDPE crystallizes and separates from the paraffin matrix and eventually forms a co-continuous structure with the paraffin phase. This structure is the reason for the sample structural integrity in DMA tests at raised temperatures and for the majority loss of the paraffin in long-term chloroform extraction tests.

#### 4. CONCLUSIONS

In this study, three different formulations of a paraffin/HDPE blend were extruded at three different processing speeds and investigated for morphology, thermal conductivity, storage modulus, thermal storage capacity, and leakage characteristics of the paraffin from the blend. Results conclude that variations in formulation have significant effects in all of the previously mentioned properties except for storage modulus where only slight effects were observed. Blends containing higher contents of paraffin showed lower thermal conductivity, higher thermal storage capacity and higher paraffin leakage amounts.

Furthermore, processing speed also is shown to have an effect on all of the investigated areas but to a lesser degree than the formulation changes. Of the processing speeds chosen for this study, 80 rpm showed the least desirable results for the thermal conductivity and extraction tests, likely due to the lower degree of dispersion between the two materials. The higher mixing speeds likely decreased the size of the paraffin pathways throughout the blend, giving the blend a more homogeneous distribution. It is therefore suggested that the processing speed for this type of blend, mixed by extrusion, be 100 rpm or higher to achieve satisfactory distribution of the two materials. Results of investigations between the mixing speeds of 100 rpm and 150 rpm showed little difference. This can be viewed as a positive result from a manufacturing standpoint, as higher processing speeds are likely to lower production costs.

In all formulations the form of the blends were maintained, even during the melt phase of the paraffin. This result, as indicated by DMA graphs, indicates that HDPE forms an interconnected phase throughout the blend, capable of the products shape.



The characterization of interconnected paraffin throughout the blend, when processed by extrusion, indicated the possibility for leakage of the paraffin from this material during use in long-term applications. Further testing is needed to investigate the leakage of paraffin from this material blend in an environment more closely related to field conditions through extensive, cyclical freeze/thaw cycles within the paraffin melt range.

Form stable PCM blends have shown great potential as a latent heat storage system. Further works based on this type of material processed by extrusion might include the addition of carbon black, expanded graphite or other thermally conductive additives that may increase the thermal conductivity of the blend as a whole. Also, variations in temperature profiles and their effect on the morphology of these blends could be another interesting investigation as higher temperatures would lower the viscosity of the HDPE further, possibly altering the morphology of the blend. Though paraffin in the blends studied for this paper was shown to not be encapsulated, higher weight percentages of HDPE could overcome this and needs to be studied.

## 5. LITERATURE CITED

- Alkan C, Sari A. fatty acids/poly(methyl methacrylate)(PMMA) blends as form-stable phase change materials for latent heat thermal energy storage. *Solar Energy* 2008; 82: 118-24.
- American Chemistry Council. Plastic Resins Industry Hit Hard by Global Economic Recession in 2008.
- Banu D, Feldman D, Haghighat F, Paris J, Hawes D. Energy-Storing Wallboard: Flammability Tests. *Journal of Materials in Civil Engineering* 1998; May: 98-105.
- Cai Y, Hu Y, Song L, Kong Q, Yang R, Zhang Y, Chen Z, Fan W. Preparation and flammability of high density polyethylene/paraffin/organophilic montmorillonite hybrids as a form stable phase change material. *Energy Conversion and Management* 2007; 48: 462-69.
- Cai Y, Song L, He Q, Yang D, Hu Y. Preparation, thermal and flammability properties of a novel form-stable phase change materials based on high density polyethylene/poly(ethylene-co-vinyl acetate)/organophilic montmorillonite nanocomposites/paraffin compounds. *Energy Conversion and Management* 2008; 49: 2055-62.
- Fang X, Zhang Z. A novel montmorillonite-based composite phase change material and its application in thermal storage building materials. *Energy and Buildings* 2006; 38: 377-80.
- Farid M. Kong WJ. Under floor heating with latent heat storage. *Power and Energy* 2002; 215: 601-09.
- Feldman D, Banu D, Hawes DW. Development and application of organic phase change mixtures in thermal storage gypsum wallboard. *Solar Energy Materials and Solar Cells* 1995; 36: 147-57.
- Gerdeen J, Lord H, Rorrer R, *Engineering Design and Composites*, CRC Press, Florida, 2006.
- Hasenohrl T. An Introduction to Phase Change Materials as Heat Storage Mediums. Project Report. Department of Energy Sciences, Lund University, Sweden 2009.
- Hu J, Yu H, Chen Y, Zhu M. Study on Phase-Change Characteristics of PET-PEG Copolymers. *Journal of Macromolecular Science* 2006; 45: 615-21.

- Inaba H, Tu P. Evaluation of thermophysical characteristics on shape-stabilized paraffin as a solid-liquid phase change material. *Heat and Mass Transfer* 1997; 32: 307-12.
- Karaiepli A, Sari A, Kaygusuz K. Thermal conductivity improvement of stearic acid using expanded graphite and carbon fiber for energy storage applications. *Renewable Energy* 2007; 32: 2201-10.
- Kosney J, Yarbrough D, Miller W, Petrie T, Childs P, Syed AM, Leuthold D. PCM-Enhanced Building Envelopes in Current ORNL Research Projects. 2006; Oak Ridge National Laboratory.
- Krupa I, Mikova G, Luyt AS. Phase change materials based on low-density polyethylene/paraffin wax blends. *European Polymer Journal* 2007; 43: 4695-4705.
- Lee C, Choi H. Crystalline Morphology in High-Density Polyethylene/Paraffin Blend for Thermal Energy Storage. *Polymer Composites* 1998; 19: 704-708.
- Lyu S, Bates F, Macosko C. Coalescence in Polymer Blends during Shearing. *AIChE Journal* 2000; 46: 229-38.
- Medina M, King J, Zhang M. On heat transfer rate reduction of structural insulated panels (SIPs) outfitted with phase change materials (PCMs). *Energy* 2008; 33: 667-678.
- Meng Q, Hu J. A poly(ethylene glycol)-based smart phase change material. *Solar Energy Materials & Solar Cells* 2008; 92: 1260-68.
- Miller C. High Density Polyethylene. *Waste Age* 2007.
- Pasupathy A, Velraj R, Seeniraj RV. Phase change material-based building architecture for thermal management in residential and commercial establishments. *Renewable and Sustainable Energy Reviews* 2008; 12: 39-64.
- Plastics News resin pricing chart. February 2010.
- Sari A, Alkan C, Karaiepli A, Onal A. Preparation, characterization and thermal properties of styrene maleic anhydride copolymer (SMA)/fatty acid composites as form stable phase change materials. *Energy Conversion and Management* 2008; 49: 373-80.

- Sari A. Form-stable paraffin/high density polyethylene composites as solid-liquid phase change material for thermal energy storage: preparation and thermal properties. *Energy Conversion and Management* 2004; 45: 2033-42.
- Su J, Liu P. A novel solid-solid phase change heat storage material with polyurethane block copolymer structure. *Energy Conversion and Management* 2006; 47: 3185-91.
- The Merck Index, thirteenth ed., Merck Research Laboratories, NJ, 2001.
- U.S. Department of Energy (DOE). Heating and Cooling.
- Tyagi V, Buddhi V. PCM thermal storage in buildings: A state of art. *Renewable and Sustainable Energy Reviews* 2007; 11: 1146-66.
- Xi P, Gu X, Cheng B, Wang Y. Preparation and characterization of a novel polymeric based solid-solid phase change heat storage material. *Energy Conversion and Management* 2009; 50: 1522-28.
- Xiao M, Feng B, Gong K. Preparation and performance of shape stabilized phase change thermal storage materials with high thermal conductivity. *Energy Conversion Management* 2002; 43: 103-08.
- Zhang Y, Ding J, Wang X, Yang R, Lin K. Influence of additives on thermal conductivity of shape-stabilized phase change material. *Solar Energy Materials & Solar Cells* 2006; 90: 1692-1702.
- Zhang YP, Lin KP, Yang R, Di HF, Jiang Y. Preparation, thermal performance and application of shape-stabilized PCM in energy efficient buildings. *Energy and Buildings* 2006; 38: 1262-69.
- Zhang X, Tao X, Yick K, Wang X. Structural and thermal stability of microencapsulated phase-change materials. *Colloid Polymer Science* 2004; 282: 330-336.
- Zhou G, Zhang Y, Wang X, Lin K, & Xiao W. An assessment of mixed type PCM-gypsum and shape-stabilized PCM plates in a building for passive solar heating. *Solar Energy* 2007; 81: 1351-60.

## 6. LIST OF FIGURES

FIGURE 1 - SEM pictures of typical 50%/50% (A), 60%/40% (B), and 75%/25% (C) paraffin/HDPE samples at 1000 times magnification.

FIGURE 2 - SEM pictures of 50%/50% paraffin/HDPE samples at processing speeds of 80 (A), 100 (B) and 150 rpm (C) at 1000 times magnification.

FIGURE 3 - SEM pictures of 60%/40% paraffin/HDPE samples at processing speeds of 80 (A), 100 (B) and 150 rpm (C) at 1000 times magnification.

FIGURE 4 - SEM pictures of 75%/25% paraffin/HDPE samples at processing speeds of 80 (A), 100 (B) and 150 (C) rpm at 1000 times magnification.

FIGURE 5 - Thermal Conductivity measurements, taken by Decagon KD2 Pro, of paraffin/HDPE blends containing 50%, 60% and 75% paraffin, compared to calculated expectations based on rule of mixtures equation.

FIGURE 6 - Thermal conductivity comparisons between neat HDPE, neat Paraffin, and three formulations at three processing speeds.

FIGURE 7 - DMA curves for three formulations compared to neat HDPE.

FIGURE 8 - DMA curves for 50%/50% formulation of paraffin/HDPE blend processed at three speeds (80, 100, 150rpm) compared to neat HDPE.

FIGURE 9 - DMA curves for 60%/40% formulation of paraffin/HDPE blend processed at three speeds (80, 100, 150rpm) compared to neat HDPE.

FIGURE 10 - DMA curves for 75%/25% formulation of paraffin/HDPE blend processed at three speeds (80, 100, 150rpm) compared to neat HDPE.

FIGURE 11 - Typical DSC curve for the Paraffin/HDPE blend (50/50 formulation shown).

FIGURE 12 - Thermal energy absorption capabilities of neat paraffin and three different formulations.

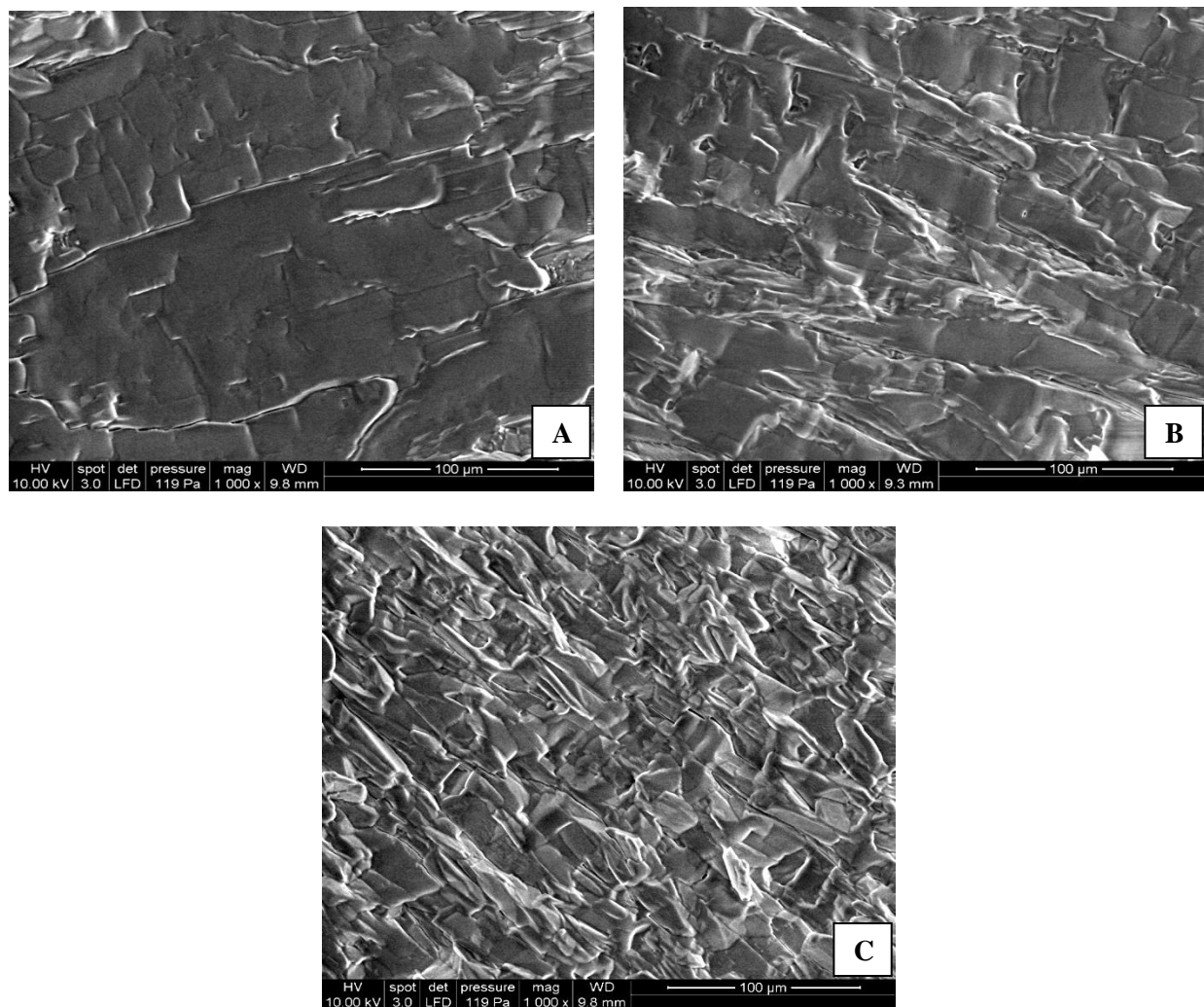
FIGURE 13 - DSC curves comparing three formulations of blends to neat paraffin and HDPE.

