

**Studies on the Crystallinity of Linear
Low-Density Polyethylene and its
nanocomposites**

BY

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| To my beloved parents and wife, my brothers, and my colleagues |

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LIST OF ABBREVIATIONS

DSC	:	Differential Scanning Calorimetry
LLDPE	:	Linear Low-density Polyethylene
LDH	:	Layered Double Hydroxide
LDHA	:	NiFe-Gr Layered Double Hydroxide
LDHB	:	MgFe-Gr Layered Double Hydroxide
LDHC	:	MgFe Layered Double Hydroxide
LDHD	:	NiFe Layered Double Hydroxide
MLS	:	Montmorillonite Layered Silicate
SSA	:	Successive Self-Nucleation and Annealing
SC	:	Step Crystallization
SEM	:	Scanning Electron Microscopy
TGA	:	thermogravimetric analysis
wt%	:	weight percent
XRD	:	X-Ray Diffraction

ABSTRACT

Full Name : Esam Khalid Fallatah

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The effect of adding four nano clays from the layered double hydroxides family; LDHA, LDHB, LDHC, and LDHD in the linear Low-Density Polyethylene matrix was studied. LDHs were incorporated in the LLDPE at 1, 2, and 3 wt% except for LDHB in which 5 wt% were added in addition to the former percentages. The previous mixed materials were compounded using HAKE Mini-Lab Extruder (Melt intercalation) and the nanocomposites were produced as sheets. The thermal properties and stability were investigated by Differential Scanning Calorimetry and Thermogravimetric Analysis, respectively. All LDHs enhanced the nucleation which slightly increased the crystallization temperatures in the nanocomposites. TGA results showed a decrement in the thermal stability except that for 1LDHB which slightly enhanced the thermal stability. The dispersion of LDHs was studied using Scanning Electron Microscopy and X-ray Diffraction. All LDHs increased the formed agglomerates with the increase of the nano-clay concentration, and they were immiscible.

ملخص الرسالة

الاسم الكامل: عصام خالد بكر فلاته

عنوان الرسالة: دراسات عن تبلور البولي إيثيلين الخطي منخفض الكثافة ومركباته النانوية

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: 1444 هجري، ربيع الآخر

في هذه الرسالة تمت دراسة تأثير إضافة أربع من المواد الصلصالية النانوية من عائلة الهيدروكسيدات ذات الطبقات المزدوجة، مضافة إلى البولي إيثيلين الخطي منخفض الكثافة. وهذه المواد الأربع المستخدمة هي هيدروكسيد الحديد المغنيسيومي مع الغرافين، هيدروكسيد الحديد النيكلي مع الغرافين، هيدروكسيد الحديد المغنيسيومي، و هيدروكسيد الحديد النيكلي. تمت إضافة الهيدروكسيدات كل على حدة إلى البولي إيثيلين بمقدار 1, 2, 3 wt% لكل هيدروكسيد باستخدام جهاز ذا قدرة على الخلط والإذابة معا. ومن ثم دراسة نتائج هذا الخلط، وهي المسماة بمركبات البولي إيثيلين النانوية. تمت دراسة التحلل الحراري باستخدام جهاز التحليل الوزني الحراري. وتمت دراسة الخواص الحرارية باستخدام جهاز المسح التفاضلي لسعرات الطاقة. وتم استخدام جهاز حيود الأشعة السينية و المسح المجهر الإلكتروني لدراسة انتشار المواد النانوية في البولي إيثيلين. جميع المواد النانوية حسنت وزادت درجة حرارة التبلور بنسب قليلة. وكذلك كانت غير قابلة للإمتزاج مع البولي إيثيلين، مع ملاحظة زيادة التكتلات المتكونة مقرونة بزيادة تركيز الهيدروكسيدات النانوية. أما نتائج التحليل الحراري أظهرت تأثيرات سلبية على البولي إيثيلين ما عدا هيدروكسيد الحديد المغنيسيومي مع الغرافين الذي أظهر نتائج محسنة للثبات الحراري.

CHAPTER 1

INTRODUCTION

Polyolefins such as polyethylene (PE), polypropylene (PP), ethylene-propylene-diene rubber (EPDM) and ethylene/ α -olefin copolymers are widely used in a plenty of applications because of its controllable properties ¹. These properties can be manipulated by different variables such as changing the molecular weight, the incorporation of linear α -olefin comonomers, the type of catalysts, the type of nano-filler [LDH , MLS, etc]. By changing the former variables, the crystallinity of polyolefins can be controlled giving a wide range of mechanical and thermal properties. Furthermore, there are various types of polyethylene which are mainly arising from branches (depend on α -olefin comonomers type) that change the nature of the material ². There are variety of branch types, starting from simple alkyl groups to ester and acid functionalities. Also, variations may arise from defects in the polymer backbone, these basically made up of vinyl groups. Additionally, the variation of defects and branches in the chain structure will let the crystallinity level to change as will. Generally, the higher the concentration of branches, the lower degree of crystallinity, the lower the density of the polymer. Polyethylene is an organic, thermoplastic, semicrystalline polymer. Generally, it has excellent thermal stability, chemical resistance and high spinnability. Thus, it has remarkable presence in producing fibers and engineering plastics processes. It has low glass transition temperature due to the absence of the strong intermolecular cohesive forces. Therefore, there are considerable

research interests to improve the strength of polyethylene. Adding LDH as an additive not reactive gives a potential offer for the improvement in physico-chemical, mechanical, optical, thermal properties. The addition of the former nano-filler will result in producing a new compound called nano-composite which has unique properties coming from the interactions at the interfaces ³. Polyolefins are widely used in our day-to-day life activities and in myriad of forms, such as fibers, films, sheets, viscous liquid, and wax. They are used in different items such as hoses, bottles, bread bags, containers, tires, outdoor-indoor carpets, bumpers, and garbage bags⁴.

1.1 Molecular Structure of Polyethylene

Polyethylene molecule is made up of a long backbone of carbon atoms linked covalently and in even number with two of hydrogen atoms linked to each carbon, methyl groups are the terminator of the chain ends. Chemically, polyethylene resins are made up of alkanes with the formula $(C_2H_4)_x$, where x is the number of polymerized monomers to form the chain which is known as the degree of polymerization. Polyethylene resins with low molecular weight (oligomers) and a degree of polymerization between 8 and 100 are waxy solids. At normal pressure and temperature, alkanes are going to be in gas or liquid phase, analogous to polyethylene with degree of polymerization less than 8. The typical degree of polymerization for PE with molecular weight starting from 1400 to 3500000 or more is ranging from 100 to 250000 or more. Polyethylene molecules can contain small amount of unsaturation and can be branched to various degrees.

1.2 Polyethylene Types

The variation on polyethylene types are mainly arises from branches that change the nature of the material. There are variety of branches type, starting from simple alkyl groups to ester and acid functionalities. Also, variations may arise from defects in the polymer backbone, these basically made up of vinyl groups. Additionally, the variation of defects and branches in the chain structure will let the crystallinity level to change as will. Generally, as the concentration of branches increases, the degree of crystallinity and the density of the polymer decreases. Table 1 illustrates unique characteristics of each type.

Table 1: Characteristics of Polyethylene types ²

Polyethylene Type	Characteristics
High Density Polyethylene (HDPE)	• Unbranched molecules. • Extremely low level of defects. • High degree of crystallinity. • High density compared to other types of polyethylene. • Can be copolymerized with a very small concentration of 1-alkenes to slightly reduce the crystallinity level. • Densities ranging (0.94-0.97) g/cm³
Low Density Polyethylene (LDPE)	• Contain substantial concentrations of branches. • Branches basically consists of butyl and ethyl groups with some long chain branches. • Low degree of crystallinity.

	• High pressure polymerization process. • Densities ranging (0.90-0.94) g/cm³
Linear Low-Density Polyethylene (LLDPE)	• Copolymers of ethylene and 1-alkenes. • 1-alkenes; primarily 1-butene, 1-hexene and 1-octene. • Co-monomer levels range 2 to 8 mole% • Both linear and branched. • Branches mostly consists of hexyl, butyl or ethyl groups but can be a variety of other alkyl groups. • The complexity of branching is lower than LDPE. • Densities ranging (0.90-0.94) g/cm³
Very low-Density Polyethylene (VLDPE)	• Specialized form of LLDPE, copolymer of ethylene with 1-alkenes. • Co-monomer levels range 8 to 14 mole% • Higher concentration of short-chain branches. • Non-crystalline polymer. • Also known as ultra-low-density polyethylene (ULDPE) • Densities ranging (0.86-0.90) g/cm³
Cross-Linked Polyethylene (XLPE)	• Cross-links may include either bridging species such as siloxanes or direct carbon–carbon bonds. • By crosslinking a gel-like network of interconnected chains is created.

	• Crystallization is greatly hindered by Cross-links. • The density of a cross-linked polyethylene is lower than that of the polyethylene resin
Ethylene-Vinyl Ester Copolymers	• Made by high pressure polymerization process as LDPE. • Ethylene-vinyl acetate (EVA) is the most commonly known amongst these copolymers. • Contain both short and long chain branches in addition to vinyl acetate groups with concentration up to 25 mole% • Greater chemical reactivity. • At low levels of acetate branches, the physical properties are like LDPE. • At high levels of acetate branches, they are elastomeric. • Ethylene-vinyl acetate copolymers exhibit higher densities at a given crystallinity level than polyethylene resins comprising only carbon and hydrogen, this is due to the presence of oxygen. • Densities ranging (0.92-0.94) g/cm³
Ionomers	• Copolymers of ethylene and an organic acid that have been neutralized to form a metal salt. • The copolymerization conditions similar to LDPE. • Contain all the branches normally found in LDPE.

	• The complicated branching structure of ionomers and the presence of polar clusters reduce their ability to crystallize. • Although the crystallinity level is low, the density is the highest among all polyethylene's due to the atomic weight of metal atoms and oxygen in the ionic clusters. • Densities ranging (0.93-0.96) g/cm³
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1.3 Properties of Polyethylene

To reach the desired physical properties, the resin and processing parameters need to be selected carefully. In addition, the semi-crystalline nature can determine the physical properties of solid polyethylene, the crystallinity of polyethylene and the factors that control it will be discussed in a separated section. It must be kept in mind that most of the properties are depending mainly on the combination of the characteristics of its non-crystalline and crystalline components and the connections that connecting them.

1.3.1 Density

Density can be used as a fair approximation to predict the physical properties, it exposes something of its semi-crystalline morphology. It is a function of branch content, molecular weight characteristics and preparation conditions. Generally, density increases as the branch concentration, rate of crystallization, or molecular weight decreases, or the degree of orientation increases. The affect of branch content on density is the highest followed by the degree of orientation and molecular weight and finally by rate of crystallization. The

presence of elements other than carbon and hydrogen in polyethylene resins will make the density to be higher when compared with homo-polymers or olefin branched materials with the same degrees of crystallinity. These elements can be non-olefinic such as vinyl acetate, methacrylic acid, and norbornene. Also, it can be chlorine and oxygen which are used for the chemical modification.

1.3.2 Thermal Properties

Generally, there is difference between semi-crystalline polymers and most of the crystalline solids, in which they exhibit a range of melting point rather than a one discrete temperature. Polyethylene shows a range of crystalline melting temperature from as low as room temperature up to 135°C. This range is because of the wide lamellar thickness distribution of the solid state. Additionally, due to the localized molecular motions in the disordered, interfacial, or crystalline regions, many secondary transitions will be exhibited by solid polyethylene.

1.3.3 Crystalline Melting Temperature (CMT)

The crystal lattice of polyethylene will be stable until the highest CMT T_m is reached. Above this point the crystallites are destroyed and amorphous, disordered melt is formed. Polyethylene goes through a change in its physical state from the semi-crystalline to the melted state over a temperature range lower than 10 °C and not higher than 70 °C. After this range polyethylene starts to become amorphous up to 140 °C, then it will char and decompose. The melting properties of polymers are usually analysed by the differential scanning calorimetry (DSC). DSC provides a graph, called a thermogram, which plots the instantaneous heat capacity of the specimen versus temperature. Generally, narrower melting distributions and higher melting peaks will be displayed for samples with low

levels of branches, low molecular weight and slow crystallization rates. Recently, the melting point of polyethylene crystals of a wide thickness has been estimated thermodynamically to be within the range of 138 – 146 °C⁵. Also, it was found that by increasing the pressure, the melting range can be shifted to higher temperatures⁶. Table 2 shows the effect of Molecular, Processing, and Morphological Characteristics on Peak Melting Temperature of Polyethylene.

Table 2: Effect of Molecular, Processing, and Morphological Characteristics on Peak Melting Temperature of Polyethylene⁷

Variable	Effect on melting temperature
Increased branch content	Decrease
Increased molecular weight	Decrease
Decreased density/crystallinity	Decrease
Increased cooling rate	Decrease
Increased orientation	Increase

1.3.4 Heat Of Fusion

The enthalpy of fusion is a measure of the amount of heat needed to convert the crystalline fraction (solid phase) to the disordered state (amorphous). Heat of fusion principally determined by two factors, these are the rate of crystallization and the degree of orientation. Generally, the higher the degree of orientation or the slower the rate of crystallization, the greater will be the enthalpy of fusion. Additionally, as the molecular weight of polyethylene increases the effect of orientation becomes more obvious. The heat of fusion of 100% crystalline polyethylene has been calculated to be 69 cal/g⁸. Table 5 lists typical heats of fusion encountered for the various classes of polyethylene⁹.

Table 3: Heats of Fusion of Various Types of Polyethylene ⁹

Polymer	Heat of fusion (cal/g)	Degree of crystallinity (%)
Very low-density polyethylene	Smaller than 15	Smaller than 22
Ethylene-vinyl acetate copolymer	7 – 35	10 – 50
Polyethylene ionomer	14 – 31	20 – 45
Linear low-density polyethylene	15 – 38	22 – 55
Low density polyethylene	21 – 37	30 – 54
High density polyethylene	38 – 53	55 – 77
Ultradrawn polyethylene fibers	Greater than 62	Greater than 90

1.4 Crystallinity of Polyethylene

Practically, due to the complicated physical nature of the molecular chains, it is impossible for polyolefins to be in a fully crystalline structure. Although, high degree of crystallinity can be attained by polymers such as Polyethylene, but it is more accurate to describe them as partially crystalline or semi-crystalline. The physical properties of polyethylene are mainly depending on the relative attributions of the non-crystalline and crystalline phases and their size, shape, connectivity, and orientation, with respect to one another.