FIGURE 14 - Leakage of paraffin (%) in 50/50 formulation by solvent extraction.

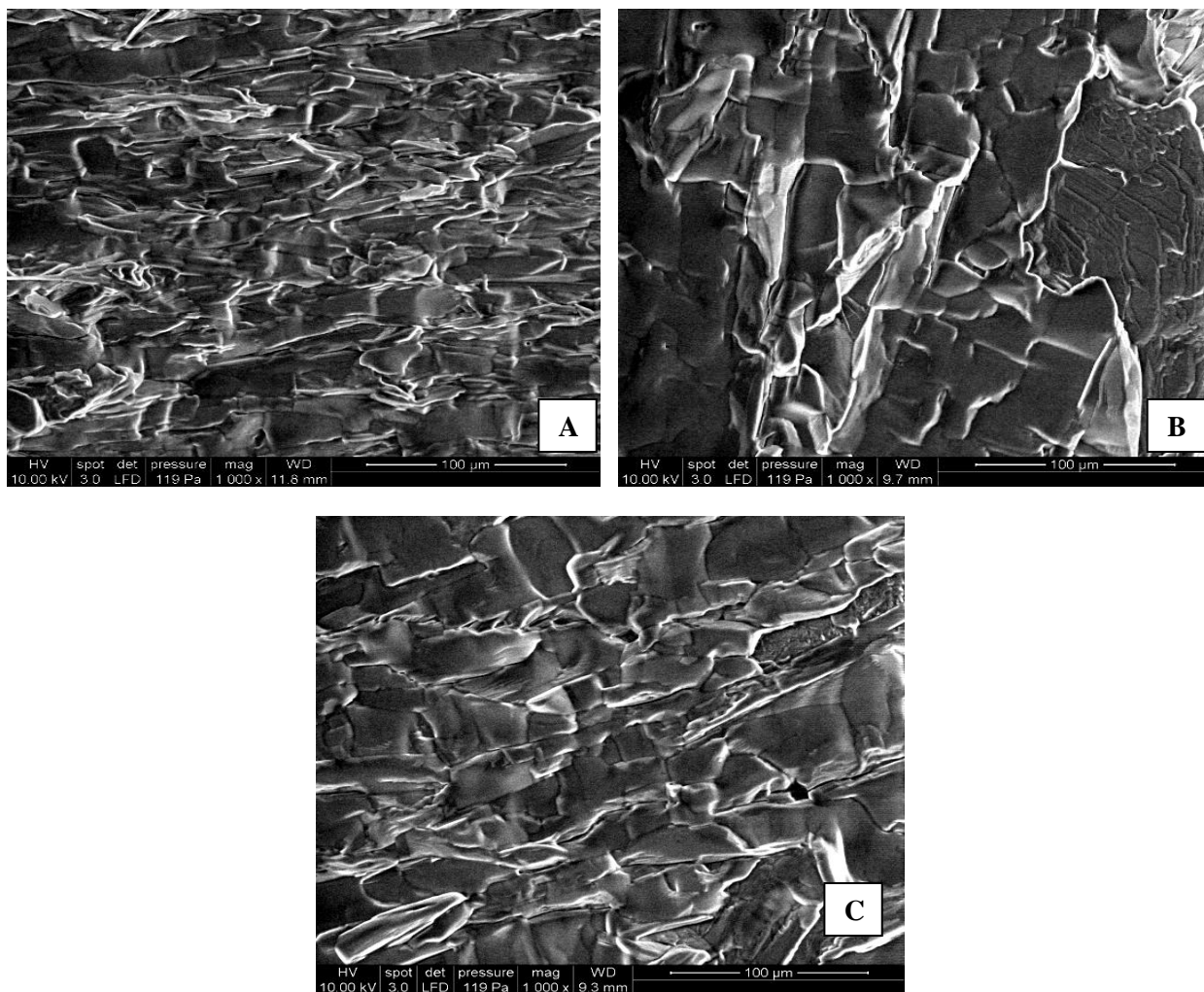
FIGURE 15 - Leakage of paraffin (%) in 60/40 formulation by solvent extraction.

FIGURE 16 - Leakage of paraffin (%) in 75/25 formulation by solvent extraction.

FIGURE 17 - Paraffin loss percentage by formulation after submerged in chloroform for the indicated times.

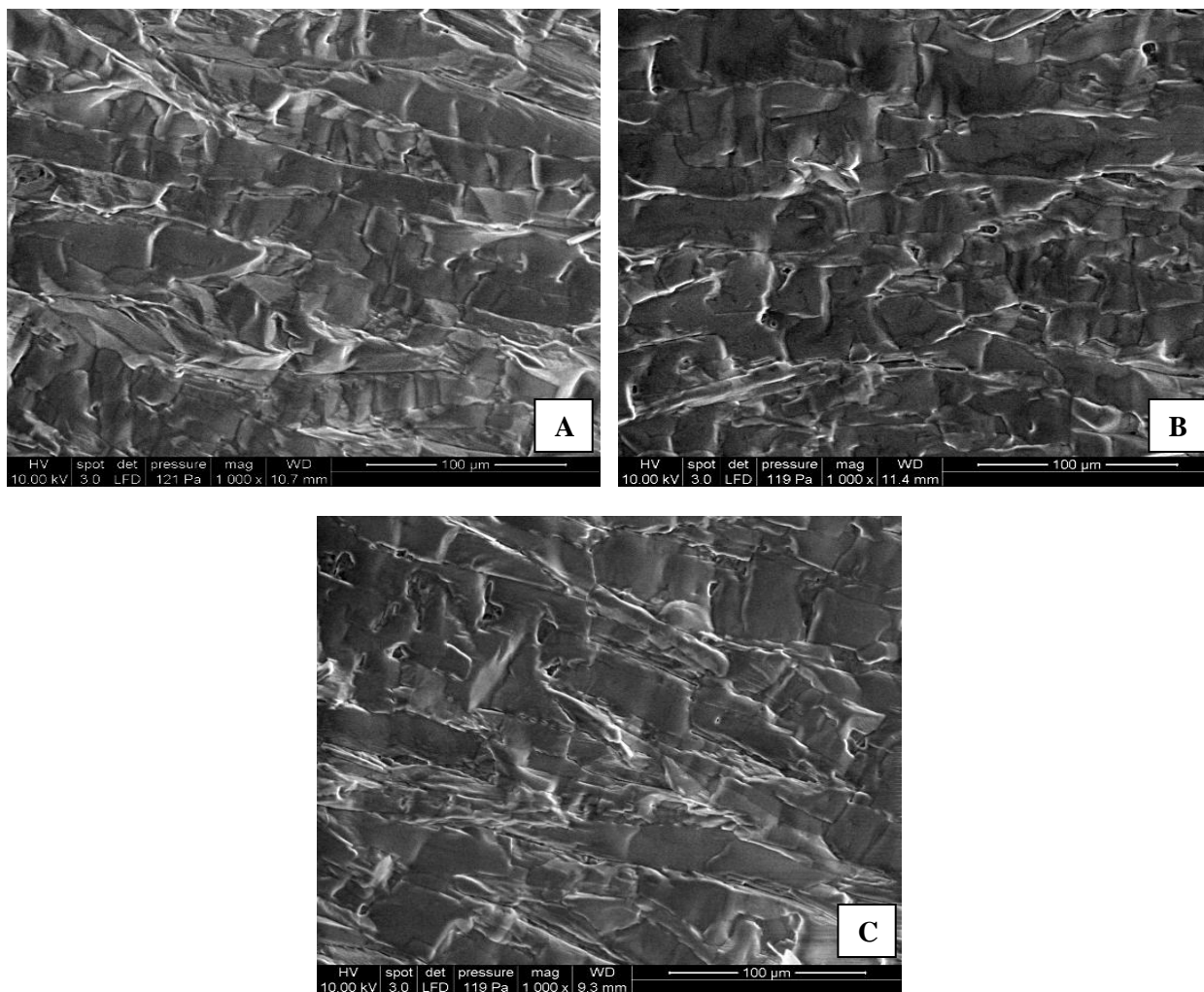


**Figure 1.** SEM pictures of typical 50%/50% (A), 60%/40% (B), and 75%/25% (C) paraffin/HDPE samples at 1000 times magnification processed at 150 rpm. Surface paraffin was removed by chloroform to show the surface of the HDPE structure.

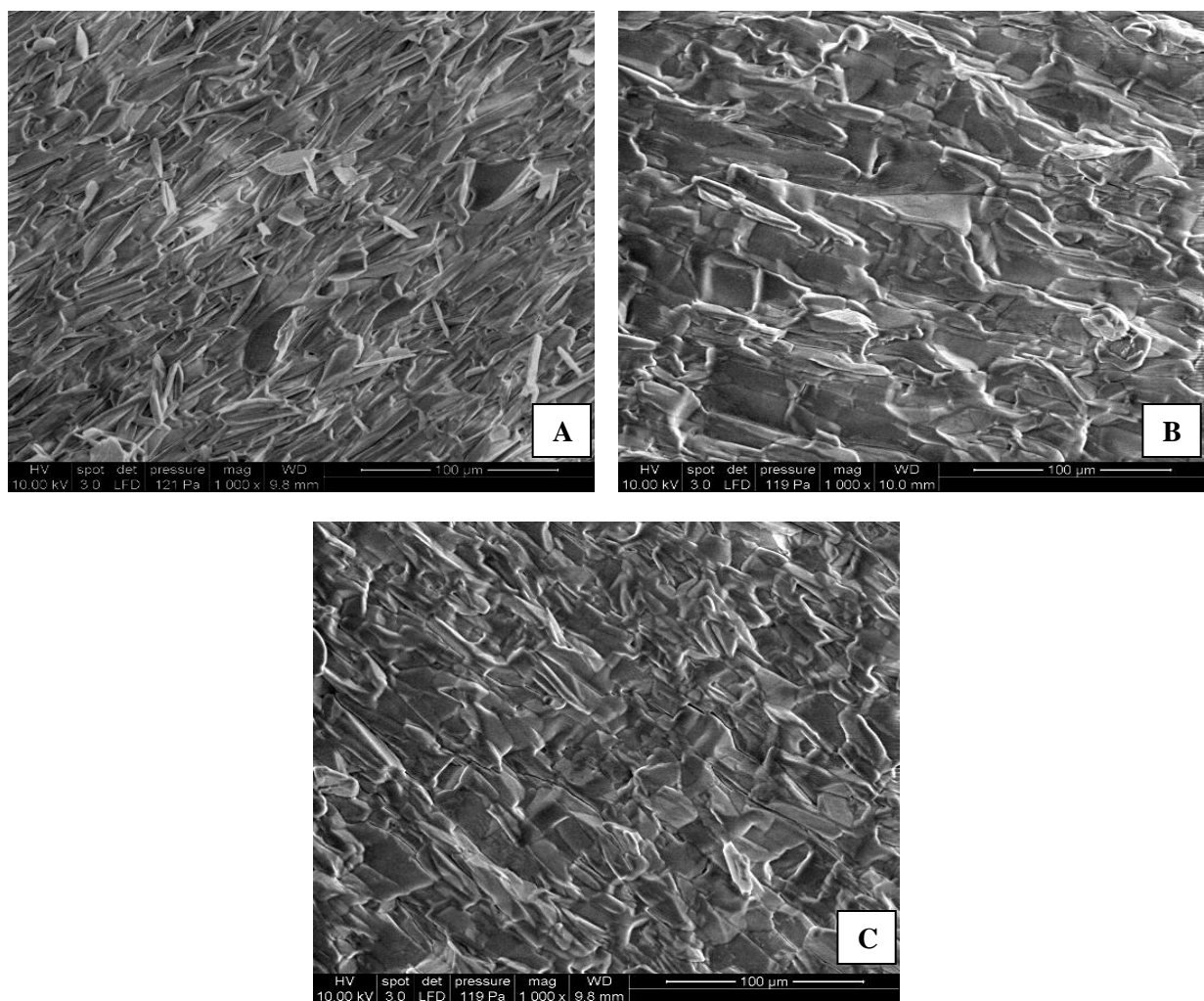


**Figure 2.** SEM pictures of 50%/50% paraffin/HDPE samples at processing speeds of 80 (A), 100 (B) and 150 rpm (C) at 1000 times magnification. Surface paraffin was removed by chloroform to show the surface of the HDPE structure.

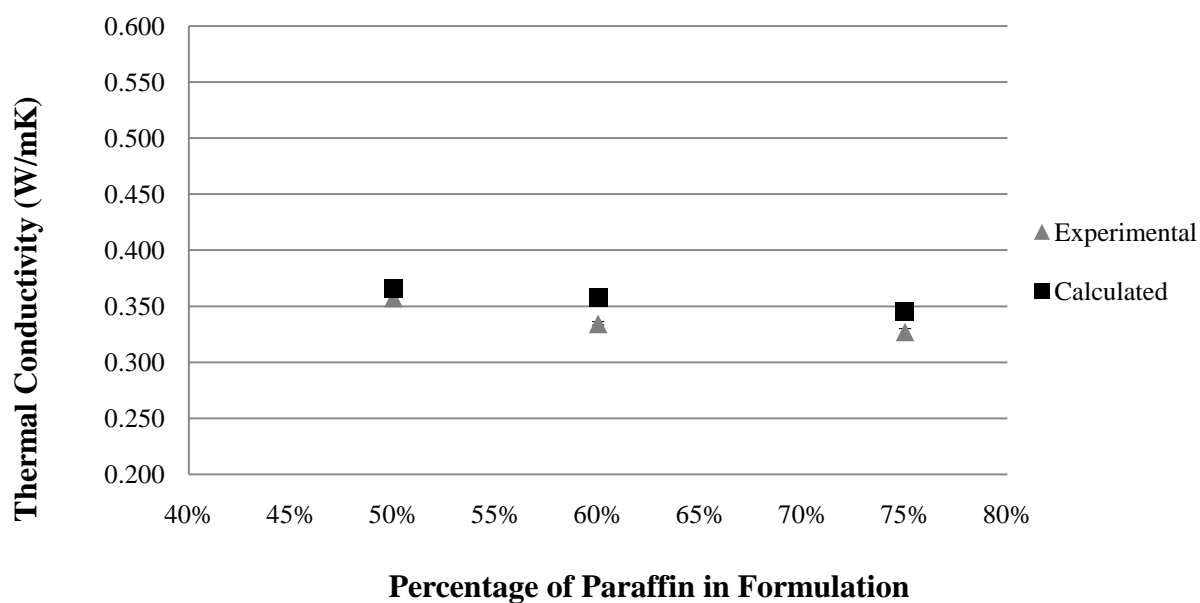




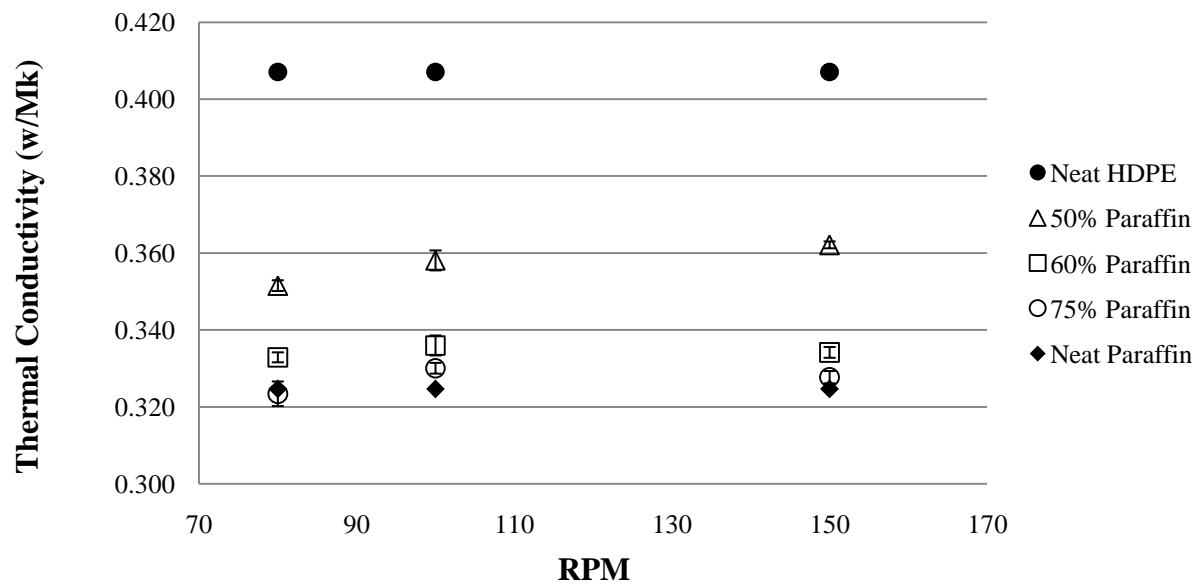
**Figure 3.** SEM pictures of 60%/40% paraffin/HDPE samples at processing speeds of 80 (A), 100 (B) and 150 rpm (C) at 1000 times magnification. Surface paraffin was removed by chloroform to show the surface of the HDPE structure.



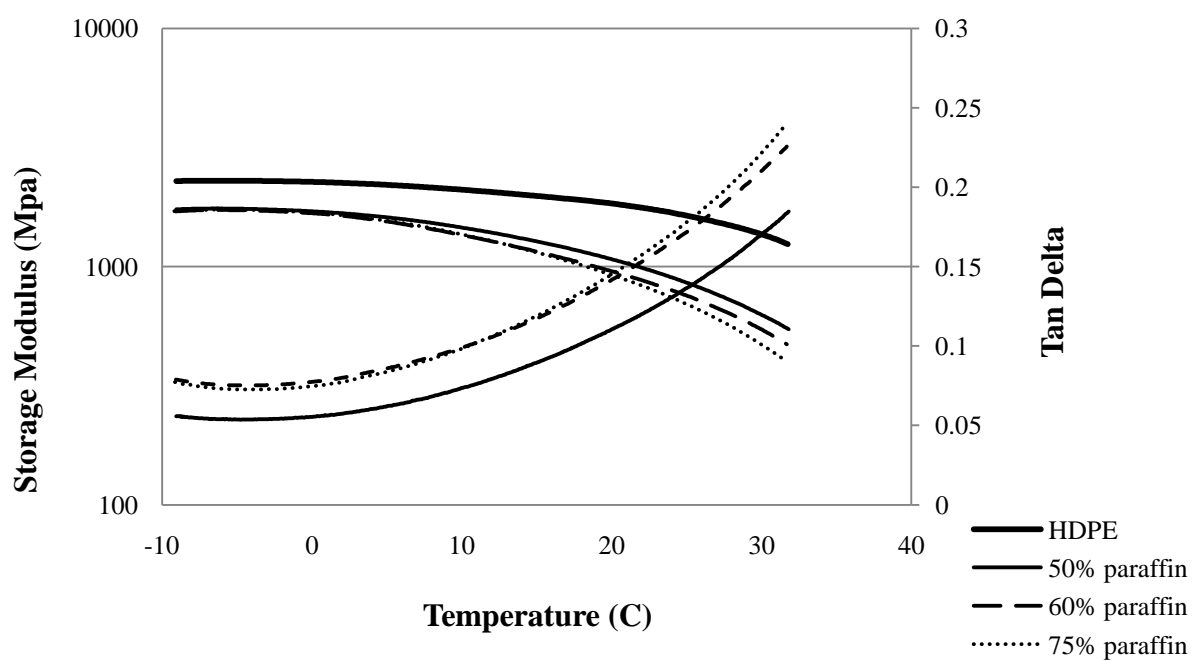
**Figure 4.** SEM pictures of 75%/25% paraffin/HDPE samples at processing speeds of 80 (A), 100 (B) and 150 rpm (C) at 1000 times magnification. Surface paraffin was removed by chloroform to show the surface of the HDPE structure.



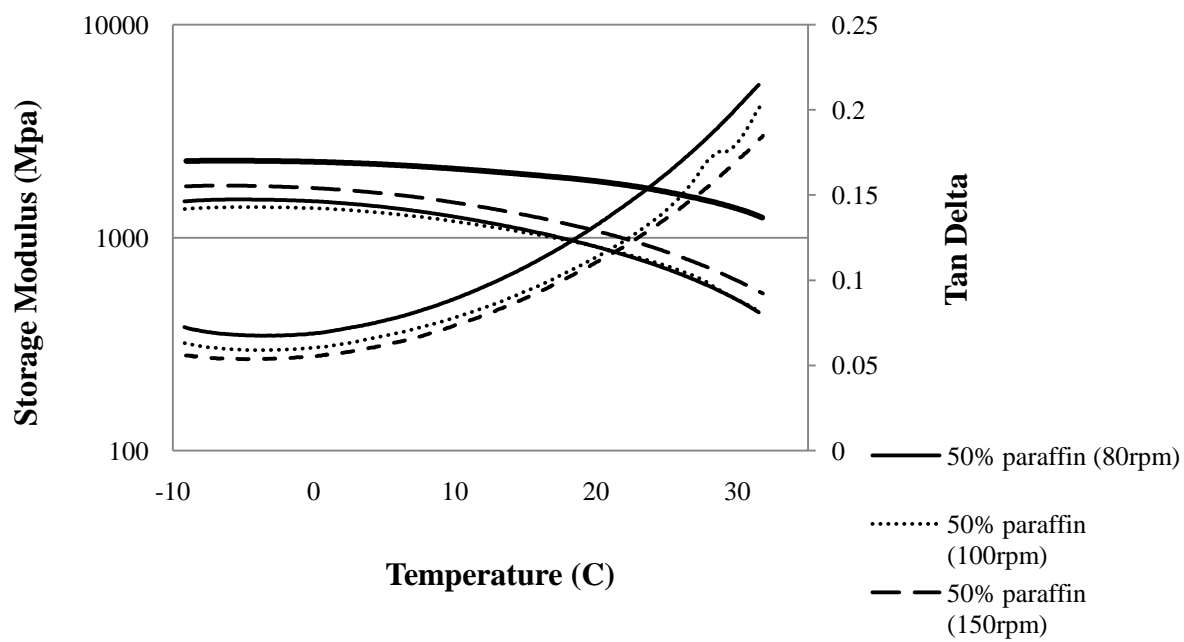
**Figure 5.** Thermal conductivity measurements of paraffin/HDPE blends containing 50%, 60% and 75% paraffin, compared to calculated expectations based on rule of mixtures equation.



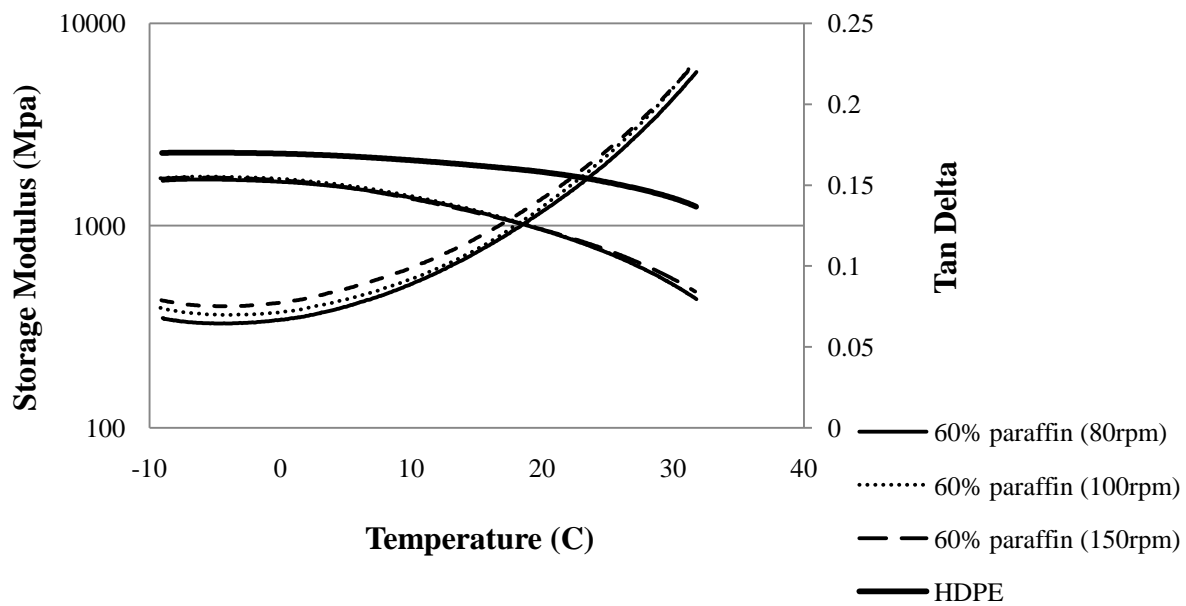
**Figure 6.** Thermal conductivity comparisons between neat HDPE, neat Paraffin, and three formulations at three processing speeds.