A semi-crystalline thermoplastic consists of spherulites. Spherulites contains amorphous material and folded flat sheet-like lamellae. During crystallization spherulites first nucleate and then grow into spheres as shown in Figure 1

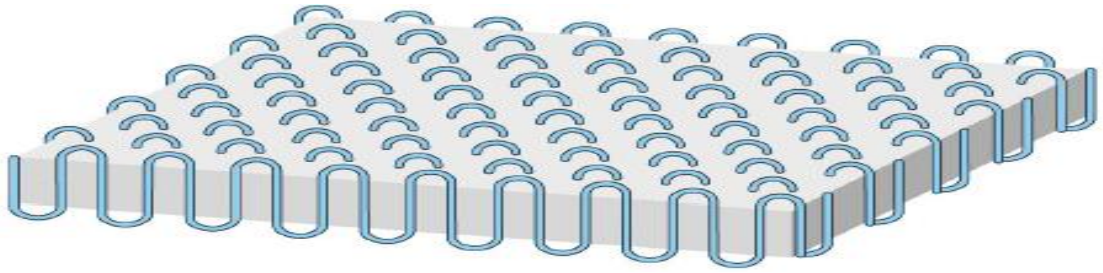


Figure 1: Crystalline Regions Comprised of “Lamellae” ¹⁰

1.4.1 Three-Phase Morphology

Semi-crystalline polyethylene is composed of three phases as shown in Figure 2. The first phase is the crystalline or ordered phase, it is made up of crystallites in which the molecular chain segments are packed in regular arrays. The second phase is the non-crystalline phase, it is made up of disordered molecular segments which are usually continuous with those in the crystallites. The disordered molecular segments comprise three types as shown in Figure 3. These types are known respectively as “tie chains”, “loops” and “’cilia’”. The third phase is the interfacial phase, also known as the partially ordered or interface region. The third phase which is the boundary between the first and second phase, consists of chain segments that demonstrate different degrees of order.

The proportion of chains forming the crystallites to that forming the disordered region is a function of the molecular weight, branching level, and crystallization conditions. The degree of connectivity between crystallites is a major factor in determining the physical properties. The amorphous is widely used to describe the non-crystalline region including the disordered and interfacial regions.

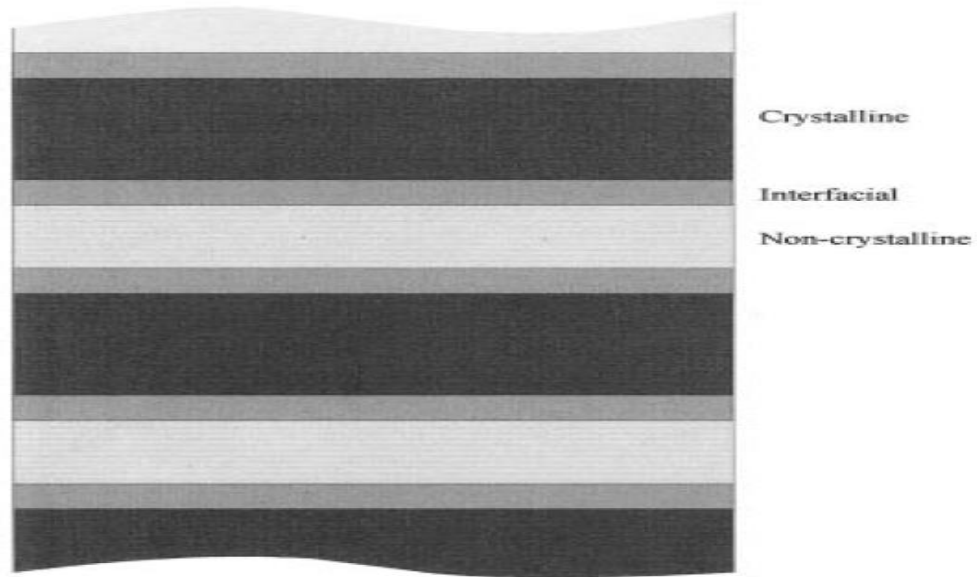


Figure 2: Schematic representation of the three phases present in solid polyethylene²

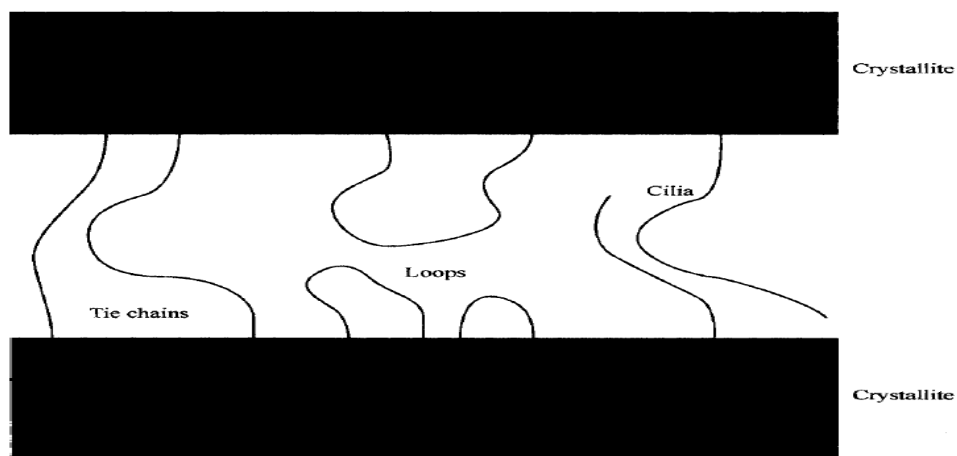


Figure 3: Tie chains, loops, and cilia in the non-crystalline phases of polyethylene²

1.4.2 Lamellae (Crystallized from the Melt)

After the development of chloro-sulfonic acid staining of the microtomed sections¹¹ and the permanganic acid etching of cut and fractured surfaces¹², the direct envisage of the

lamellar morphologies become possible by using transmission electron microscope. Atomic force microscopy and ruthenium tetroxide vapor staining techniques have been recently used to study the arrangement of lamellae in polyethylene^{13,14}. Generally, the higher degree of crystallinity of a sample, the more organization of lamellae with it. “lamella” and “crystallite” are usually used interchangeably when referring to polyethylene morphology. Specifically, lamellae are a specific type of crystallites, which is a microscopic crystal.

1.4.3 Crystallization Mechanism

Thermodynamically, polyethylene crystallizes when the conditions that make the crystalline phase more stable than the disordered one are satisfied. The structure of the disordered state is affected by both internal and external factors. The internal factors are mainly depending on molecules, such factors as the molecular weight distribution, molecular weight, concentration, type and distribution of branches. The external factors which mainly depend on surrounding conditions include temperature, pressure, shear, concentration of solution, and polymer solvent interactions.

Thermodynamically, following Gibbs equation $\Delta G = \Delta H - T\Delta S$, as the temperature of a given system becomes lower, the crystallization driving force will become greater. Kinetically, the crystallization process will become slower with the increment on viscosity

associated with the decreasing of temperature. So, the precise mechanism of crystallization is determined by balancing the kinetic and thermodynamic factors.

1.4.4 Crystallization Kinetics

The crystallization kinetics of a sample is controlled by the rate of crystal growth and the rate of nucleation. The high viscosity of polyethylene will hinder the motion of molten chains during the crystallization and consequently decreases the crystallization rate. Also, the formation of thick lamellae will be inhibited. In addition, the crystallization rate can be influenced by such independent variables like temperature and orientation. The crystallization rate will be slow at high temperature close to the equilibrium melting temperature, because the chemical potential is small. In contrast, the slow occurrence of crystallization at low temperature is due to the high molecular weight and branching those inhibited the movement of chains. Studying the crystallization processes is better to be conducted using the most two common methods, these are the differential scanning calorimetry and hot stage optical microscopy. In the former method, the heat flow is measured as a function of time and temperature. In the second method, the progress of growth of spherulites is observed.

For any given polymer, the highest rate of crystallization typically occurs at an absolute temperature approximately equal the equilibrium melting temperature multiplied by 0.8. In the case of linear polyethylene, the maximum rate would be around 60 °C.

1.4.5 Interlamellar Connections

Connections between crystallites can be by covalent or/and ionic bonds. The covalent bonds are present on all polyethylene specimens, while the ionic bonds require the presence of a polar comonomer. Covalent connections include the direct tie chains and entangled loose loops coming from another lamella.

1.5 Layered Double Hydroxide

The following is a summary of what Costa et al¹⁵ mentioned about the advantages of the LDH:

- LDHs are reactive materials, they are made up by an endothermic decomposition reaction which produces water and metal oxide residue. Thus, because of this property the thermal stability could be improved.
- Anionic surfactants could be used to modify the LDH, they are mainly used to increase the number of the available surfactants.
- LDHs are more efficient in providing the reinforcement of the polymer at lower filler concentration. Also, they can be prepared with high purity in the laboratory with changeable chemical compositions and homogeneous structure.
- The reinforcing efficiency of the LDH or any clay-polymer nanocomposites depends mainly on the dispersion in the polymer.
- LDHs are non-poisonous as the Halogens which are harmful for the human health and the environment. Unfortunately, Halogens were widely used as FR. Thus, the search is avoiding Halogens (Halogen free flame retardants).

1.6 Differential Scanning Calorimetry

Generally, the thermal analysis of polyethylene is conducted by heating or cooling of a sample at a controlled rate, while the physical characteristics is being monitored. The change in heat capacity is determined by using DSC. DSC is a technique used to determine the thermal properties of polyethylene related to essential morphological investigations and real live applications. DSC is conducted by dynamic calorimetric analysis of a sample in which its temperature is being increased at controlled rate. This is obtained by measuring the heat capacity of a sample as a function of temperature while heating or cooling. The results are presented in a plot known as a thermogram in which the heat flow is plotted as a function of temperature. Melting and crystallization processes are represented by endothermic and exothermic peaks respectively as shown in Figure 4 & 5. The material transition such as glass-rubber transition is reflected by a step change as illustrated in Figure 6. Figure 7 comprises all reflected peaks.

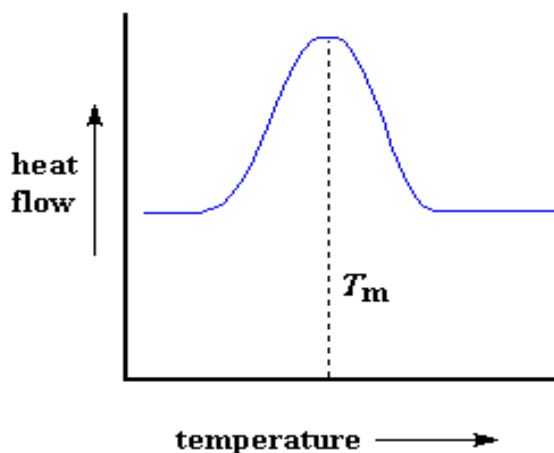


Figure 4: Typical polymer thermogram for Melting process by DSC (Endothermic peak)¹⁶

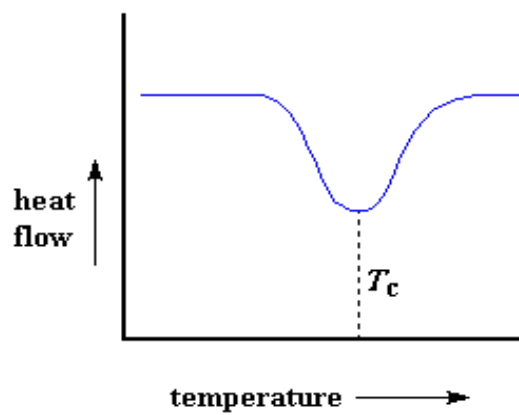


Figure 5: Typical polymer thermogram for Crystallization process by DSC (exothermic peak)¹⁶

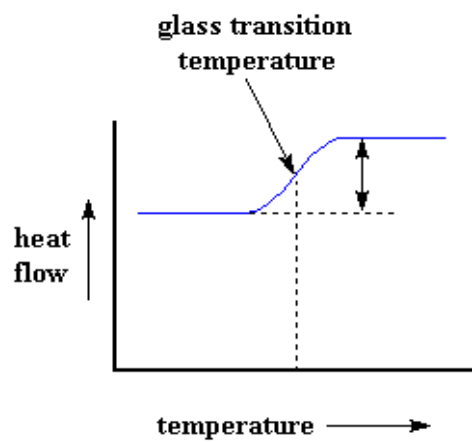


Figure 6: Typical polymer thermogram for Glass-rubber transition by DSC¹⁶

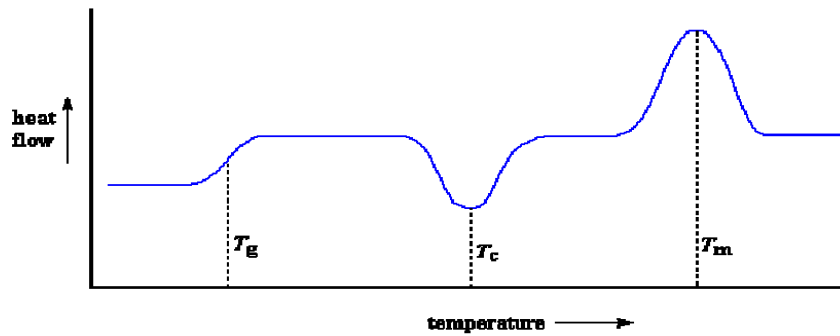


Figure 7: Typical polymer thermogram for Crystallization, melting and material transition peaks by DSC¹⁶

There are two basic types of DSC, both are capable to obtain accurate measurements on samples within the range of 1 -20 mg. In both types small aluminium sample pans are used to encapsulate the specimens on, the pans are placed in a sample chamber to compare it with an empty reference pan. Also, a computer is used to regulate the rates and monitor the temperatures.

In the first type shown in Figure 8, the heat flow to the sample chamber through the sample support is maintained at constant rate, whereas the temperature of the sample pan is recorded with respect to the reference pan. This type is called the heat flux DSC.

The second type shown in Figure 9, is known as the power compensating type. In this device, the temperature of the reference and the sample pans is increased at a constant rate, whereas the flow of heat required to change the temperature is recorded. A precision of a few hundredths of a degree is obtained when the temperature of the sample and reference pans are determined using both types of DCS.

Another method can be used instead of the linear rate of temperature change by using a harmonic thermal oscillation overlaid over a linear temperature ramp. The results are

analogous to the linear temperature ramp but the temperature fluctuates at a fixed frequency. Each peak represents a fixed increment in temperature higher or lower than the preceding one. This method was developed to differentiate non-reversible from reversible phenomena. It is helpful when a reversible step transition (such as the glass–rubber transition) is found in the areas of a non-reversible event such as chemical decomposition, melting or crystallization.

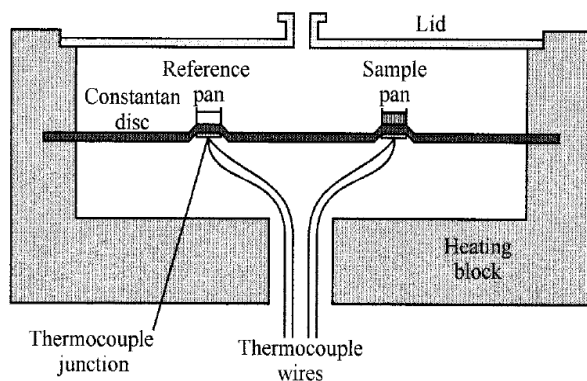


Figure 8: The Heat flux DCS, constant heat flow into the sample ²

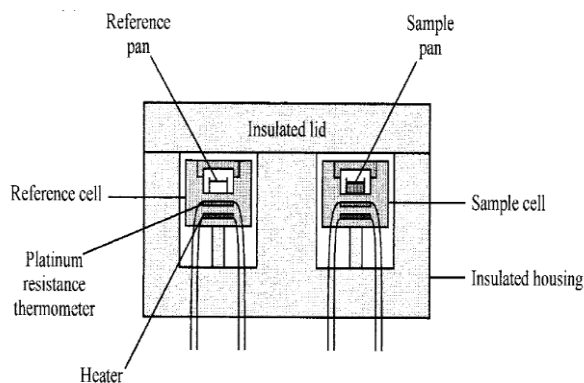


Figure 9: The power compensation DSC, modulated heat flow to maintain specific temperature ramp ²

1.6.1 Melting and Crystallization Temperature in DSC

Generally, the melting temperature can be recorded from the thermogram by noting the position of the maximum endothermic peak. Practically, it is not that simple because the polyethylene specimen includes innumerable lamellae. Each lamella has its own melting temperature which is largely dependent upon its thickness. Melting occurs over a range of temperatures due to the wide range of lamella thicknesses. Many experiments were conducted to determine an absolute melting point or a unique melting temperature but unfortunately the net result of these trials is that there is no such thing as an absolute point.

Practically, thermograms of polyethylene are usually reported using a sample size between 5 and 15 mg at cooling or heating rates of 5 – 20 °C/min. The accuracy of the data can be influenced by the calibration of the instrument, which is achieved by using samples of high purity metals or crystalline compounds. Practically, it is preferred to take down the melting thermogram of the same specimen twice following the “first melt/recrystallization/second melt” process. During the first melt the thermogram is recorded in which it reflects the sample’s original thermal history. It is better to heat the sample to a temperature 20 to 50 K above the melting region. Then, under controlled conditions the sample is cooled to recrystallize. After that, the sample is heated again to melt and the thermogram is recorded, it is termed as the second melt. The second melt can be used to compare samples that have undergone the same recrystallization step. The observed variations reflect the differences in molecular characteristics. The consideration of melting point determination will be applied to the determination of the crystallization temperature. Commonly, crystallization temperature is recorded at the minimum exothermic peak. The deviation between the melting and crystallization peak temperature increases as the rate of temperature ramp

increases. Crystallization usually occurs on cooling from the melt, and the rate of it strongly depend on temperature. The occurrence of crystallization may take place during the heating run, when the sample is in a non-equilibrium state, which is caused by special treatment such as quenching ⁹. When recording crystallization and melting temperature data, it is important to note the sample size, sample configuration (film, powder etc), thermal history, the cooling or heating rate, and whether the stated temperature was applicable to the onset or the peak maximum or conclusion of melting ².

1.6.2 Degree of Crystallinity in DSC

The degree of crystallinity of semi-crystalline polymers such as polyethylene can be calculated using the heat of fusion taken from the thermogram. The obtained heat of fusion is compared with the estimated value of the complete crystalline polyethylene to estimate the fraction of the sample in the crystal lattice. Commonly, the heat of fusion of the complete 100% crystalline polyethylene [HDPE] is within the range of [66 – 70] cal/g. Usually, it is taken to be 69 cal/g ¹⁷. For linear polyethylene (pure crystalline) Mathot, Pijpers, 1983, proposed the following equation¹⁸:

$$\Delta_{fus}h(T) = 293 - 0.3092 \times 10^{-5}(414.6 - T)^2 (414.6 + 2T)$$

Where the temperature is in Kalvin and the heat of fusion is in J/g. The heat of fusion of polyethylene can be estimated using Mathot, Pijpers, 1983, 1989 procedure, as following: Firstly, a straight line is drawn from the start of melting to its end, as shown in Figure10 represented by the red line. Secondly, the temperature (T) at which the crystallinity occur

should be marked. Then, if the experimental curve does not intersect the drawn line ($T > T^*$, e.g. T_2 in Figure 11), only area A1 (Blue Area) has to be evaluated. If there is an intersection between the experimental and the drawn line ($T < T^*$, e.g. T_1 in figure 19), area A2 (Green Area) must be subtracted from area A1 (Yellow Area). The calculated area is measured in cal/g or J/g, which is the heat of fusion of the semi-crystalline polyethylene. Finally, the degree of crystallinity can be approximated using the following: If no intersection occurred then $w_c(T) = \frac{A1 \text{ (Blue Area)}}{\Delta_{fush}(T)}$, otherwise $w_c(T) =$

$$\frac{A1 \text{ (Yellow Area)} - A2 \text{ (Green Area)}}{\Delta_{fush}(T)}$$

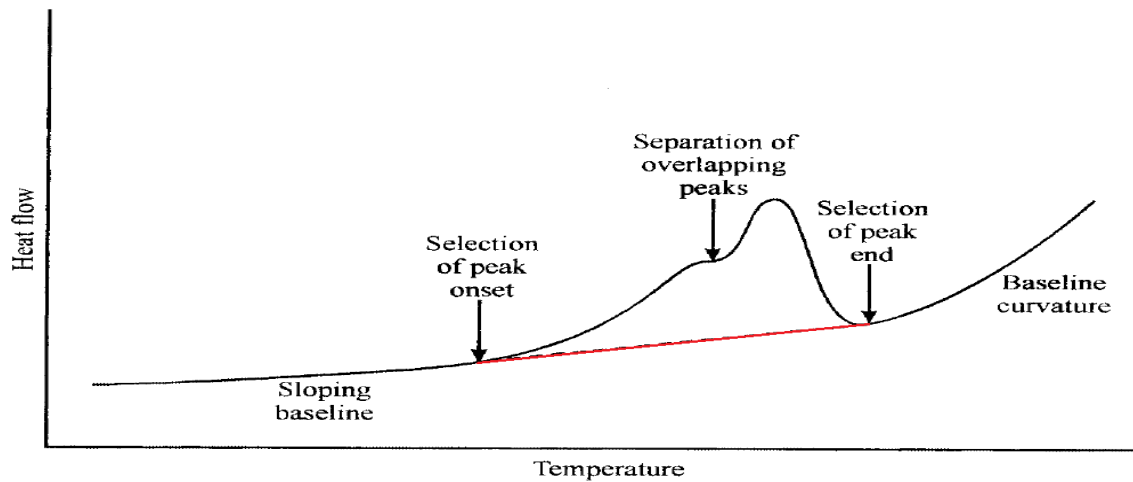


Figure 10: Thermogram of low density polyethylene illustrating some of the selection of the baseline under the peak ²

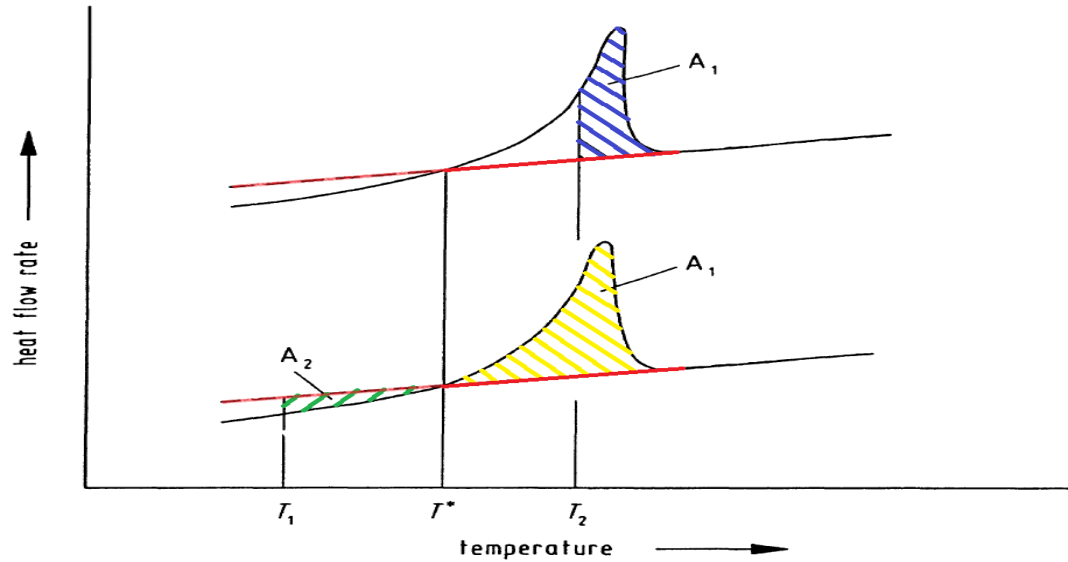


Figure 11: Degree of crystallinity estimation based on the procedure of Mathot, Pijpers, 1983, at two different temperatures $T_1 < T^*$ and $T_2 > T^*$, where T^* is the temperature of intersection of the drawn line and the experimental curve²

1.7 Thermal Fractionation by Calorimetric Methods

Many properties of polyethylene are affected by the overall level of branching and its distribution. The range of branches found in the polyethylene is reflected by the molecular weight distribution. The distribution of concentration of branches is also referred as the chemical composition distribution (CCD). The chemical composition distribution of polyethylene can be approximately determined by calorimetric investigation of its dissolution or melting properties. The temperature of dissolution or melting of a lamella is a function of its thickness. Differential scanning calorimetry provide information about the distribution of lamellar thicknesses reflected by a plot of the heat required to melt the lamellae as a function of temperature. Additionally, calorimetric thermal fractionation can

produce both intramolecular (short chain branching) and intermolecular (Long chain branching) fractionation.

When a branched polyethylene is cooled slowly from the melt, its melting characteristics can be analysed, and the chemical composition distribution can be qualitatively understood. This is because the distribution of crystallite thicknesses is a function of branching distribution. The higher temperature peak corresponds to the highly crystalline (lightly branched) molecules, whereas the lower temperature peak corresponds the lightly crystalline (highly branched) molecules. A qualitative or semi-quantitative data of CCD can be obtained using DSC. DSC is used by different methods such as: solvated thermal analysis fractionation STAF², stepwise isothermal segregation SIST¹⁹, step crystallization SC²⁰, DSC index²¹, successive self-nucleation/annealing SSA^{22,23} and fractional DSC, FDSC²⁴. Although calorimetric methods are simple, they suffer from high co-crystallization and low resolution because of the low mobility of the polymer chains in the melt.

1.7.1 Step Crystallization

In this technique, the polymer is melted at temperature above its melting temperature to erase any thermal history and then, allowed to crystallize under progressive isothermal temperature with one or several cooling rates.

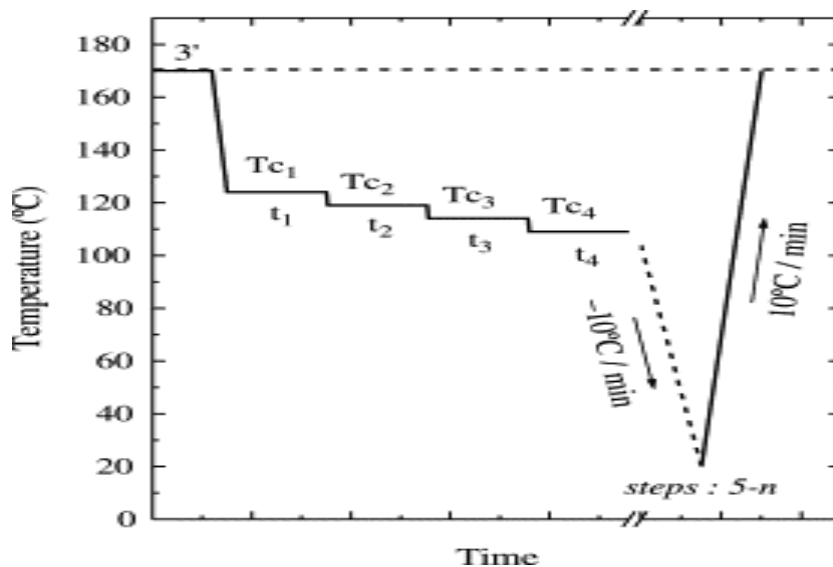


Figure 12: The applied temperature program for the Step Crystallization (SC) method ²⁵

A representative outcomes of SC fractionation is taken from the result of the Starck work²⁰, as shown in Figure 12. Starck used a copolymer of ethylene with 4.2molar% 1-butene. He applied the SC method with progressively seven isothermal stages, in a temperature range of 128-92°C. The temperature difference between each stage is 6°C and the time at each crystallization temperature is varying within the range of [120 - 150 min]. Fig. 1-18, the top graph, represents the DSC results of a copolymer produced by Ziegler – Natta (ZN) catalyst without using the fractionation methods in which it shows bimodal melting endotherm which mainly caused by the catalyst active sites. Five sharp peaks can be seen for the same copolymer after using the SC as a fractionation method and mostly they will be created during the annealing which occur within the isothermal steps between 122 and 92°C. The last peak which is at 87.5°C, is the melting temperature of the thinnest crystallites created during the cooling to room temperature. The length of the methylene sequence (MSL) mostly affects the thickening of the crystallites which will affect the heat of fusion

consequently. The fractionation method gave an advantage on distinguishing the thickest crystallites which can be reflected by the highest melting point peak whereas the area under this peak represents the amount of the fraction. The progressive small peaks after the highest melting point represent the melting points for the thinner crystallites those are produced by shorter MSL. Stable crystals or Crystals that are closer to equilibrium will be produced when lengthy holding times is used at each T_c , in which the annealing and lamellar thickening are favoured ²⁶.