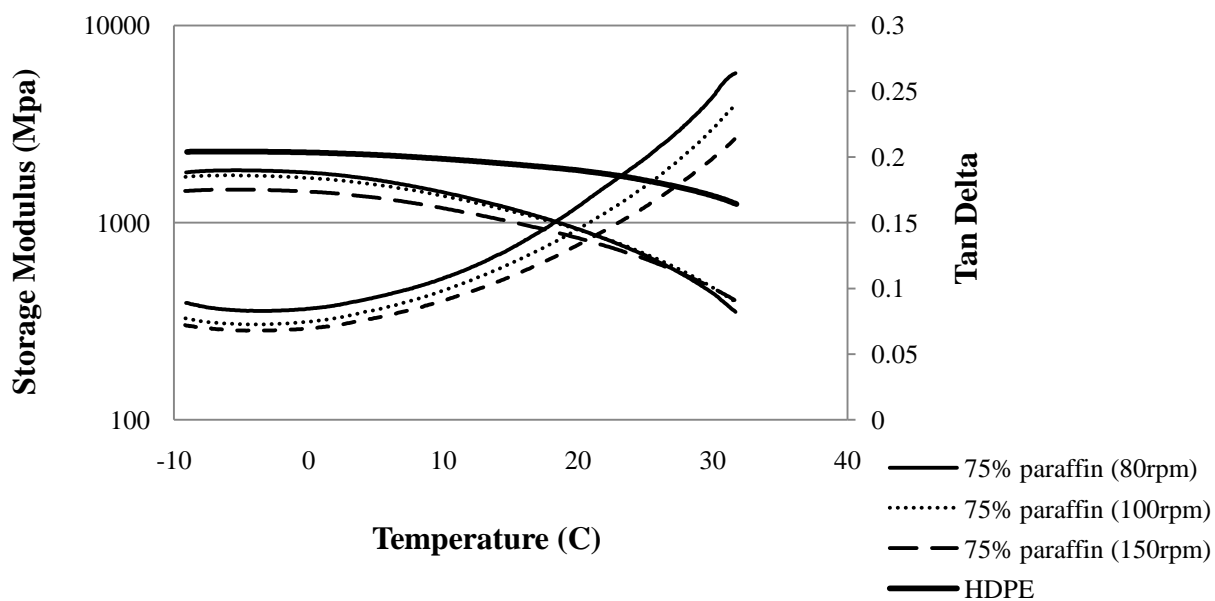
**Figure 7.** Representative DMA curves for three formulations compared to neat HDPE.



**Figure 8.** DMA curves for 50%/50% formulation of paraffin/HDPE blend processed at three speeds (80, 100, 150rpm) compared to neat HDPE.

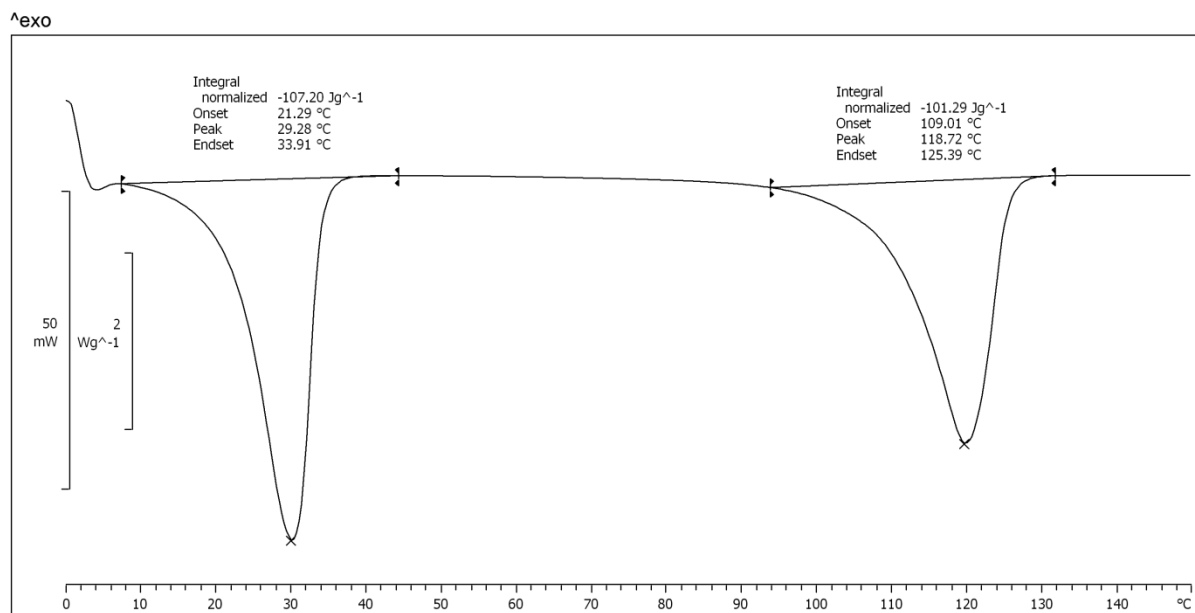


**Figure 9.** DMA curves for 60%/40% formulation of paraffin/HDPE blend processed at three speeds (80, 100, 150rpm) compared to neat HDPE.



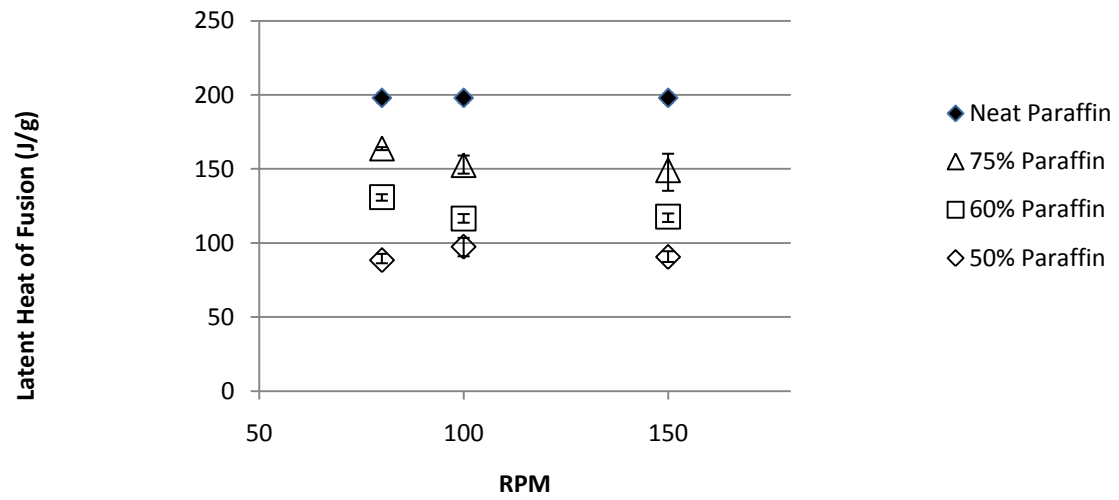
**Figure 10.** DMA curves for 75%/25% formulation of paraffin/HDPE blend processed at three speeds (80, 100, 150rpm) compared to neat HDPE.



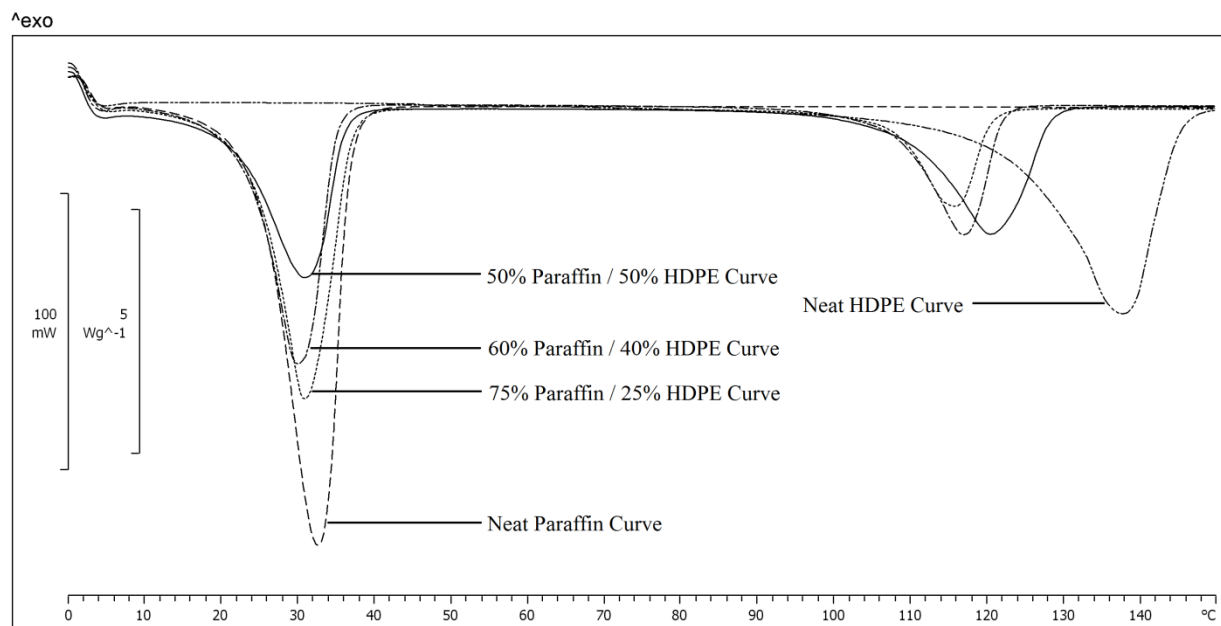


**Figure 11.** Typical DSC curve for the Paraffin/HDPE blend (50/50 formulation shown).

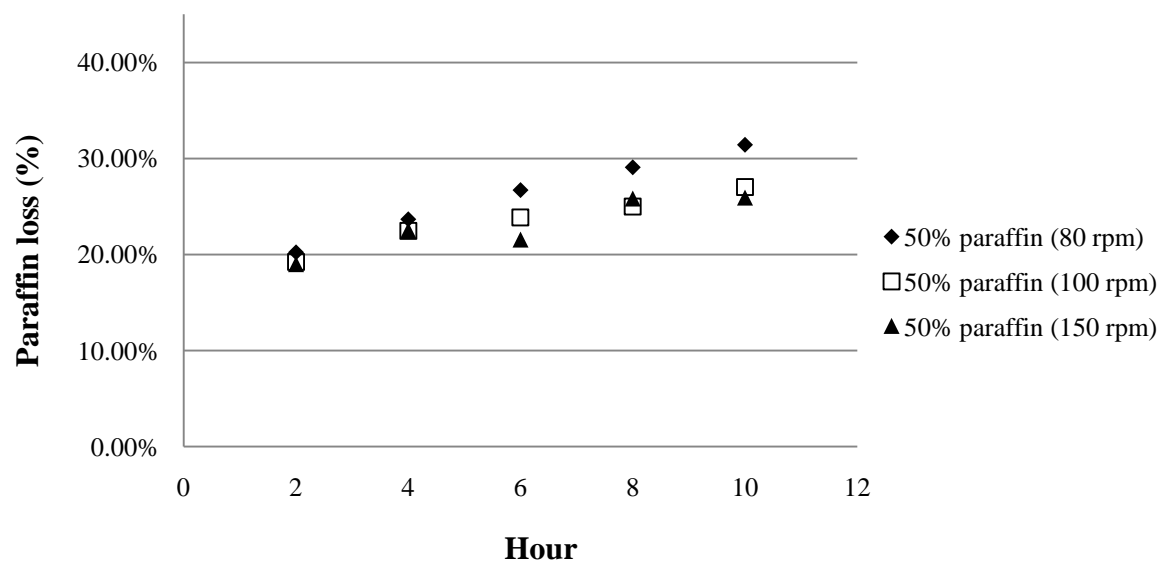
## Latent Heat of Fusion of Formulations



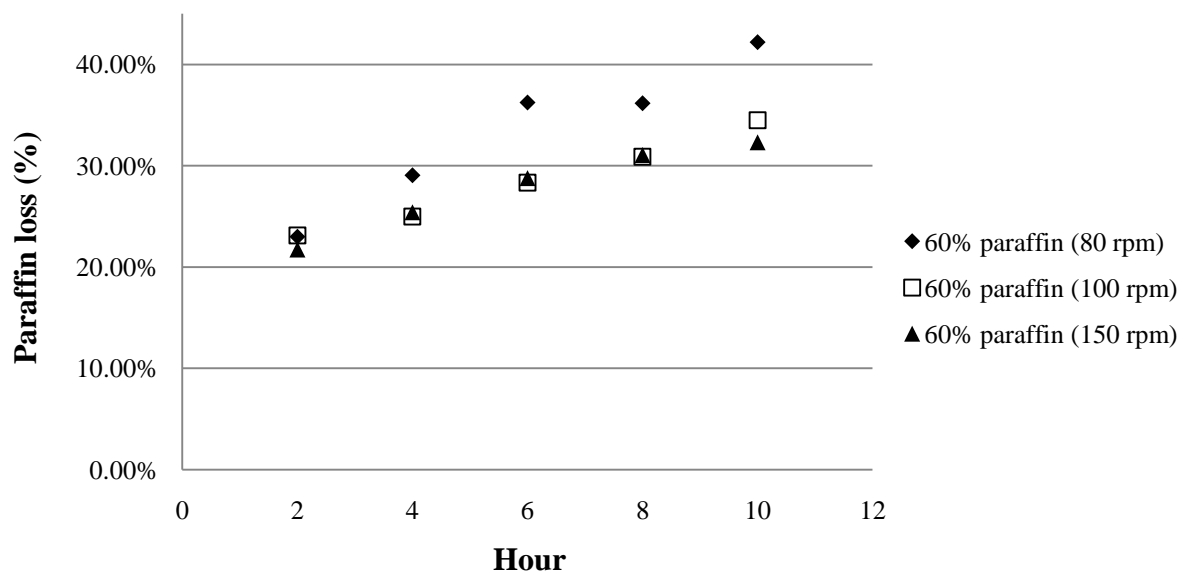
**Figure 12.** Thermal energy absorption capabilities of neat paraffin and three different formulations.



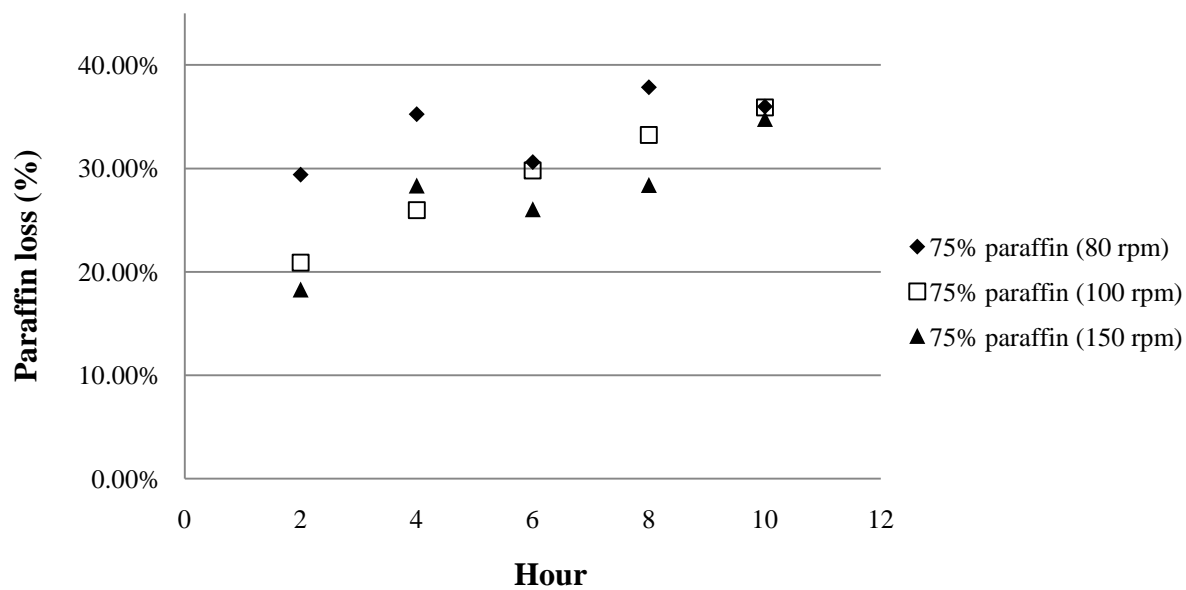
**Figure 13.** DSC curves comparing three formulations of blends to neat paraffin and HDPE.



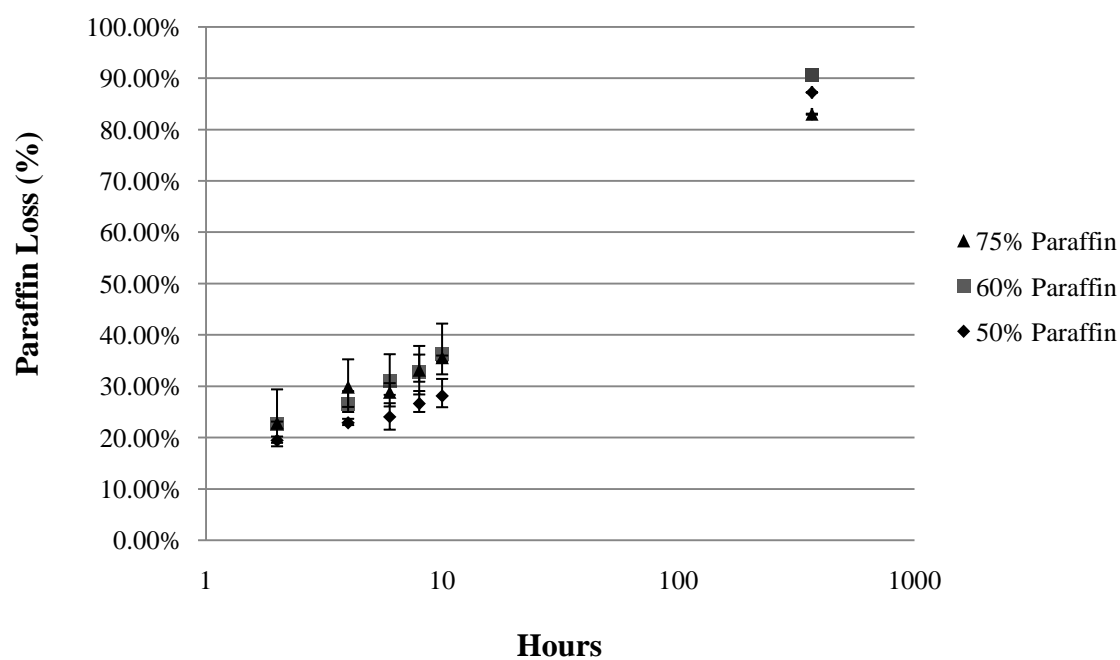
**Figure 14.** Leakage of paraffin (%) in 50/50 formulation by solvent extraction.



**Figure 15.** Leakage of paraffin (%) in 60/40 formulation by solvent extraction.



**Figure 16.** Leakage of paraffin (%) in 75/25 formulation by solvent extraction.



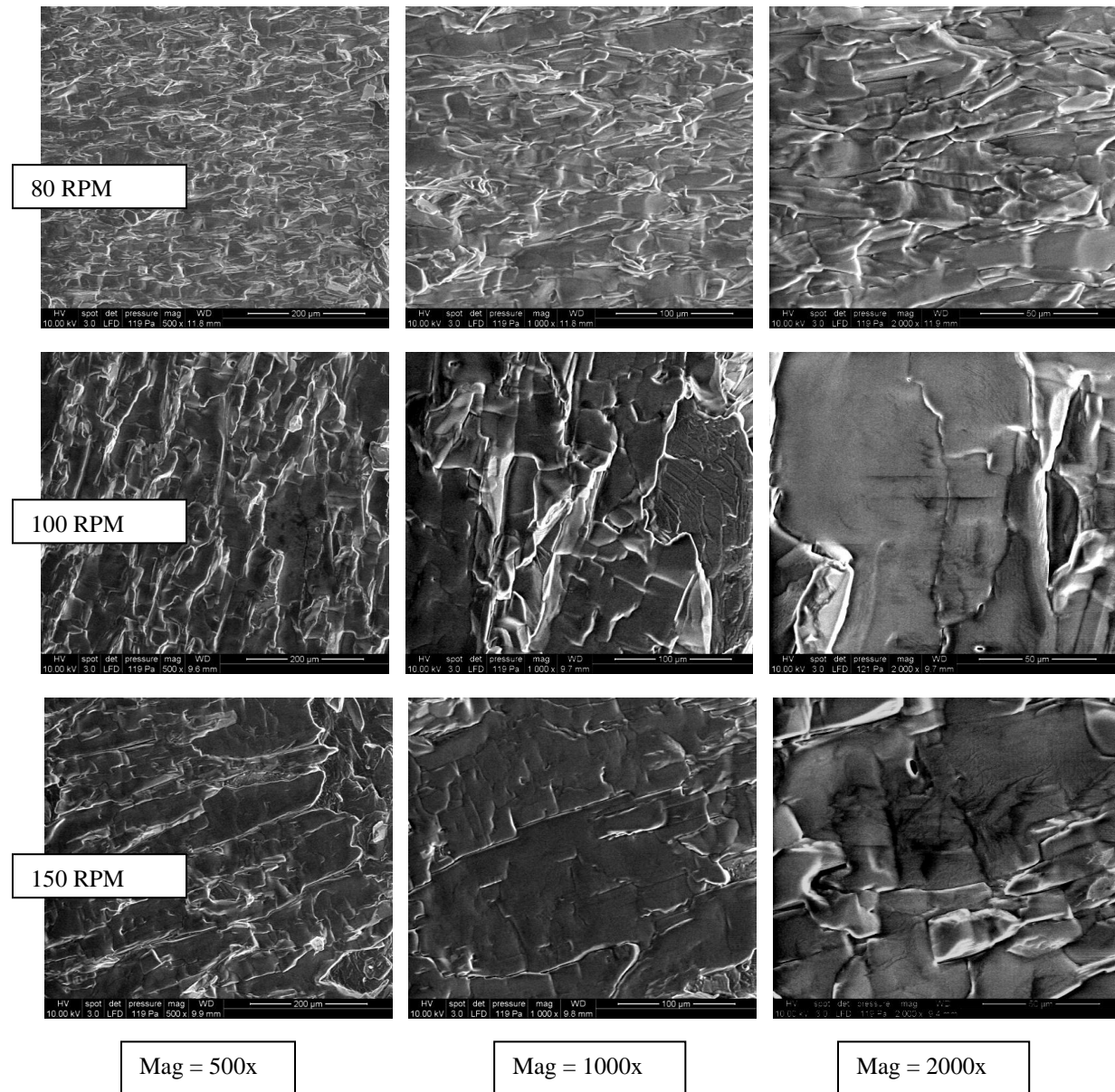
**Figure 17.** Paraffin loss percentage by formulation after submerged in chloroform for the indicated times.