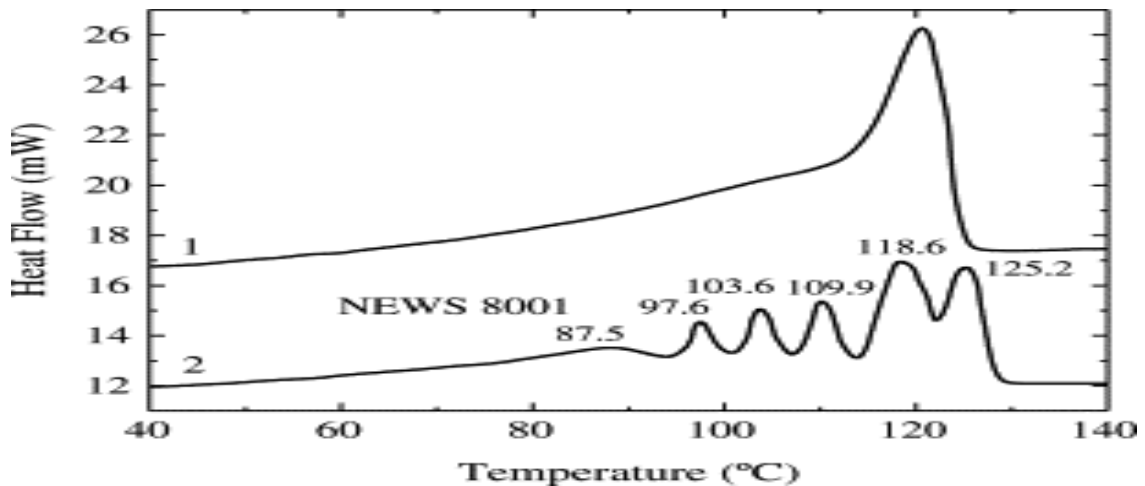


Figure 13: DSC heating scans (5 °C/min) for a copolymer of ethylene with (4.2 mol%) 1-butene, before (top) and after SC fractionation (bottom). Starck Studies of the comonomer distributions in low density polyethylenes using temperature rising elution fractionation and stepwise crystallization by DSC²⁰

1.7.2 Successive Self-Nucleation and Annealing

SSA method is conducted by the involvement of the partial melting of crystallites followed by recrystallization using the self-nucleation process, since there are small crystal fragments that were not destroyed during the melting process. The experimental procedure of successive self-nucleation and annealing method can be summarized from Muller et al. ²³ work as following:

First, the sample should be kept for about 3 min in the melt under a temperature at least 25°C higher than the maximum melting point temperature (T_m) of the polymer. The reason of choosing this high temperature as the initial melting temperature, is to rubout all previous thermal history.

Second, at a typical constant rate of 10 or 20°C/min the sample is cooled to a low enough minimum temperature to allow and enhance the crystallization during the cooling process. The minimum peak which appeared in this step is called the standard crystallization temperature ($T_{s,c}$). After that, the sample is kept at the former minimum temperature for not more than 5 min.

Third, the temperature of the sample is elevated from the previous temperature up to a chosen temperature by heating the sample under constant rate of 10 or 20°C/min. The chosen temperature is referred as the self-nucleation or self-seeding temperature (T_s). It is preferable to choose the final melting temperature of the polymer sample to be the self-seeding temperature, this is done by performing a pre-studies of the self-nucleation point before applying the SSA method. After that, the sample will be kept at this temperature for about 5 min.

Fourth, the sample is cooled again at constant rate of 10 or 20°C/min from T_s down to the minimum temperature chosen in 2nd step, and kept for about 5 min. Through this step the polymer fractions those were melted at the self-seeding temperature will recrystallize again within the cooling cycle according to the domain as described in table 7.

Fifth, again at constant rate the sample is heated up by a rate of 10 or 20°C/min from the minimum up to a temperature (T_{s2}) 5°C lower than the previous T_{s1} . After that, the sample

is kept at this new temperature (T_{s2}) for about 5 min. This step is important for the process, because the fractionation window (temperature interval) that will be used for fractionation is going to be determined.

Sixth, the fourth and fifth steps will be repeated progressively by lowering T_s using the fractionation window. It is better to keep the chosen temperature interval constant along the fractionation. Finally, the sample is heated at constant rate of 10 or 20°C/min from the minimum temperature up to the melting temperature that has been chosen in 1st step. A schematic representation of this method is shown in Figure 14.

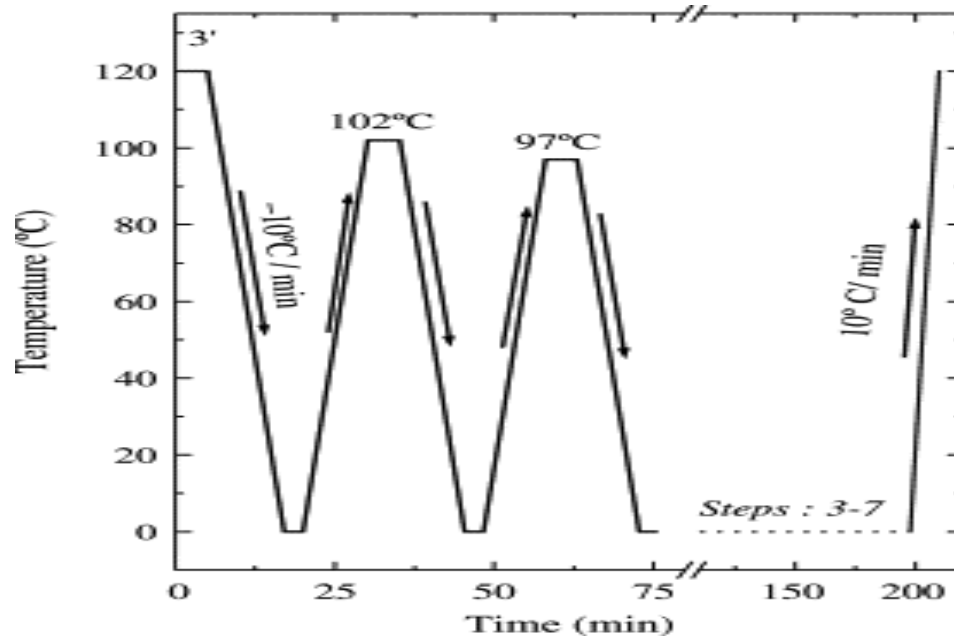


Figure 14: Thermal program for Successive Self-nucleation and annealing process ²⁵

Fillon et al²⁷ summarised the characteristics of each domain of the self-nucleation as shown in Table 4. A typical example to explain the Domains is that for HPB as shown in Figure 15 & 16. Figure 15 shows the cooling runs after the self-seeding temperature is achieved

while Figure 16 shows the following heating runs. For T_s span ranging between 120°C and 113°C, there is no difference in the obtained crystallization temperatures, because the sample is melted completely at T_s . While that at T_s span ranging between 112 °C and 102 °C, the sample is not melted completely, so the sample will recrystallize by self-nucleation, which produces sample with higher densities during the cooling and consequently a higher crystallization temperature will be obtained. For T_s below or equal 101 °C, the crystallization temperatures is much higher than those obtained from other domains, since the crystallization occurs immediately just below T_s . The last temperature that encourages self-nucleation without annealing is the optimum or ideal self-nucleation temperature or the minimum T_s Temperature. Lower than this optimum temperature annealing will start,

in which it can be detected by DSC during the heating run as shown in Figure 17 represented by the two melting peaks.

Table 4: Domains of self-nucleation according to Fillon et al. ²⁷

DOMAIN	CHARACTERISTICS
I	• Complete melting at T_s occurs. ○ The sample will recrystallize at the standard T_c. ○ Almost no variance between the new crystallization temperature and the standard temperature. ○ Constant nucleation density is obtained.
II	• Also, called exclusive self-nucleation. • No annealing occurs, only self-nucleation. • Detected above the final melting temperature, specifically starts at the optimum self-nucleation temperature. • At T_s, most of the polymer crystals will melt and small crystal fragments will not. • The small fragments will act as self-nuclei. ○ The sample will recrystallize at a higher temperature than the standard T_c. ○ An increase on density is obtained.
III	• Self-nucleation and annealing occurs ➤ The sample will recrystallize immediately, just below T_s

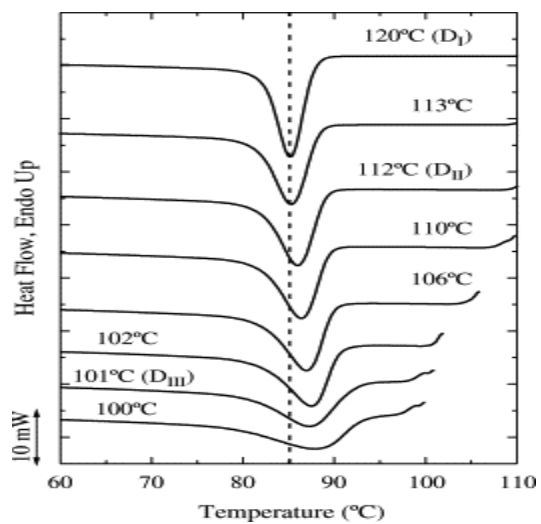


Figure 15: DSC cooling scans with cooling rate of (10 °C/min) from the indicated Ts temperatures ²⁵

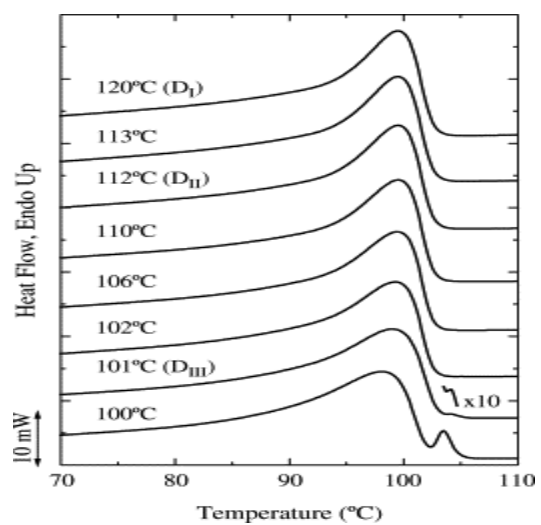


Figure 16: Self-nucleation of a model HPB. Subsequent DSC heating scans (10 °C/min) ²⁵

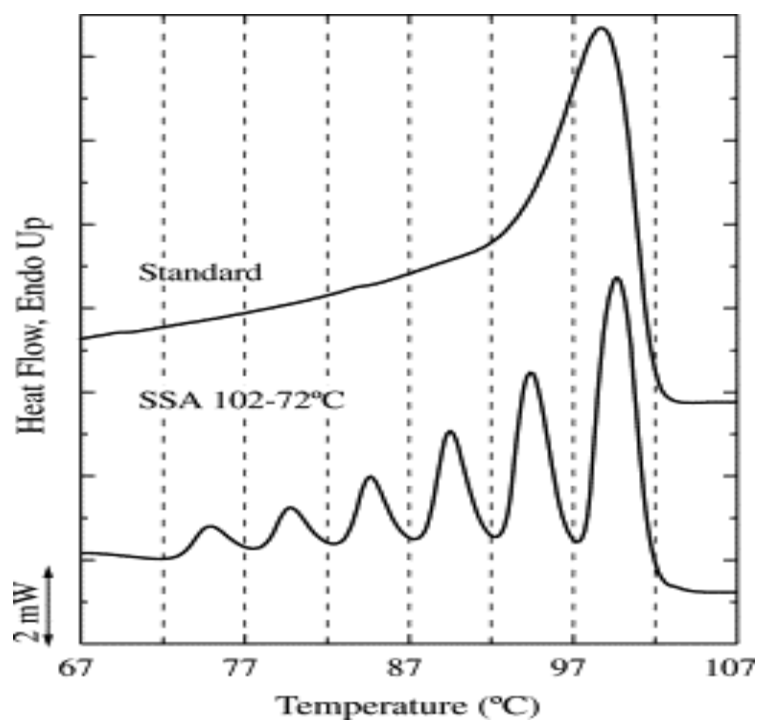


Figure 17: DSC heating scans (10 °C/min) for HPB before (top) and after SSA fractionation (bottom) ²⁵

CHAPTER 2

LITERATURE REVIEW

2.1 Calorimetric Methods

2.1.1 Step Crystallization

A successful results of thermal fractionation methods can be achieved by an appropriate selection of the experimental variables. The most important variables are: the initial crystallization temperature, the fractionation window (The temperature variance between the stages), number of the isothermal steps, holding time for each crystallization temperature, cooling rate from the melt, cooling rates between the progressive isothermal steps and the final heating rate.

In Varga et al. works^{28,29}, the SC method has been conducted by melting a LDPE sample at 150°C, then cooled to 108°C, after that it was cooled further to room temperature. In their work several fractionation windows 44, 20, 10, 5, and 3°C have been applied. After the evaluation of these fractionation windows, the authors concluded that the best resolution will be obtained by using a fractionation window of 3°C intervals.

Depending on the work of Alamo et al.³⁰, the initial crystallization temperature has been selected by Vandermiers et al.³¹ to be 121 °C. In this work, it is reported that the molecular segregation processes in polyethylene blends (different hydrogenated polybutadienes) are favoured at temperatures above 120 °C.

The optimum first crystallization temperature for VLDPE have been selected by Chen et al.³² to be 116°C. They achieved this temperature by proposing a cooling rate of 0.08°C/min to determine the onset crystallization temperature. The fractionation window used by them was 4°C starting from 116 °C down to 24 °C. they observed that, the use of wider windows of fractionation will reduce the resolution of the fractionation while the shorter windows will cause an overlapping of the melting of the fractions generating bad resolution.

Mullar and Arnal in their review recommended to use controllable cooling rates. Because most of the cooling systems those are used in DSC are able to handle rates as high as 60°C/min under control. However, it is preferred to use much higher values but it depends on the efficiency of the used cooling system²⁵.

After the comparison between 50 and 100 min, Chen et al.³² have decided to use 50 min as a holding time at each crystallization temperature, since they found a comparable quality of fractionation. Also, the effect of holding time at each crystallization temperature was studied in a wider time range 30 min to 24 h by Keating and McCord²⁴. They found that sufficient thermal fractionation can be obtained by applying holding times within the time range of [4 - 6 h] for samples with different molecular weights. Also, using 1 h as a holding time at each crystallization temperature can be used to perform the fractionation of low molecular weight materials, as found by Keating and McCord²⁴. Which is close to the time employed by Chen et al.³². Although better resolution seemed to be obtained by

using longer holding times, the technique becomes impractical, and the probability of sample degradation will be higher when high temperatures are used.

Regarding the heating rates, catalyst reorganization can be averted by using relatively fast rates during the scan as recommended ³³. The effect of heating rate on the quality of fractionation of LLDPE have been studied by Starck ²⁴. He decided to use a heating rate of 5°C/min, at which the best signal resolution can be obtained as observed. However, if mass compensation is performed, higher scanning rates might also give better or similar results as found by Pijpers et al. ³⁴.

2.1.2 Successive Self-Nucleation and Annealing

The most important variables during SSA treatment are the first T_s temperature, the fractionation window, the time spent at each T_s , the heating and cooling rates during the thermal conditioning steps.

In the third step of SSA method, which previously mentioned in Muller et al.²³ and Arnal et al.³⁵ Muller had recommended to use the optimum self-nucleation temperature (minimum T_s) which is in Domain II to be the first self-seed temperature T_s . So, the polymer will always be at the same starting condition. Another advantage of using the minimum T_s , is that the crystallization process doesn't anymore reflect the overall transition process which include both nucleation and growth, while it represents either secondary nucleation or growth only. Also, the SSA fractionation results will not depend anymore on the heterogeneities content of any sample or the catalytic residues.

Muller and Arnal ²⁵ recommended the use of fractionation window of 5 °C, depending on how the fractions are separated and how wide is the range of melting temperature of the

polymer under study. Their recommendation has been given after the use of different fractionation windows 5, 2.5 and 1^oC with a DSC heating scan rate of 10^oC/min. Bad resolution was observed by using windows less than 5^oC.

Arnal et al.²³ have recommended a holding time of 5 min to be used on SSA fractionation. In their works, 5 and 15 min holding times were tested to fractionate a commercial LLDPE. They observed that the generation of new fractions was not enhanced with the increment in holding time. So, they used 5 min as holding time otherwise time consumption would be high with 15 min which is impractical.

In the work of Arnal et al.²³, different heating rates (20, 10 and 5 ^oC) have been tested in the fractionation of an approximately 10 mg of commercial LLDPE, using SSA method. They observed that the best time resolution is obtained by using 10 ^oC/min as a heating rate. However, fast heating rates such as 50 ^oC/min can be employed as recommended by Pijpers et al.³⁴ with the reduction of the mass of the sample which is performed by Muller et al.²⁵. The mass of the sample must be conveniently decreased to avoid any superheating effects. Muller et al. found that, the quality of the fractionation by this adaption is still good with an advantage of reducing the fractionation time which means lower time consumption.

Muller et al.^{23,35,36} found that SSA method is more practical when compared with SC. This is because by SSA higher resolution of thermal fractionation can be obtained for ethylene/ α -olefin copolymers than SC. Also, the fraction separation of the SSA method is better because of the progressive fractional melting steps after the crystallization steps. The main difference between SC and SSA, is that in the former only step cooling is applied, while in SSA a series of cooling and heating cycles are conducted.

SSA is capable to yield quantitative or qualitative information about short chain branch distributions, distribution of lamellar thickness in the sample and polydispersity Index of the SCB distribution ²⁵. SSA has been used in variety of applications such as: the characterization of functionalized materials, the characterization of cross-linked polyethylene, the characterization of oxidative degradation and biodegradation products, the study of miscibility in polyethylene blends, and the evaluation of confinement effects.

SSA can provides fast and helpful data about the functional group locations those are inserted onto polyolefin backbone by grafting which is a copolymerization method. Knowing that, by the new functional groups, the components of immiscible polymer blends can be more compatible^{37,38}. Because of the location of tertiary and primary carbons which are in the amorphous regions, Thermal fractionation cannot detect grafting reactions onto the mentioned carbons. While it does so, if the radical of functional groups attacked the secondary carbons of the main chain of polyethylene^{39,40}. A typical example for the characterization of grafted product was found in the works of Arnal et al.^{35,36}. In their works, they used an ULDPE with a density of 0.875 g/cm³ and 88 CH₃/1000C, in which it is grafted by Maleic Anhydride (MAH). They found that as the initiator or/and MAH concentrations increases, the grafting degree will increase, while the melting temperatures and degree of crystallinity will decrease. Eventually, SSA is more useful in the conformation of the reaction mechanism than FTIR and ¹H NMR. This might be because of the difficulty in postulating the reaction mechanism based only on FTIR and ¹H NMR ²⁵.

The ability of SSA to provide information about the important changes in chemical structure before the degradation of polyethylene takes place ⁴¹ added more advantage to

this technique. It can be employed to characterize the failures of the coating wires during service live and to provide a thermal history of the used coats as an insulator for the high voltage wires^{35,42}. Polyethylenes degradation was recently studied by SSA method and reported in^{43,44}. The degree of crosslinking has been studied by Varga et al.²⁸. In their work, they studied the crosslinking of HDPE and observed that as crosslinking increases, the number of endothermic peaks obtained after the final melting scan also increases.

Additionally, the confinement effects on thermal fractionation by the chain restrictions a segregated di-block copolymer can be evaluated by SSA. The topological restriction is caused by the micro-phase separated morphology (matrix, lamellae, cylinders and spheres) of the block and the covalently linked side blocks. Lorenzo et al.⁴⁵ studied the topological confinement of different morphologies of poly (ethylene -b- styrene) block by varying the level of polystyrene contents. They found that the higher melting temperature fractions gradually disappear as the topological confinement increases.

The diluent effect of poly(ethylene-ran-propylene) block upon SSA thermal fractionation has been studied by Lorenzo et al.⁴⁵⁻⁴⁷. From their works, it can be concluded that to generate SSA fractionation nearer to thermodynamic equilibrium the use of solvents or diluents might be useful to avoid the use of very long fractionation times.

2.2 Linear Low-density polyethylene

LLDPE is a copolymer of ethylene with 1-alkene, basically 1-hexene, 1-octene, 1-butene or propylene. The comonomer level is ranging between 2 and 8 mole%. The density is ranging between 0.918 and 0.935 g/cm³. Melting temperatures are ranging between 100 and 125°C. Degree of crystallinity from calorimetry are [22-55] %². LLDPE has low

modulus, low tensile strength, improved toughness (caused by the short chain branches, SCB) and high melt strength (Caused by long chain branches, LCB), which leads to processing advantages.

2.3 Layered Double Hydroxides

LDHs belong to the anionic clay minerals which are used for the preparation of polymer-layered crystal nanocomposites. LDHs are made up of hydroxides sheets or metal oxide which are positively charged with water molecule and intercalated anions.^{48,49} LDH has the general formula $[M^{II+}_{1-x}M^{III+}_x(OH)_2]^{x+}(A^{m-})_{x/m} \cdot yH_2O]^{x-}$ where M^{II+} is a divalent metal ion (Such as Mg^{2+} , Zn^{2+} , Ca^{2+} , etc.), M^{III+} is a trivalent metal ion (Such as Al^{3+} , Co^{3+} , Fe^{3+} , Cr^{3+} , etc.), and A^{m-} is an anion (Such as Cl^- , CO_3^{2-} , NO_3^- , etc.)⁵⁰

X-Ray Diffraction analysis showed that the LDH cations are located in the same layer, while the water molecule and the anions are in the interlayer region. This contradicting the first hypothetical structure which was hypothesized by Feithnecht. The first hypothetical structure is representing the LDH with intercalated hydroxide layers.⁵¹

LDHs have a basic layer structure based on $[Mg(OH)_2]$ which is called brucite. The brucite is a CdI_2 type, and it is linked with small polarizable ions and polarizing cations. They consist of hydroxide ions which surrounding octahedrally the magnesium ions. By the edge-sharing, these octahedral units can form infinite number of layers in which the hydroxide ions are sitting perpendicularly to the plane of the layers. Then, the former layers will stack on the top of each other to create a 3D structure.⁵²

LDHs which are synthesized conventionally are highly hydrophilic materials. They can be either microcrystalline or amorphous with hexagonal habit, in which the dominant faces are developed parallel to the hydroxide metal layers. The adjacent layers of LDHs are strongly bounded to each other.

LDHs have symmetrical shape synthetic nano-fillers and size, with a strongly active surface. Their functionalization can be designed to produce carbon dioxide and water. Figure 18 shows the structure of the LDHs.

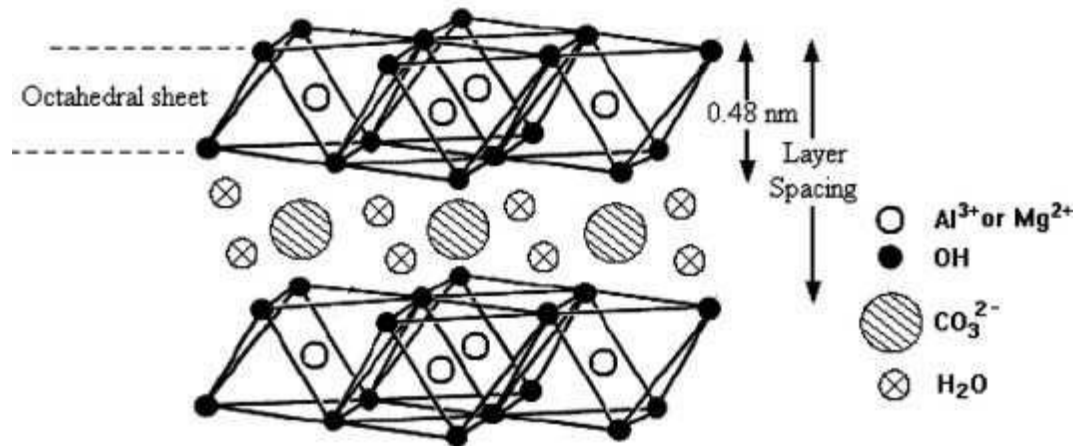


Figure 18: LDH Structure⁵²

The number of the synthesized metal-anion combinations and the possible prepared compositions is high. Thus, it is an advantage of the LDH compared to the other layered materials. The charge density of LDH is high and can be tuned by the metal ratio. The charge density of the LDH layers is affected by the metal ratio since it consists of divalent and trivalent metal cation. The higher the divalent to trivalent ratio will result in a lower charge density. That means if the trivalent metal increased, the more positive the charge

will be. Also, by controlling the particle size distribution and the particle size, LDH can be synthesized as a stabilizing agent.⁵³

The dispersion of the metal ions is homogeneous. Also, they are thermally stable even at reducing conditions. Also, they have high specific surface area and good anion exchange capacities. The basic properties of LDH depends mainly on the calcination temperature and the compositions. The former LDH properties were summarized by Del Hoyo.⁵¹

2.3.1 Applications of LDH

LDHs are inexpensive since they are easy to be synthesized, versatile and are flexible in composition. Thus, they are widely used as a potential source of a variety of actual catalysts, catalyst precursors or catalyst supports.^{53,54}

By the anion-exchange and the surface adsorption, LDHs can be used to remove the negatively charged species since they have high specific surface area and good anion exchange capacities.^{55,56}

LDHs are biocompatible, have the ability to intercalate alkaline character and anionic drugs and have changeable chemical composition. Thus, they can be used in pharmaceutical formulations and in medicine as well.^{57,58}

Because of the high conductivity of LDHs and their ability to exchange intercalated ions, they were used in nanocomposite electrolyte systems. They are found in systems such as the fabrication of thin-film type Li-polymer secondary batteries.⁵⁹

LDHs have the ability to improve the thermal stability of the functional polymer material and the ability in formulating flame retardant materials. The former properties are attributed to the synergistic effects between the LDH and polymer.^{60–63}

LDHs can be used especially for polyethylene and polypropylene as scavengers or acid neutralizers. Also, LDHs are useful as UV ray absorbents, adsorbents for heavy metal anions from waste waters, viscosity control agents, smoke suppressors, in separation processes. Also, they can be useful as an agent for moisturizing, anti-inflammatory, and anti-aging.^{51,64}

2.4 Polymer Nanocomposites

Because of the interaction between the clay and the polymer at the nanoscale level, the properties have been enhanced. Three different types of dispersion can be produced due to the addition of the nano-clay in the polymer. These types are the Micro-composite, intercalated, and exfoliated dispersion.

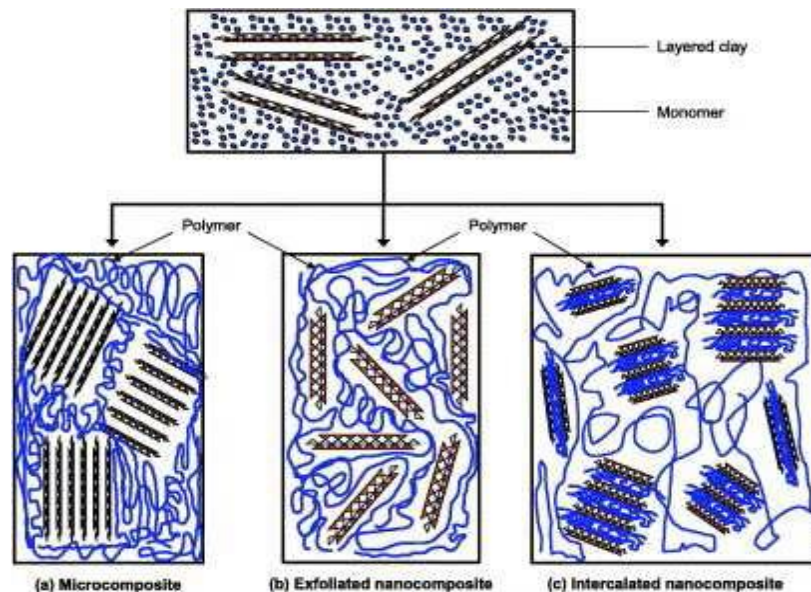


Figure 19: Illustration of the (a) micro-composite (b)exfoliated nanocomposite (c) intercalated nanocomposite⁶⁵

In the micro-composite dispersion, the clay particles will not be penetrated but surrounded by the polymer chains as shown in figure 19 (a). In intercalated nanocomposite, the clay galleries will be penetrated by the polymer chains resulting in an expansion of these galleries as shown in figure 19(c). In exfoliated nanocomposites, the clay galleries are highly disordered and completely disrupted due to the extensive penetration of the polymer chains leading to the delamination as shown in figure 19(b).