## **7. APPENDIX**

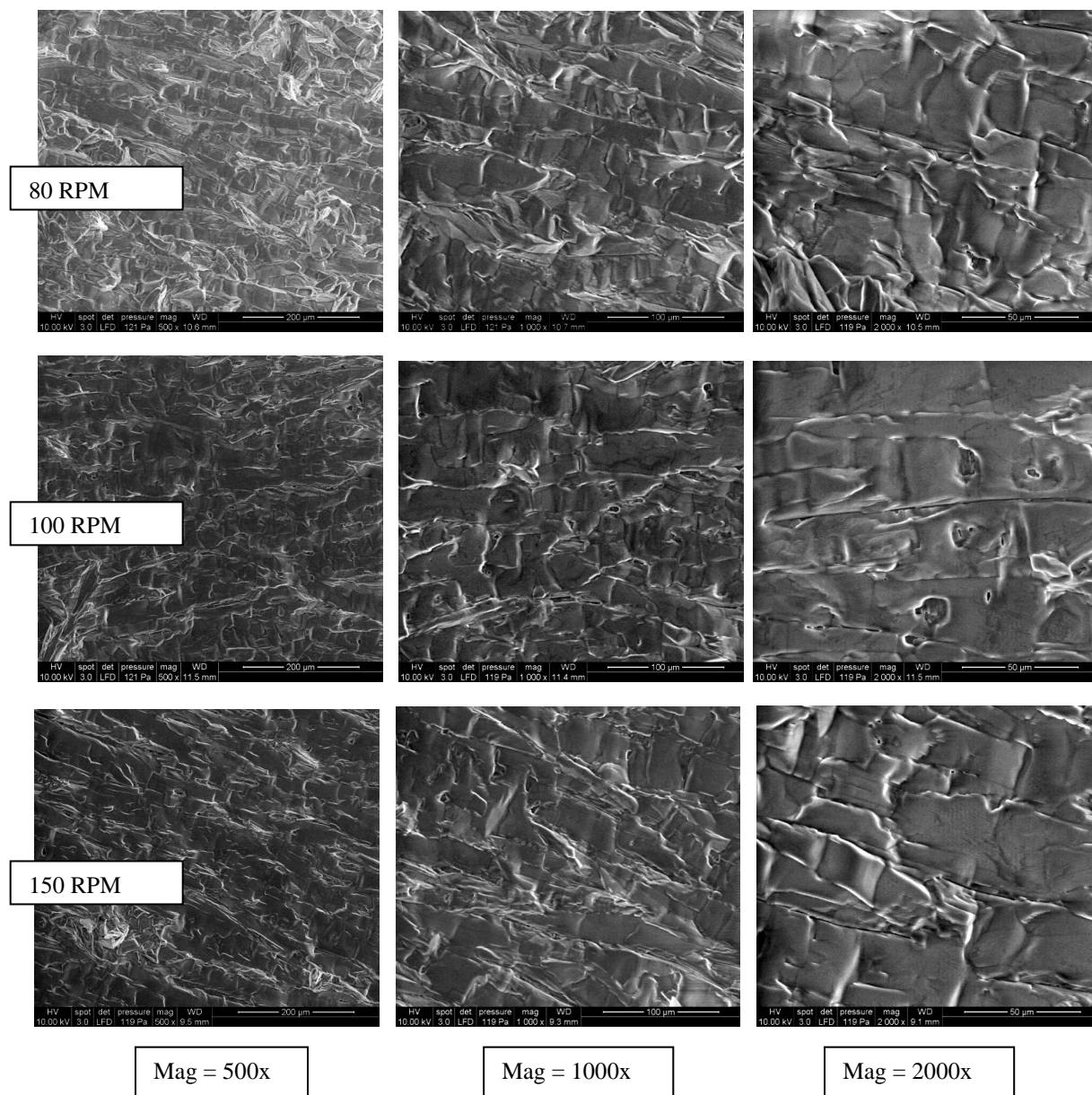


## 7.1 SEM

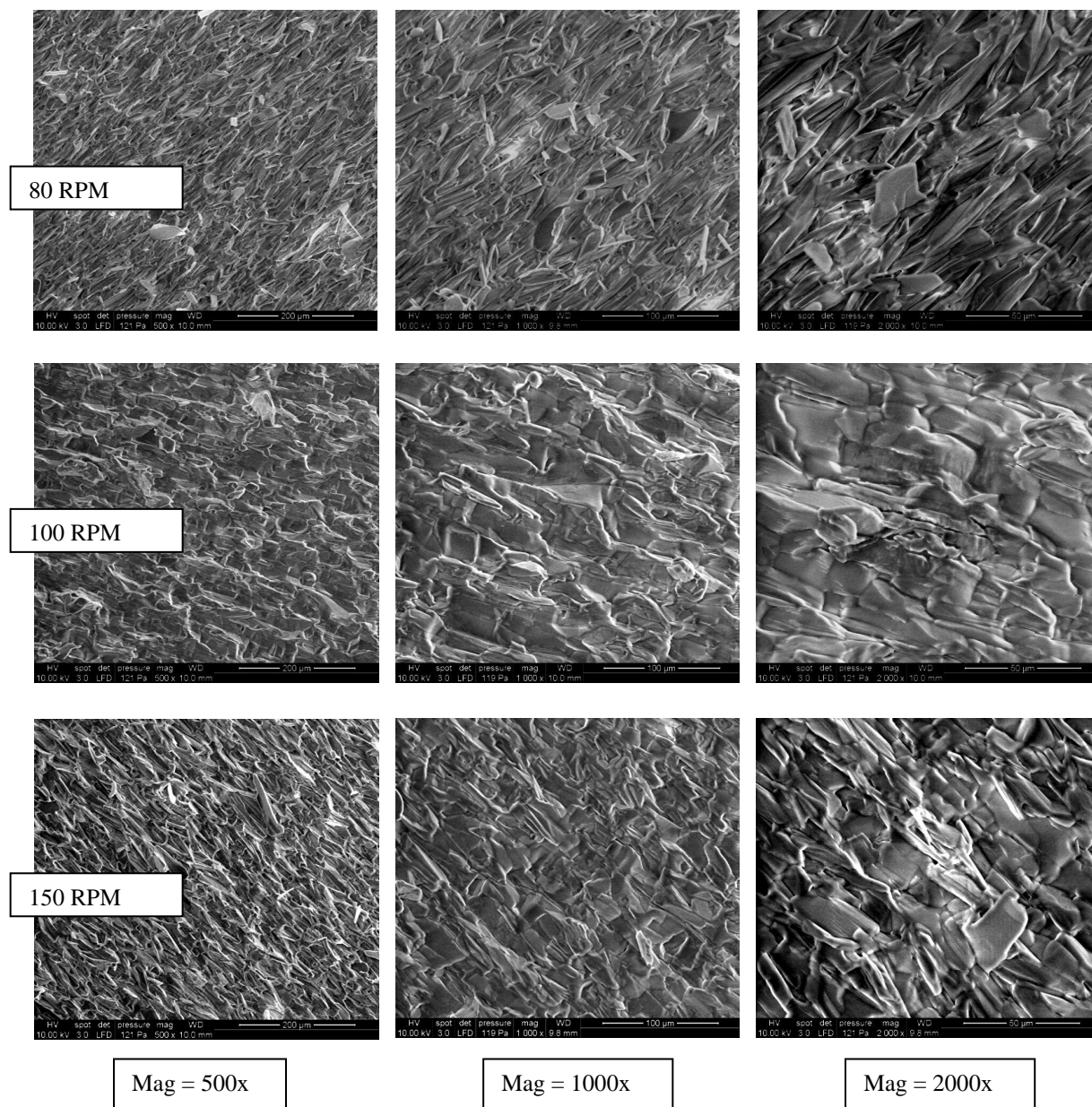
**Figure 7-1-1.** FE SEM micrographs 50% Paraffin/ 50% HDPE formulations (paraffin removed)



**Figure 7-1-2.** FE SEM micrographs 60% Paraffin/ 40% HDPE formulations  
(paraffin removed)



**FIGURE 7-1-3.** FE SEM micrographs 75% Paraffin/ 25% HDPE formulations  
(paraffin removed)



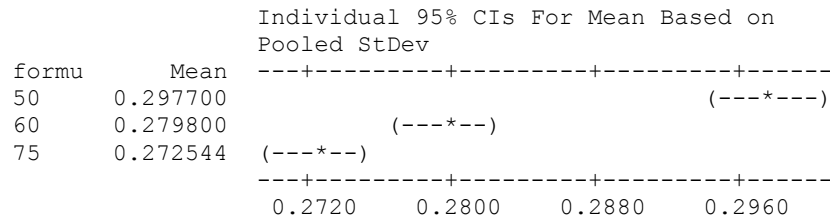
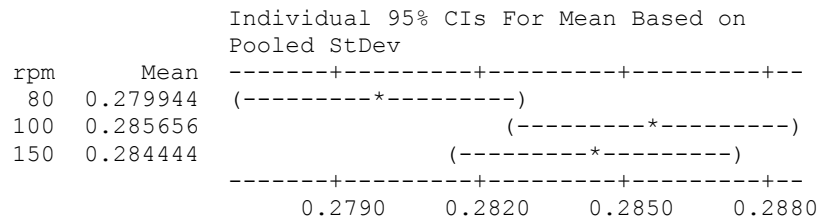
## 7.2 Thermal Conductivity

**Table 7-2-1.** Thermal Conductivity - Analysis of Variance - Minitab

Two-way ANOVA: W/(mK) versus rpm, formulation

Source	DF	SS	MS	F	P
rpm	2	0.0001630	0.0000815	4.54	0.025
formulation	2	0.0030176	0.0015088	83.99	0.000
Interaction	4	0.0000680	0.0000170	0.95	0.460
Error	18	0.0003233	0.0000180		
Total	26	0.0035719			

S = 0.004238    R-Sq = 90.95%    R-Sq(adj) = 86.92%



Formulation	<b><u>Thermal Conductivities (W/mK)</u></b>		
	Processing Speed		
	<b>80</b>	<b>100</b>	<b>150</b>
<b>Neat Paraffin</b>	0.325 (speed n/a)		
<b>75/25</b>	0.323	0.330	0.328
<b>60/40</b>	0.333	0.336	0.334
<b>50/50</b>	0.352	0.358	0.362
<b>HDPE</b>	0.407 (speed n/a)		

**Table 7-2-2.** Mean thermal conductivity results for three different formulations at three different processing speeds.

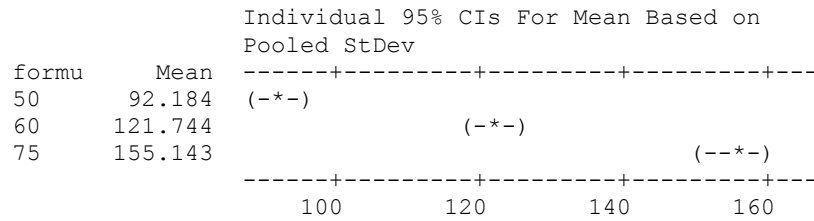
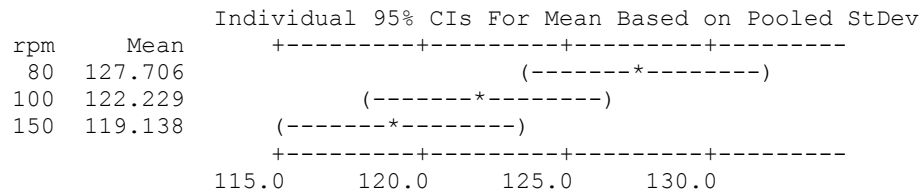
### 7.3 DSC

**Table 7-3-1.** Thermal Energy Storage Capacity - Analysis of Variance - Minitab

#### Two-way ANOVA: J/g versus rpm, formulation

Source	DF	SS	MS	F	P
rpm	2	338.9	169.43	4.45	0.027
formulation	2	17859.3	8929.65	234.30	0.000
Interaction	4	528.1	132.04	3.46	0.029
Error	18	686.0	38.11		
Total	26	19412.3			

S = 6.173 R-Sq = 96.47% R-Sq(adj) = 94.90%

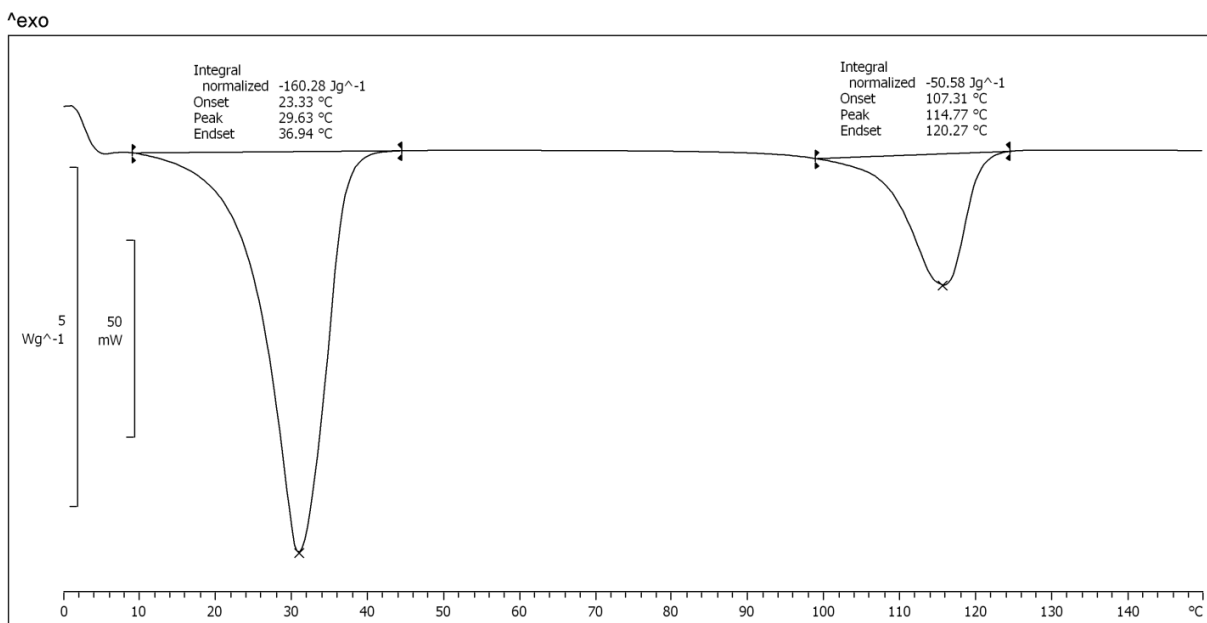


**Thermal Energy Storage Capacities (J/g)**

Formulation	Processing Speed		
	80	100	150
<b>75/25</b>	163.71	152.67	149.05
<b>60/40</b>	130.91	116.46	117.86
<b>50/50</b>	88.49	97.55	90.51