2.4.1 Synthesis of polymer-clay nanocomposites

Polymer clay nanocomposites are prepared by three methods which are in-situ polymerization, melt intercalation, and polymer solution intercalation.

CHAPTER 3

EXPERIMENTAL

This study will be based on blending of selected LLDPE samples with different nano fillers.

Detailed objectives are:

- To perform degradation study of the produced blends by using TGA
- To study the effect of the filler type and content on the crystallinity of ethylene copolymer.
- To study the melting and crystallization behavior of LLDPE/LDHs nanocomposites using DSC.
- Investigate the dispersion of the nano-clay in the polymer using SEM and XRD.

3.1 Materials

The LLDPE was taken from SABIC (KEMYA) in the form of pellets. LDHs have been prepared in the laboratory using the following, Iron(III) nitrate nonahydrate ($\text{FeH}_{18}\text{N}_3\text{O}_{18}$), Nickel(II) nitrate hexahydrate ($\text{H}_{12}\text{N}_2\text{NiO}_{12}$), Magnesium nitrate hexahydrate ($\text{H}_{12}\text{MgN}_2\text{O}_{12}$), *i*-Graphene nanosheets (GNS), Hydrazine (N_2H_4), Sodium hydroxide (NaOH) pellets, and Deionized water. The LLDPE is specified as the Polyethylene (PE). NiFe, NiFe-Graphene, MgFe, and MgFe-Graphene are designated as LDHs through the study.

3.1.1 NiFe-Graphene LDH Preparation

1 molar of NaOH solution was prepared by dissolving 40 grams of NaOH pellets in 1 liter of DI water. 10 mL of the former NaOH solution then placed in a graduated cylinder with

50 mL of DI water to make 0.2 molar of NaOH for GNS sonication according to the formula $M_1V_1=M_2V_2$. Then, 500 mg of GNS was ultrasonicated in the (0.20 M) NaOH solution for 1 hour at 100 amplitudes. After that, 4.04 grams of Iron(III) nitrate nonahydrate, 8.73 grams of Nickel(II) nitrate hexahydrate, and 50 mL of DI water were mixed in a 500 mL round bottom flask under magnetic stirring for 15 minutes at 60°C and 450 rpm as agitation speed. After that, the sonicated GNS solution was placed with the prepared solution of the precursor salts ($\text{Ni}^{2+}:\text{Fe}^{3+}$) in addition to three drops of Hydrazine under magnetic stirring at 90°C and rotation speed of 900 rpm . Consequently, by using the prepared (1.0 M) NaOH solution the pH was maintained at 10 ± 0.5 . Then, the suspension was allowed to be refluxed for 24 hours, while the resultant solution was kept under vigorous magnetic stirring at $90\pm10^\circ\text{C}$ and rotation speed of 900 rpm. Subsequently, the mixture was centrifuged for 5 minutes at 4500 rpm and washed by DI water four times. Then, the mixture was centrifuged for the last time but was washed with ethanol instead of DI water. After that, the dense suspension was dried in the oven for 24 hours at 60°C. Finally, the dried dense suspension was grinded to powder. Knowing that Hydrazine was used as a reducing agent to reduce the GNS and adjust the pH. Also, since the ratio of $\text{Ni}^{2+}:\text{Fe}^{3+}$ was chosen to be 3:1, and the atomic weight of Ni and Fe are 290.79 gram/mole and 404 gram/mole, respectively. It was possible to calculate the required quantities of each salt as: $m_{\text{Fe}} = 404 \times 0.01 = 4.04$ grams, and $m_{\text{Ni}} = \frac{3}{1} \times \frac{290.79}{404} \times 4.04 = 8.73$ grams.

3.1.2 MgFe-Graphene LDH Preparation

1 molar of NaOH solution was prepared by dissolving 20 grams of NaOH pellets in 500 mL of DI water. 10 mL of the former NaOH solution then placed in a graduated cylinder with 40 mL of DI water to make 0.25 molar of NaOH for GNS sonication according to the formula $M_1V_1=M_2V_2$. Then, 500 mg of GNS was ultrasonicated in the (0.25 M) NaOH solution for 33 minutes at 100 amplitudes. After that, 4.04 grams of Iron(III) nitrate nonahydrate, 7.6923 grams of Magnesium nitrate hexahydrate, and 50 mL of DI water were mixed in a 500 mL round bottom flask under magnetic stirring for 15 minutes at 60°C and 450 rpm as agitation speed. After that, the sonicated GNS solution was placed with the prepared solution of the precursor salts ($Mg^{2+}:Fe^{3+}$) in addition to three drops of Hydrazine under magnetic stirring at 90°C and rotation speed of 900 rpm . Consequently, by using the prepared (1.0 M) NaOH solution the pH was maintained at 10 ± 0.1 . Then, the suspension was allowed to be refluxed for 24 hours, while the resultant solution was kept under vigorous magnetic stirring at $90\pm10^\circ\text{C}$ and rotation speed of 900 rpm. Subsequently, the mixture was centrifuged for 5 minutes at 4500 rpm and washed by DI water four times. Then, the mixture was centrifuged for the last time but was washed with ethanol instead of DI water. After that, the dense suspension was dried in the oven for 24 hours at 60°C. Finally, the dried dense suspension was grinded to powder. Knowing that Hydrazine was used as a reducing agent to reduce the GNS and adjust the pH. Also, since the ratio of $Mg^{2+}:Fe^{3+}$ was chosen to be 3:1, and the atomic weight of Mg and Fe are 256.41 gram/mole and 404 gram/mole, respectively. It was possible to calculate the required quantities of each salt as: $m_{Fe}= 404*0.01 = 4.04$ grams, and $m_{Mg}=\frac{3}{1} \times \frac{256.41}{404} \times 4.04 = 7.6923$ grams.

3.1.3 MgFe LDH Preparation

1 molar of NaOH solution was prepared by dissolving 40 grams of NaOH pellets in 500 mL of DI water. After that, 4.042 grams of Iron(III) nitrate nonahydrate, 7.6930 grams of Magnesium nitrate hexahydrate, and 50 mL of DI water were mixed in a 500 mL round bottom flask under magnetic stirring for 15 minutes at 60°C and 450 rpm as agitation speed. After that, the precursor salts ($\text{Mg}^{2+}:\text{Fe}^{3+}$) solution temperature was raised to 90°C under magnetic stirring at rotation speed of 900 rpm. Consequently, by using the prepared (1.0 M) NaOH solution the pH was maintained at 10 ± 0.28 . Then, the suspension was allowed to be refluxed for 24 hours, while the resultant solution was kept under vigorous magnetic stirring at $90 \pm 10^\circ\text{C}$ and rotation speed of 900 rpm. Subsequently, the mixture was centrifuged for 5 minutes at 4500 rpm and washed by DI water four times. Then, the mixture was centrifuged for the last time but was washed with ethanol instead of DI water. After that, the dense suspension was dried in the oven for 24 hours at 60°C. Finally, the dried dense suspension was grinded to powder. Knowing that, since the ratio of $\text{Mg}^{2+}:\text{Fe}^{3+}$ was chosen to be 3:1, and the atomic weight of Mg and Fe are 256.41 gram/mole and 404 gram/mole, respectively. It was possible to calculate the required quantities of each salt as:

$$m_{\text{Fe}} = 404 \times 0.01 = 4.04 \text{ grams, and } m_{\text{Mg}} = \frac{3}{1} \times \frac{256.41}{404} \times 4.04 = 7.6923 \text{ grams.}$$

3.1.4 NiFe LDH Preparation

1 molar of NaOH solution was prepared by dissolving 40 grams of NaOH pellets in 500 mL of DI water. After that, 4.0399 grams of Iron(III) nitrate nonahydrate, 8.7305 grams of Nickel(II) nitrate hexahydrate, and 50 mL of DI water were mixed in a 500 mL round bottom flask under magnetic stirring for 15 minutes at 60°C and 450 rpm as agitation

speed. After that, the precursor salts ($\text{Ni}^{2+}:\text{Fe}^{3+}$) solution temperature was raised to 90°C under magnetic stirring at rotation speed of 900 rpm . Consequently, by using the prepared (1.0 M) NaOH solution the pH was maintained at 10 ± 0.07 . Then, the suspension was allowed to be refluxed for 24 hours, while the resultant solution was kept under vigorous magnetic stirring at $90\pm10^{\circ}\text{C}$ and rotation speed of 900 rpm. Subsequently, the mixture was centrifuged for 5 minutes at 4500 rpm and washed by DI water four times. Then, the mixture was centrifuged for the last time but was washed with ethanol instead of DI water. After that, the dense suspension was dried in the oven for 24 hours at 60°C . Finally, the dried dense suspension was grinded to powder. Knowing that, since the ratio of $\text{Ni}^{2+}:\text{Fe}^{3+}$ was chosen to be 3:1, and the atomic weight of Mg and Fe are 290.79 gram/mole and 404 gram/mole, respectively. It was possible to calculate the required quantities of each salt as:

$$m_{\text{Fe}} = 404 \times 0.01 = 4.04 \text{ grams, and } m_{\text{Ni}} = \frac{3}{1} \times \frac{256.41}{404} \times 4.04 = 7.6923 \text{ grams.}$$

3.1.5 LLDPE/LDH nano-composites Preparation

Each LDH was blended with the LLDPE using the MiniLab – Compounder⁶⁶. In this device, the nanocomposite materials are hot blended using a conical twin screw extruder in a batch process. The compounder was preheated to 160°C and various mixtures with 1, 2, and 3% by weight of each nano-clay were prepared from the melt at a rotation speed of 50 rps for 8 minutes. The PE and NiFe-Graphene LDH nanocomposites are designated as 1LDHA, 2LDHA, and 3LDHA. The PE and MgFe-Graphene LDH nanocomposites are designated as 1LDHB, 2LDHB, and 3LDHB. The PE and MgFe LDH nanocomposites are designated as 1LDHC, 2LDHC, and 3LDHC. The PE and NiFe LDH nanocomposites are designated as 1LDHD, 2LDHD, and 3LDHD. Since the total weight of each sample 6 grams, that means a nanocomposite comprising 99% by weight PE (5.94 gram) and 1% by

weight NiFe-Graphene LDH (0.06 gram) is designated as 1LDHA. Knowing that, the preparation of each sample was repeated 3 times, the results of each were averaged.

3.1.6 Fourier-transform infrared spectroscopy

FTIR were used to assure the presence of Gr/LDHs organic functional group. The samples were prepared using the KBr pellet technique. Then, the spectra of the Gr/LDH nanofillers were obtained using PerkinElmer FTIR spectrometer (model 16F-PC) in the range of 4000 – 400 cm^{-1} .

3.2 Dispersion

Samples are characterized by the X-ray diffraction (XRD) and the scanning electron microscopy (SEM) to approximately determine if an exfoliated or intercalate nanocomposite was obtained.

3.2.1 Scanning Electron Microscopy

The SEM is a device used to characterize and observe the inorganic and organic materials on a micrometer to nanometer scale. A precisely electron beam is impacted on the interested area to show the microstructure. The interaction of the electron beam with the specimen will produce signals such as x-rays, secondary electron, and backscattered electrons. The produced signals then used to characterize the sample specimen. The SEM images have a large depth of field and a high resolution. Thus, it is very useful for the compositional analysis and topographical analysis.⁶⁵

The fractured surfaces were prepared after immersing the samples in a Liquid Nitrogen. The liquid nitrogen will make the sample hard and breakable because the sample temperature will be reduced to a temperature below the glass-rubber temperature otherwise

the sample will be soft and un-breakable. Then, the samples were gold coated for 60 seconds under vacuum using sputter coating. This coating was used to avoid charging while imaging. The microstructure of the specimens was observed with TESCAN Lyra-3 Field Emission Dual Beam (Electron/Focused Ion Beam) system combined with high-resolution field emission scanning electron microscope (FE-SEM).

3.2.2 X-Ray Diffraction

XRD is a device used to investigate the fine structure of matter. The use of this technique started after 1912 when von Laue's discovered that, X-rays are diffracted from crystals. At the beginning, XRD was used only for the crystal structure determination. Now, it is not only used for the former purpose but to such different investigations as stress measurement and chemical analysis. Also, nowadays XRD is used for the determination of the orientations of one crystal or in polycrystalline aggregate, for the measurement of particle size, and to study the phase equilibria.

Samples are prepared as thin circular films with a diameter of 1cm. Then, the investigation was carried out using Ultima IV XRD (from Rigaku) operated at 40 mA and 40kV with CuK alpha radiation ($\lambda = 1.54060$). The diffraction angel (2θ) was selected in the range of 3 – 70 degrees at a scanning rate of 0.5°/min.

3.3 Thermal Analysis

The degradation properties of LLDPE nanocomposites were studied by thermogravimetric analysis (TGA). The effect of LDH on the thermal properties of LLDPE nanocomposites was studied by the differential scanning calorimetry (DSC).

3.3.1 Differential Scanning Calorimetry

DSC is a technique based on power compensation used to measure the required energy to establish an approximately zero temperature difference between an inert reference material and a substance. The reference and the substance are going to be subjected to a similar temperature system in an environment cooled or heated at a controlled rate. The measured amount of the evolved or absorbed energy in a particular transition will be given by the obtained heat flow data. That means the calorimetric measurements can be obtained directly by this technique.

The thermal properties such as the melting and crystallization behavior of the LLDPE nanocomposites were studied using differential scanning calorimetry (DSC Q – 1000) TA instrument. The device was calibrated using elemental indium sample. 5 – 7 mg of sample was used for each run. At the beginning the sample was heated from 25°C to 170°C at heating rate of 10 °C/min. Then, it is cooled down from 170°C to 25°C at a cooling rate of 10 °C/min. After that, it is heated again from 25°C to 170°C using the heating rate of the first cycle.

The crystallinity of nanocomposites was calculated by using the following⁶⁷ basic equation:

$$X_c = \frac{\Delta H}{(1 - \varphi)\Delta H^o} \times 100\%$$

Where φ is the weight percent of LDH; ΔH is the integrated enthalpy of fusion; ΔH^o is the enthalpy of fusion of 100% crystalline polyethylene which is taken as 287.3 J/g in this thesis work^{68,69}.

3.3.2 Thermogravimetric Analysis

TGA is a device used to measure the weight change of a sample as a function of time which is called isothermal mode or as a function of temperature which is called the scanning mode. Weight changes occur during chemical reaction, evaporation, sublimation, and decomposition, magnetic or electrical transformations. TGA is used to characterize the thermal stability and the decompositions of materials under different conditions. Also, it is used to study and compare the effect of additives on polymer behavior. The change of weight of the sample can be measured and plotted either relatively as a percentage of the starting mass or absolutely in milligrams versus time or temperature.

The study of the thermal stability of the LLDPE nanocomposites was performed using SDT-Q600 TGA by TA instruments. Around 10 mg of different samples were heated from 30°C to 800°C at a heating rate of 10°C/min.

CHAPTER 4

RESULTS AND CONCLUSION

4.1 LDH Characteristics

LDHs which were prepared based on Daud et al⁷⁰ review paper were characterized by FTIR, XRD, and TGA. This is important for the study because it gives valuable information about the prepared material especially the presence of the organic group of LDHs and graphene. This presence means a successful preparation was made otherwise a failure and a new preparation should be conducted. Also, the presence of LDH in the polymer nanocomposite can be detected by the obtained XRD signals from this characterization.

4.1.1 FTIR LDH RESULTS

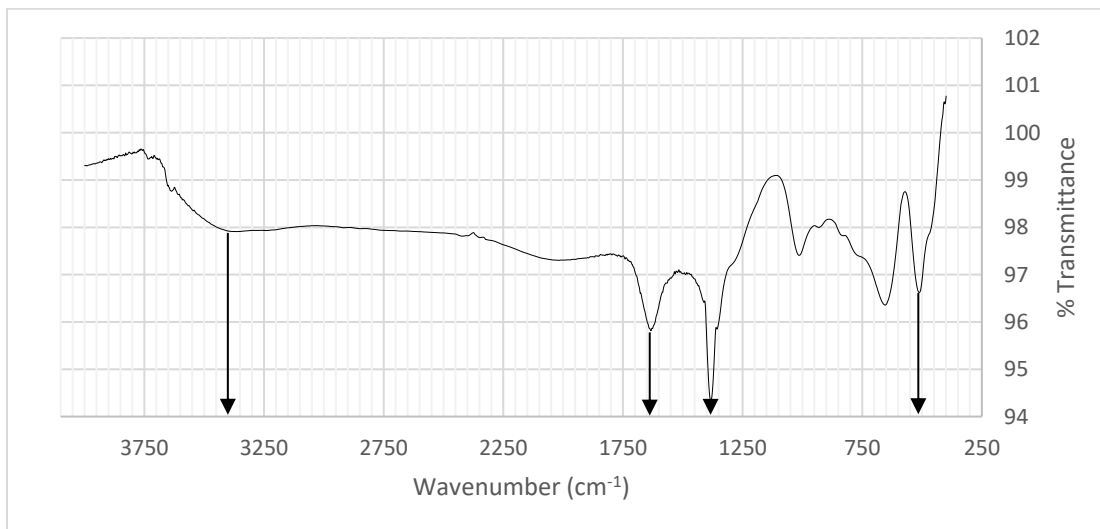


Figure 20: NiFe LDH, FTIR Result

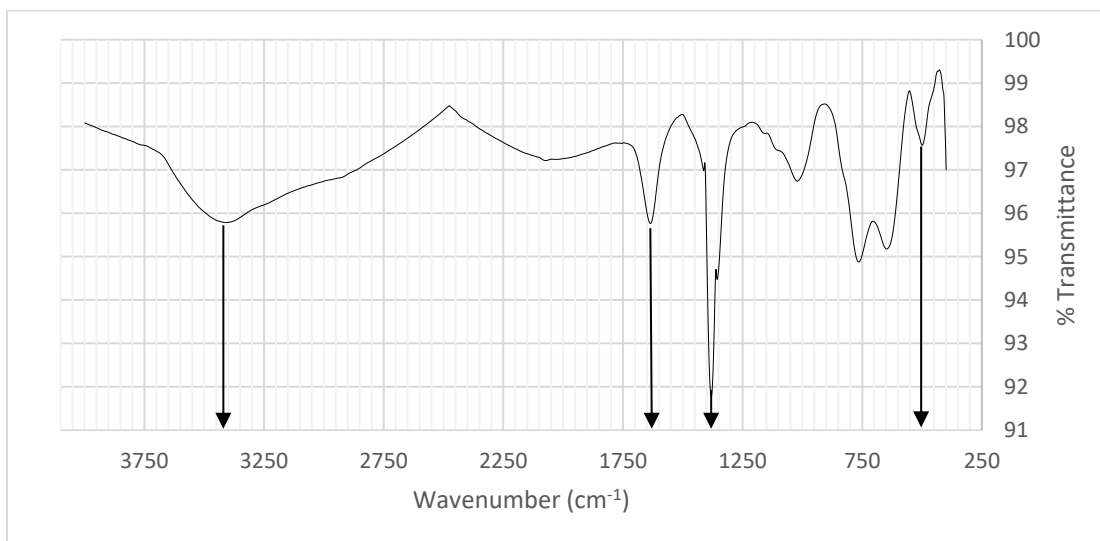


Figure 21: NiFe-Gr LDH, FTIR Result

The adsorption peak observed in figure 20 & 21 around 3400 cm^{-1} is due to the hydroxyl group and the overlapping stretching vibrations of the interlayer water ⁷¹. The peak that caused by bending vibration of the interlayer water can be seen in figure 20 & 21 around 1630 cm^{-1} ⁷¹. The metal oxide absorption peak can be observed within the $450 - 900\text{ cm}^{-1}$

region for NiFe-Gr LDH as shown in figure 21 while for NiFe LDH it can be observed at 450 - 850 cm^{-1} region as shown in figure 20. The results are close to what have been observed by N Hidayati et al.⁷¹ with a small shift which depends on the used device. The vibration peak which caused by the layered material (nitrate) can be observed at around 1380 cm^{-1} ⁷¹. While that for the layered double hydroxide (vNi-O) can be seen at around 495 cm^{-1} ⁷¹. Graphene absorption peak would be shown at around 3400 cm^{-1} and 1610 cm^{-1} ¹ due to the stretching hydroxyl group and the skeletal aromatic vibrations, respectively.^{60,72} The later cannot be seen because of the overlapping.

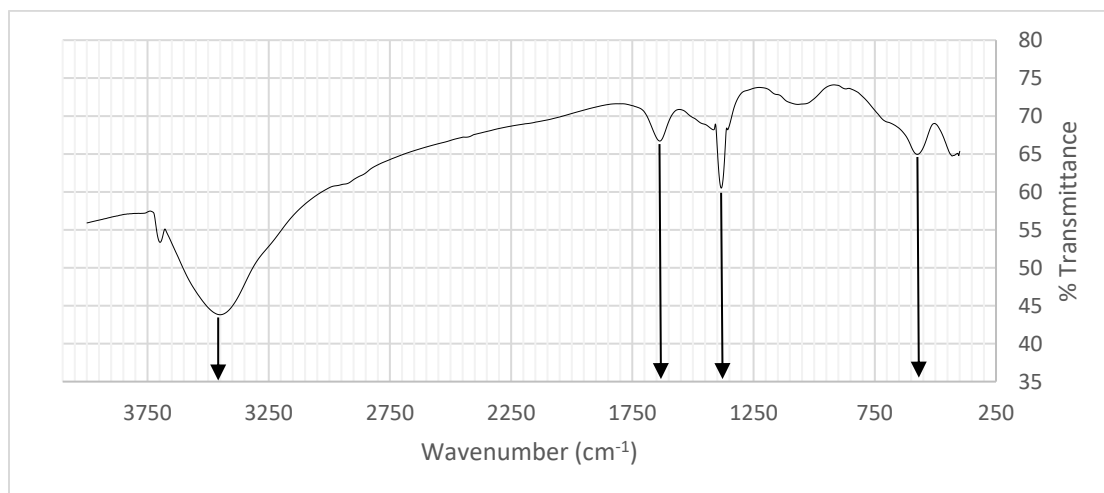


Figure 22: MgFe LDH, FTIR Result

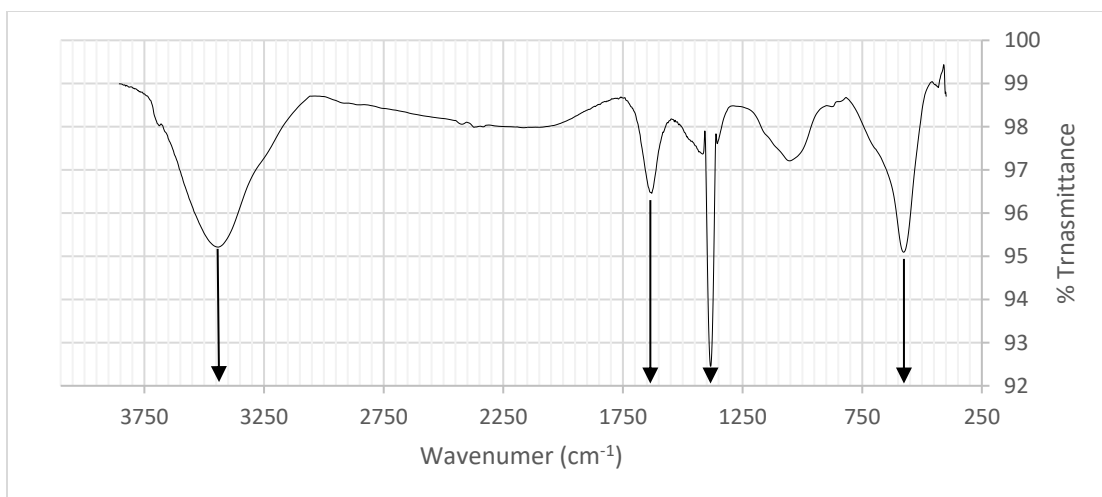


Figure 23: MgFe-Gr LDH, FTIR Result

The adsorption peak observed in figure 22 & 23 around 3450 cm^{-1} are due to the hydroxyl group and the overlapping stretching vibrations of the interlayer water ⁷¹. The peak that caused by bending vibration of the interlayer water can be seen in figure 22 & 23 around 1630 cm^{-1} ⁷¹. The metal oxide absorption peak can be observed in $500\text{ -}700\text{ cm}^{-1}$ region for both MgFe-Gr LDH and MgFe LDH. The results are close to what have been observed by N Hidayati et al. ⁷¹ but with a shift which depends on the used device. The vibration peak which caused by the layered material (nitrate) can be observed at around 1380 cm^{-1} ⁷¹. While that for the layered double hydroxide (vMg-O) can be seen at around 580 cm^{-1} ⁷¹. Graphene absorption peak would be shown at around 3400 cm^{-1} and 1610 cm^{-1} due to the stretching hydroxyl group and the skeletal aromatic vibrations, respectively.^{60,71} The later cannot be seen because of the overlapping.