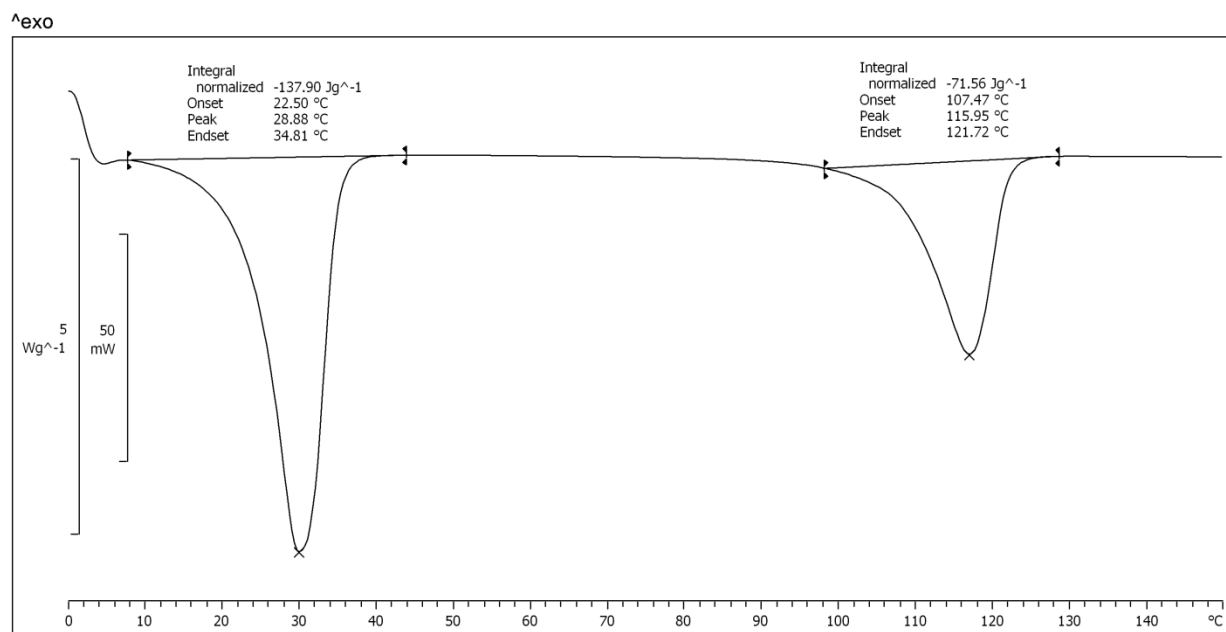
**Table 7-3-2.** Mean thermal energy storage capacities results for three different formulations at three different processing speeds.

### 7.3 DSC

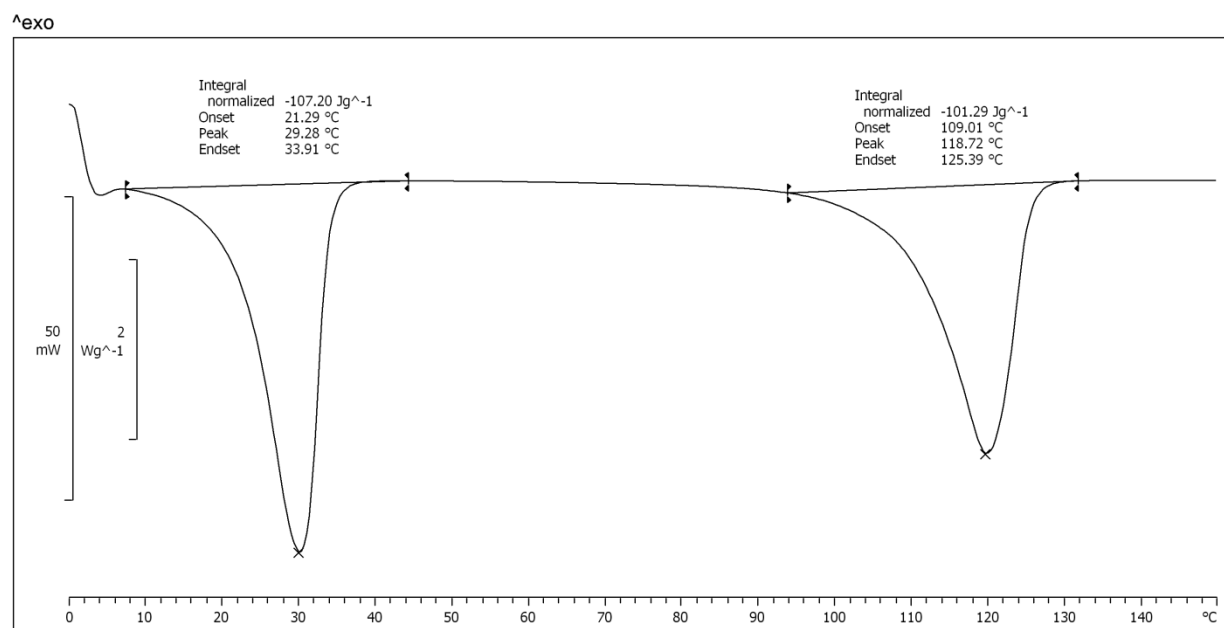


**Figure 7-3-1.** Typical DSC curve for the Paraffin/HDPE blend (75/25 formulation shown).





**Figure 7-3-2.** Typical DSC curve for the Paraffin/HDPE blend (60/40 formulation shown).



**Figure 7-3-3.** Typical DSC curve for the Paraffin/HDPE blend (50/50 formulation shown).

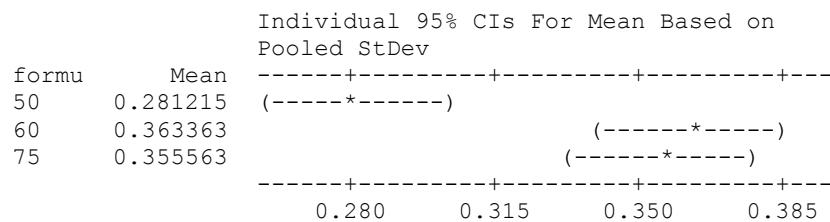
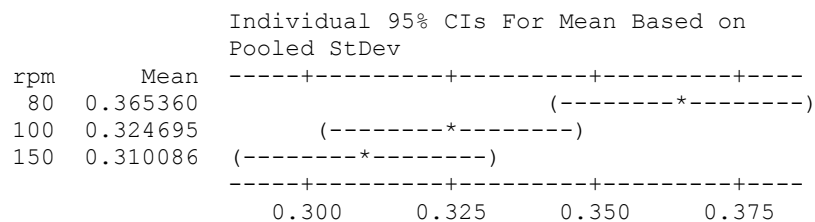
## 7.4 Leakage

**Table 7-4-1.** Leakage of Paraffin after 10 hours - Analysis of Variance - Minitab

Two-way ANOVA: % Loss versus rpm, formulation

Source	DF	SS	MS	F	P
rpm	2	0.0147671	0.0073835	7.37	0.005
formulation	2	0.0370106	0.0185053	18.46	0.000
Interaction	4	0.0067793	0.0016948	1.69	0.196
Error	18	0.0180412	0.0010023		
Total	26	0.0765982			

S = 0.03166    R-Sq = 76.45%    R-Sq(adj) = 65.98%



**Paraffin Leakage after 10 hours (%)**

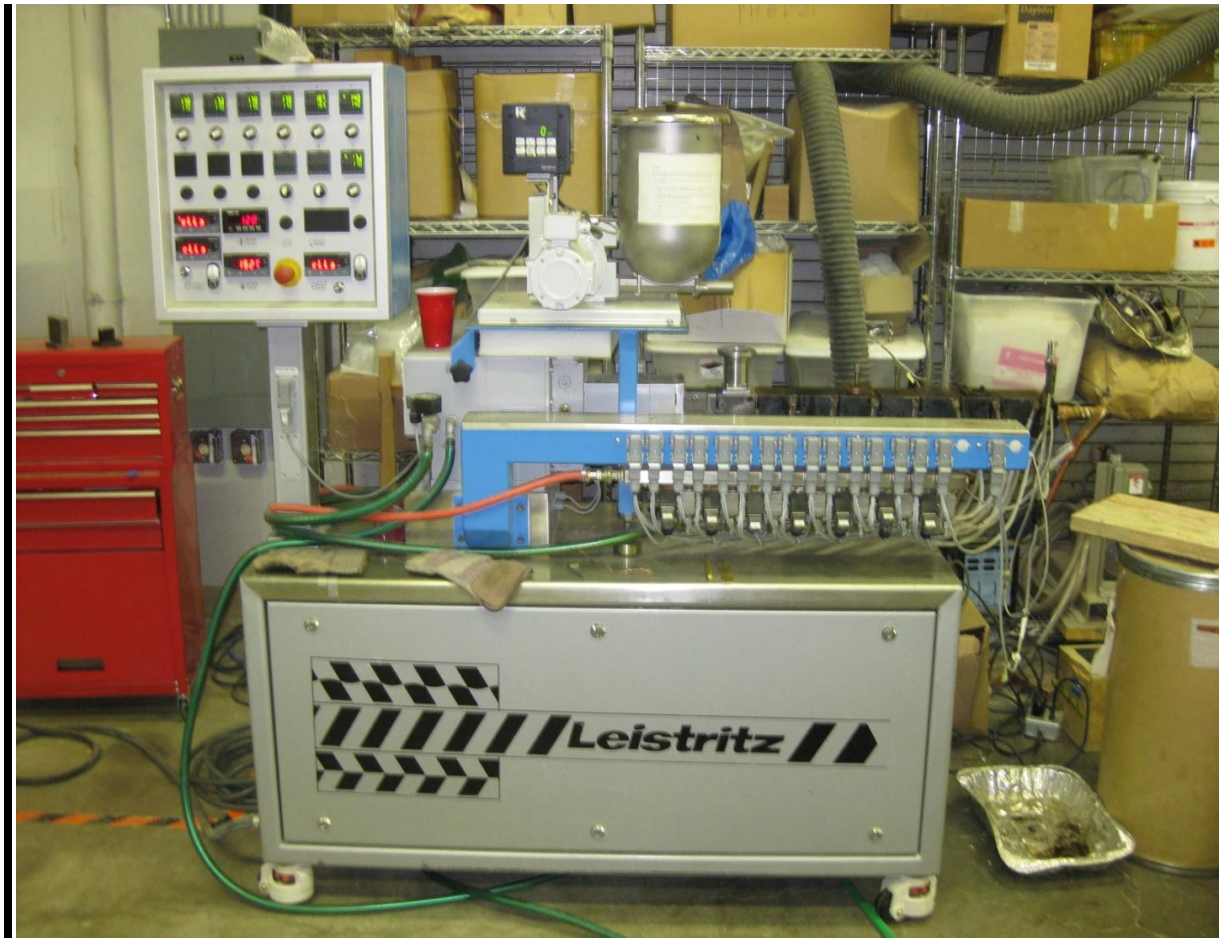
Formulation	Processing Speed		
	80	100	150
<b>75/25</b>	36.0%	35.9%	34.8%
<b>60/40</b>	42.2%	34.5%	32.3%
<b>50/50</b>	31.4%	27.0%	25.9%

**Table 7-4-2.** Mean paraffin leakage results for three different formulations at three different processing speeds. Samples were submerged in a solvent (chloroform) bath for 10 hours.

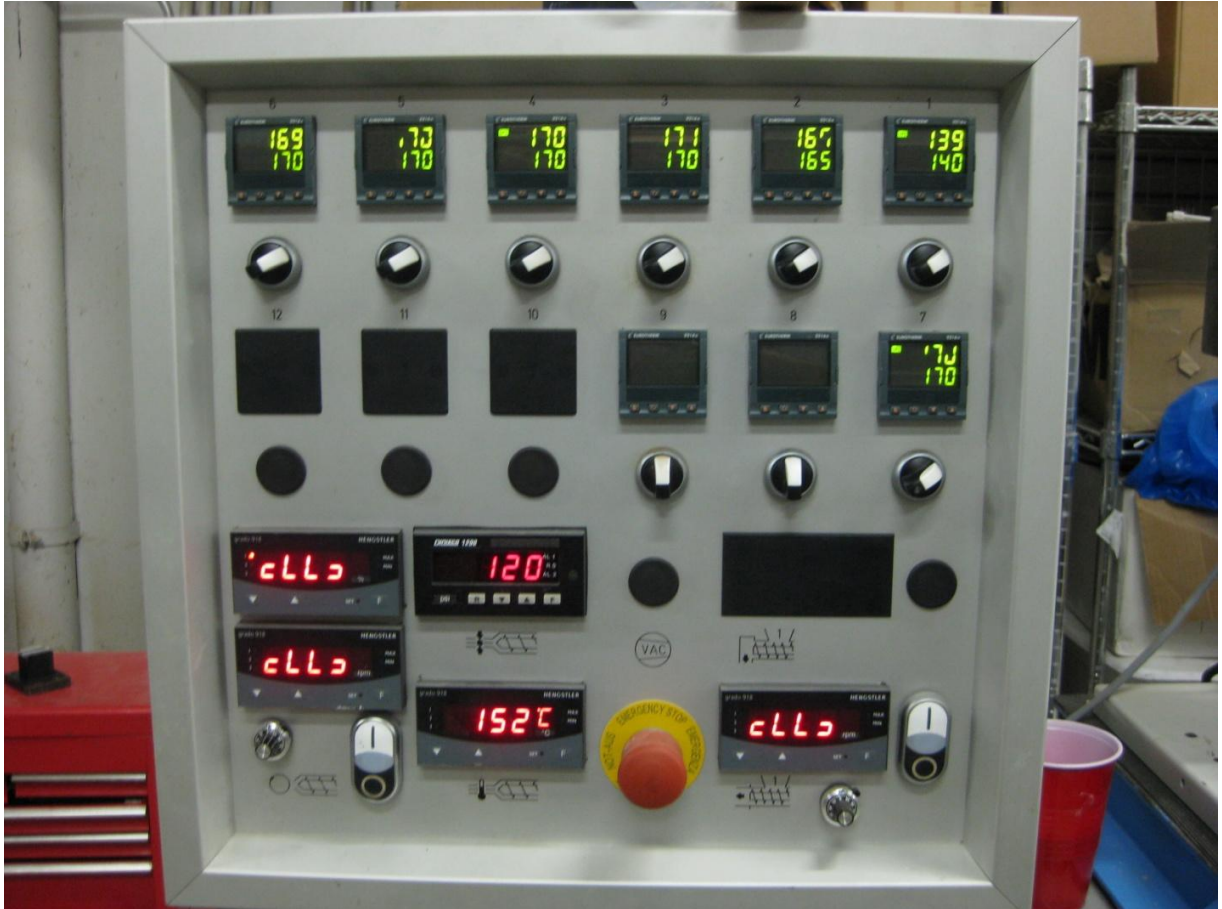
## *7.5 Processing*

### **Prescriptive Method for Extrusion Processing of Form-Stable Phase Change Materials**

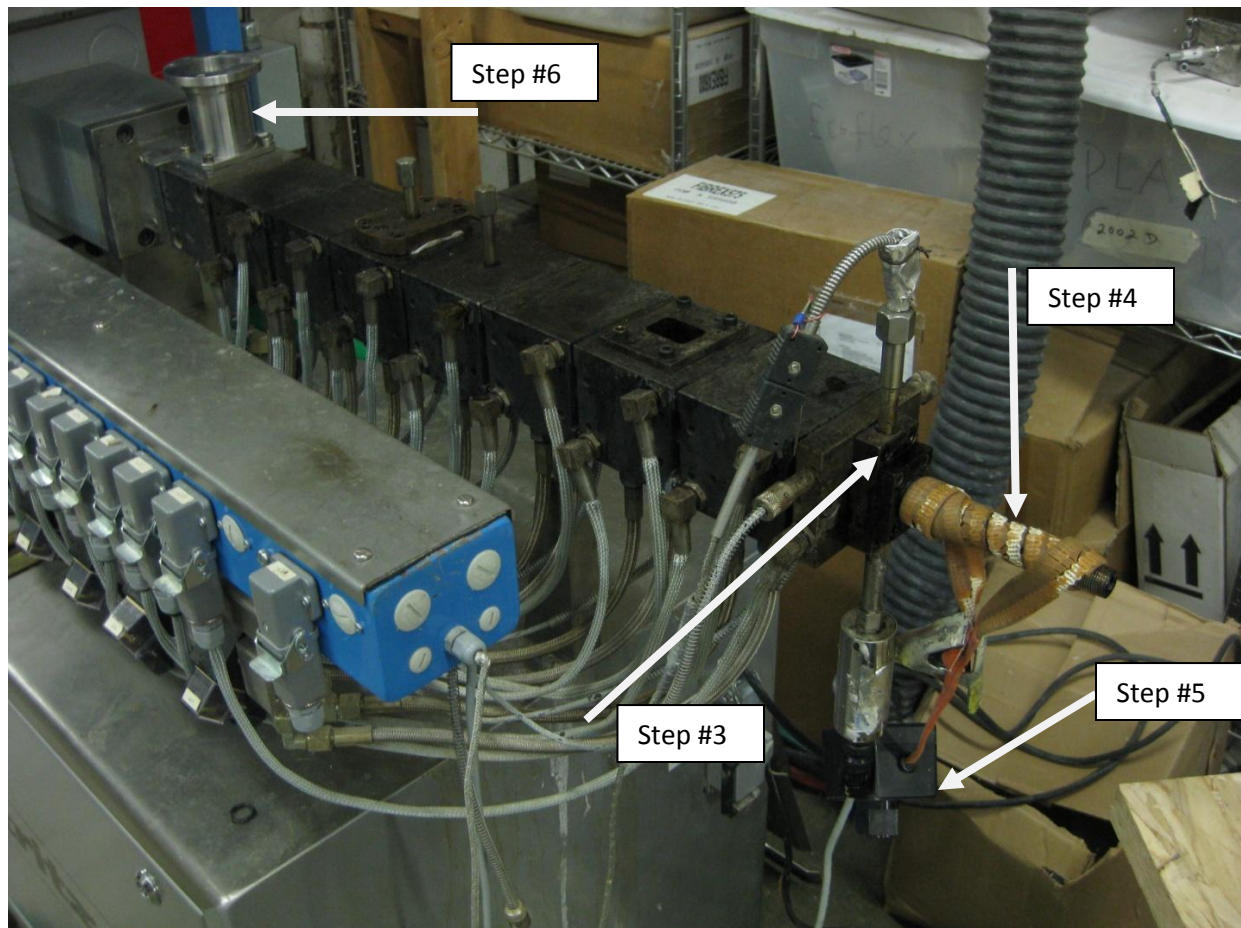
Step 1: Turn on extruder and adjust heating zones to desired temperatures.



Step 2: Allow extruder to heat up until all temperature zones have met the set points of 'Step 1', then purge the extruder with neat HDPE powder until the material produced is free of all debris and foreign material.



- Step 3: Manually remove ALL material from the extruder output by removing the output die and cleaning. NOTE: if there is material left in this area or throughout the extruder, the HDPE/paraffin blend will not transfer through the extruder, but out the vent instead.
- Step 4: Attach pipe to the exit of the extruder and wrap with heat-tape.
- Step 5: Turn on heat-tape, allow warming, and then remove any material obstructing the inside of the pipe.
- Step 6: Remove the feed throat of the extruder.



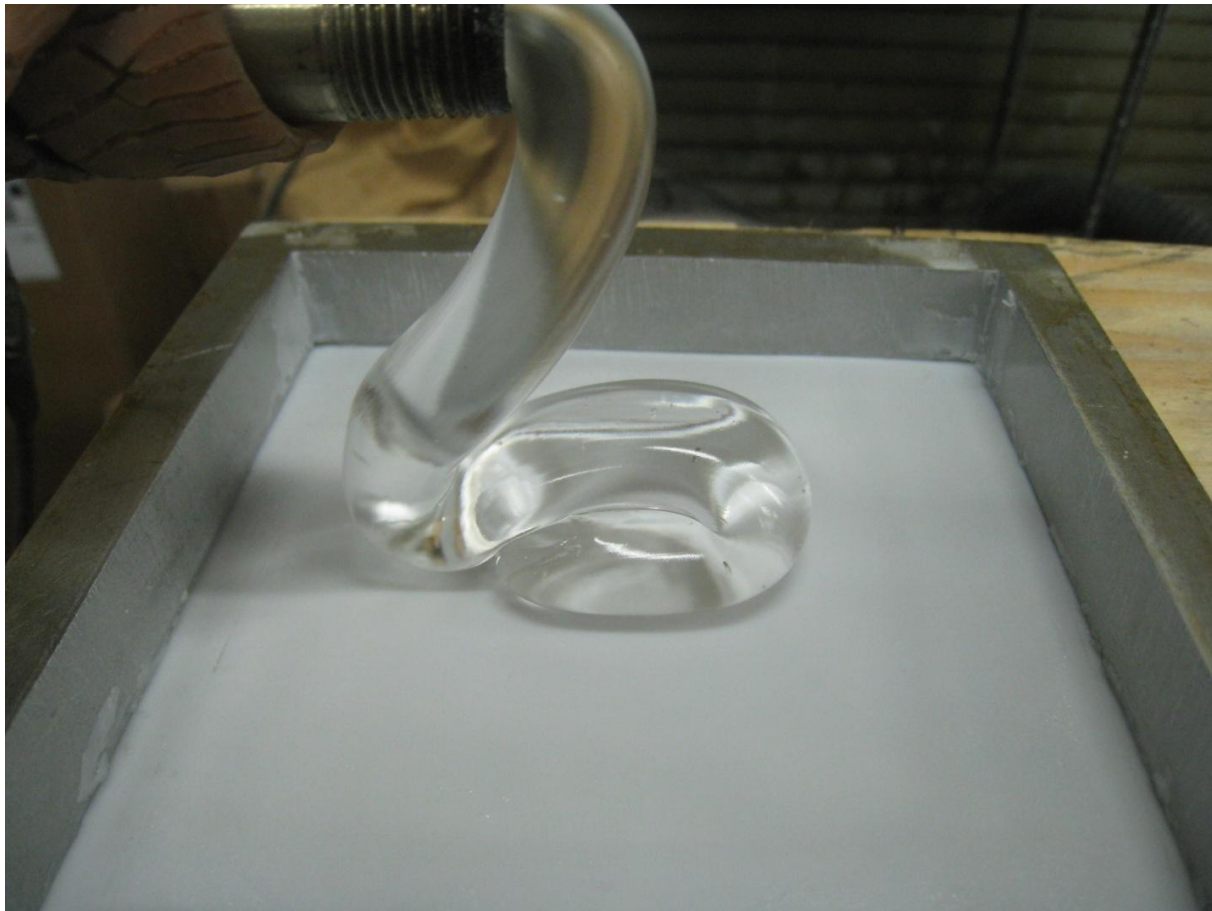


- Step 7: Prepare neat paraffin in liquid form by heating.
- Step 8: Combine neat HDPE powder and neat paraffin (liquid) in a beaker by desired weight percentages. Total mixture weight for one batch is equal to 450 grams.
- Step 9: Mix slurry with a glass stirring rod until the slurry is a homogeneous mixture. Continue mixing this slurry throughout the entire processing stage until all of the slurry has been transferred to the extruder.





- Step 10: Turn on and adjust the processing speed (rpm) of the extruder.
- Step 11: Pour some of the slurry into the feeding area of the extruder. When close to being filled, stop pouring and continue mixing the slurry in the feeding area to ensure the best dispersion of the materials. NOTE: Do not put the glass stirring rod too far into the feeding area; keep away from the extrusion screws!!
- Step 12: Continue this process as needed.
- Step 13: Allow the material to exit the extruder for a few minutes (being caught in a pan so as not to make a mess) allowing any other foreign material to pass through the extruder.
- Step 14: Once the material exiting the extruder is clean, place the form under the exit pipe and collect the material.



Step 15: Continue until the form is full or all of the slurry is depleted.



Step 16: Turn off the extrusion screws ( $\text{rpm} = 0$ ) and allow material to cool naturally until solid.

Step 17: Repeat steps 8 through 16 as needed for additional samples, formulations or processing speeds.