4.1.2 XRD LDH RESULTS

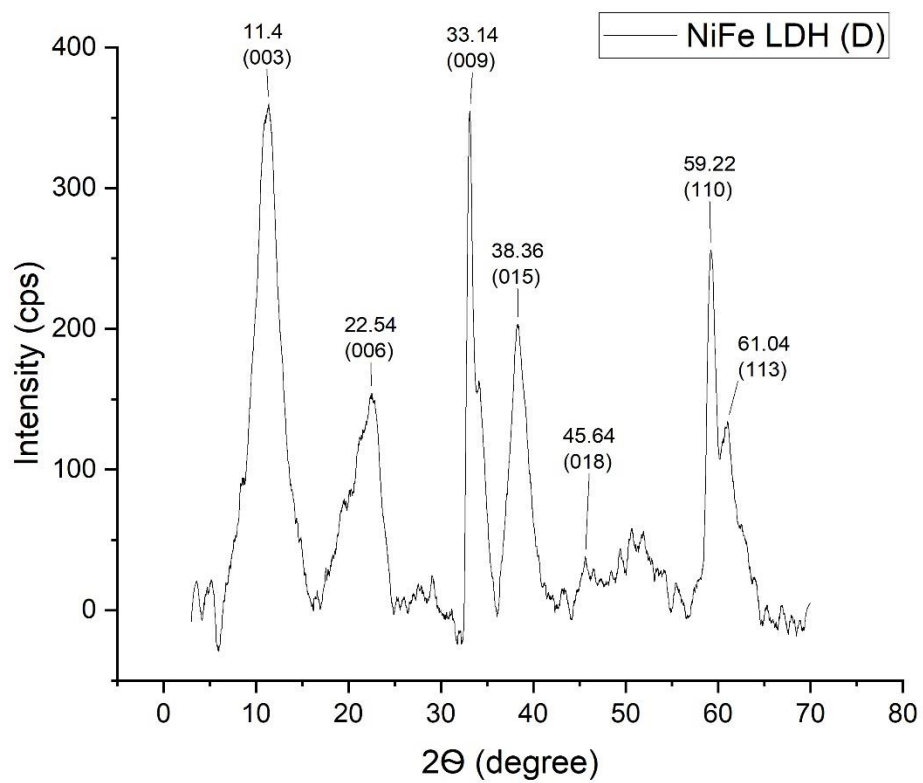


Figure 24: NiFe LDH, XRD Result

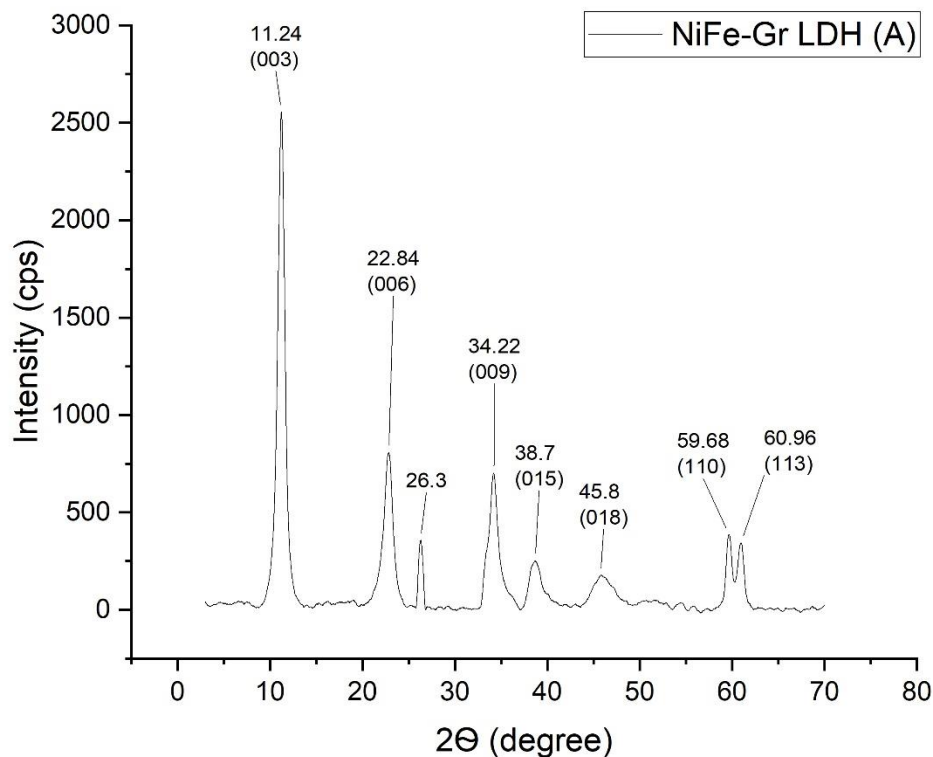


Figure 25: NiFe-Gr LDH, XRD Result

As it can be seen in Figure 25, Graphene has an intense crystalline peak around $2\theta \approx 26^\circ$ as observed by Duad et al.⁶⁰ which relates to C(002) plane obtained from graphene spectrum⁷³. While Figure 24 shows no peak at $2\theta \approx 26^\circ$ because of graphene absence. Both Figures 24,25 show diffraction peaks at 2θ around 11° , 23° , 34° , 39° , 46° , 59° , and 61° reflected by the LDH which corresponds to (003), (006), (012), (015), (018), (110), and (113) crystal structure planes⁷³, respectively. The d spacing at $2\theta \approx 11^\circ$ for NiFe LDH is 7.69 Å, while that for NiFe-Gr LDH is 7.867 Å. This increment caused by the addition of Graphene which enhanced the intensity.

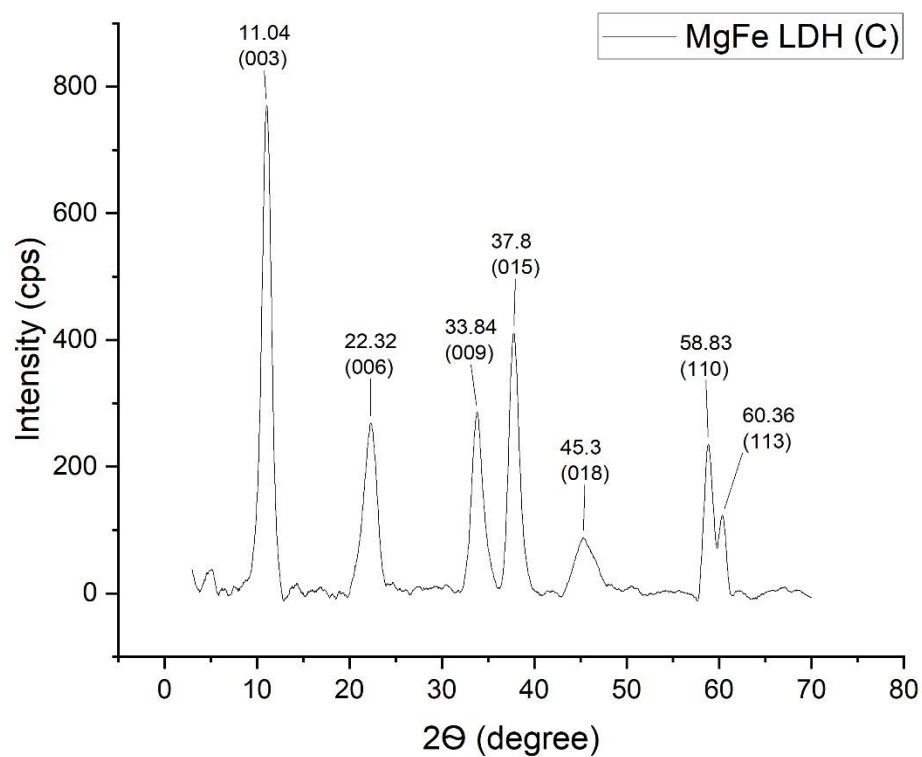


Figure 26: MgFe LDH, XRD Result

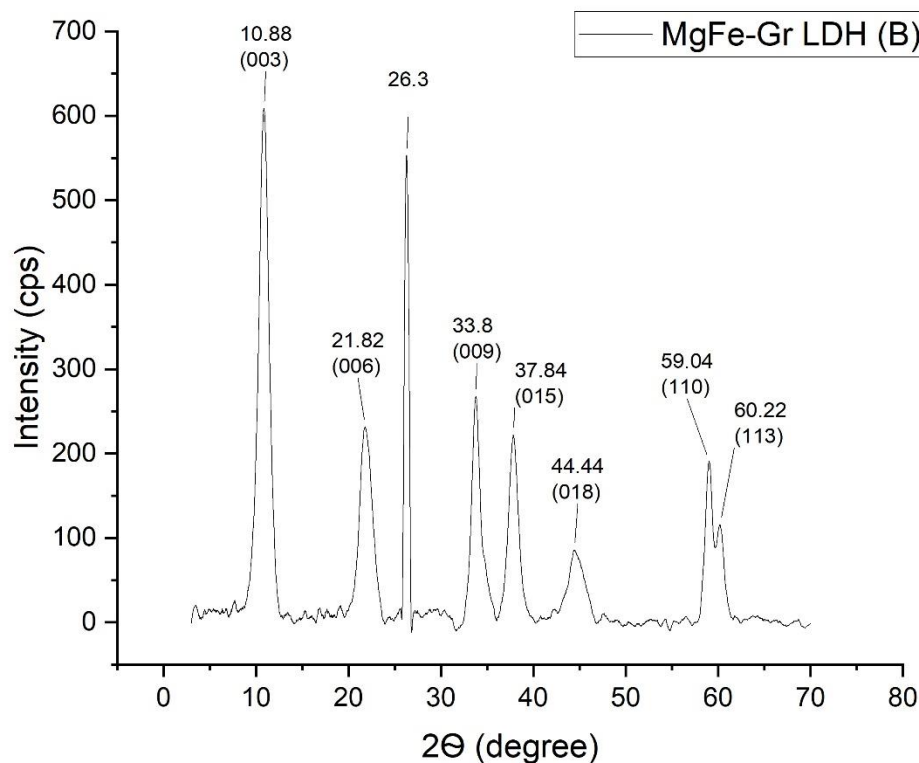


Figure 27: MgFe-Gr LDH, XRD Result

As it can be seen in Figure 27, Graphene has an intense crystalline peak around $2\theta \approx 26^\circ$ as observed by Duad et al.⁶⁰ which relates to C(002) plane obtained from graphene spectrum⁷³. While Figure 26 shows no peak at $2\theta \approx 26^\circ$ because of graphene absence. Both Figures 26,27 show diffraction peaks at 2θ around 11° , 23° , 34° , 39° , 46° , 59° , and 61° reflected by the LDH which corresponds to (003), (006), (009), (015), (018), (110), and (113) crystal structure planes⁷⁴, respectively. The d spacing at $2\theta \approx 11^\circ$ for MgFe LDH is 8.019 Å, while that for MgFe-Gr LDH is 8.167 Å. This increment caused by the addition of Graphene which enhanced the intensity. The discussion of MgFe (Gr/without Gr) LDH

is like the previous because of the hydrotalcite-like LDH family have almost the same reflections⁷⁵.

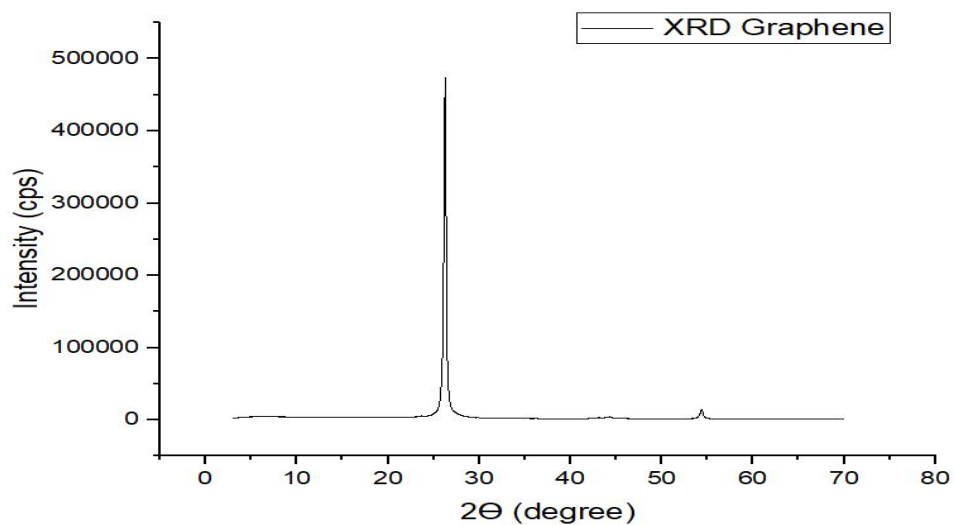


Figure 28: Graphene XRD Results

The presence of graphene can be easily detected by its XRD intensity peak which is within the region of 2θ (25 – 30 degree) as shown in figure 28. This peak can be noticed clearly in figures 27 & 25 because of the graphene. While in figures 26 & 24 it is not shown because the LDHs were prepared without graphene.

4.1.3 MgFe (-Gr) and NiFe (-Gr) LDH Structure - XRD RESULTS

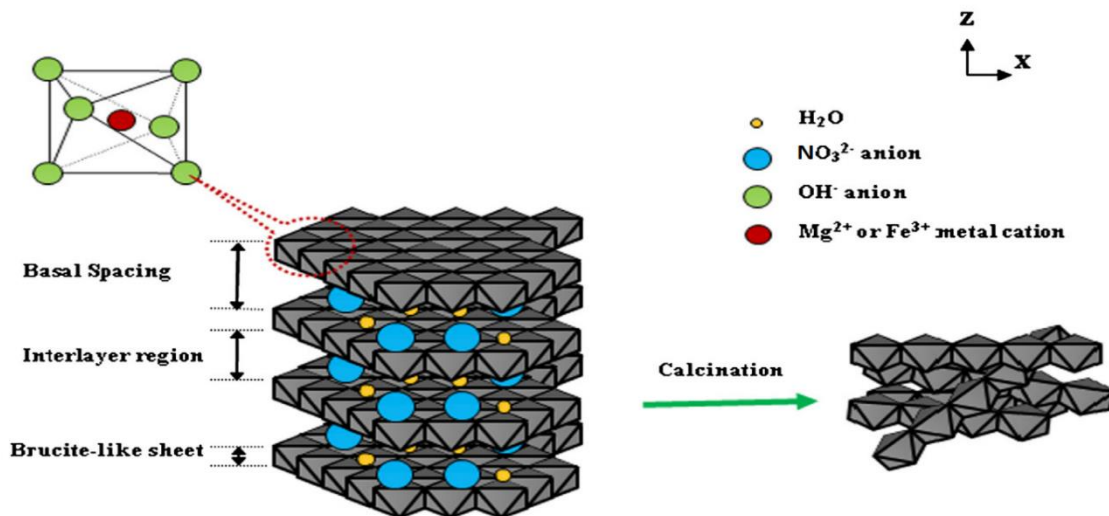


Figure 29: illustration of LDH structure ⁷⁴

As shown in figure 29 which is an illustration of LDH structure, the LDH is formed from stacked layers on top of each other building a three-dimensional network. These layers will be held together by hydrogen bonding. They would be represented by the 3R type if the lattice c parameter is almost three times the d spacing for the peak which corresponds to (003) ⁷⁶⁻⁷⁹. $d(003)$ is the basal spacing between adjacent brucite like layers which can be found from the XRD results at around $2\theta \approx 11^\circ$. Lattice c parameter can be approximated by $c=d(003)+2d(006)+3d(009)$ ⁷⁴. The Cation to cation distance in the brucite-like layers can be calculated by $a=2d(110)$ ⁷⁴. In this work all the LDH's corresponds to 3R types as it can be noticed from table 5. Figure 24, 25, 26 & 27 shows three sharp, intense peaks at $2\theta \approx 11^\circ$, 23° and 34° which is ascribed to the good crystallinity of the well-developed stacking layers with a perfect structural integrity. Also, it is an attribution to the processing of the hydrotalcite structure. The presence of the peaks at around $2\theta \approx 34^\circ$, 39° , 46° is an

indication that the stacking layers have 3R structure type ⁸⁰. As it can be seen in table 5, there is a small decrement in c-parameter with the absence of graphene due to the small amount of the co-intercalated water molecule within the interlayer region ⁸¹

Table 5: X-ray patterns of LDHs

Name	a-parameter (Å)	c-parameter (Å)	d-spacing (Å)	2 θ (°)	FWHM (°)
NiFe-Gr LDH	3.04	25.81	7.87	11.24	0.79
MgFe-Gr LDH	3.13	26.48	8.17	10.83	1.34
NiFe LDH	3.10	20.17	7.69	11.5	5.12
MgFe LDH	3.15	23.92	8.02	11.02	1.37

4.1.4 TGA LDH RESULTS

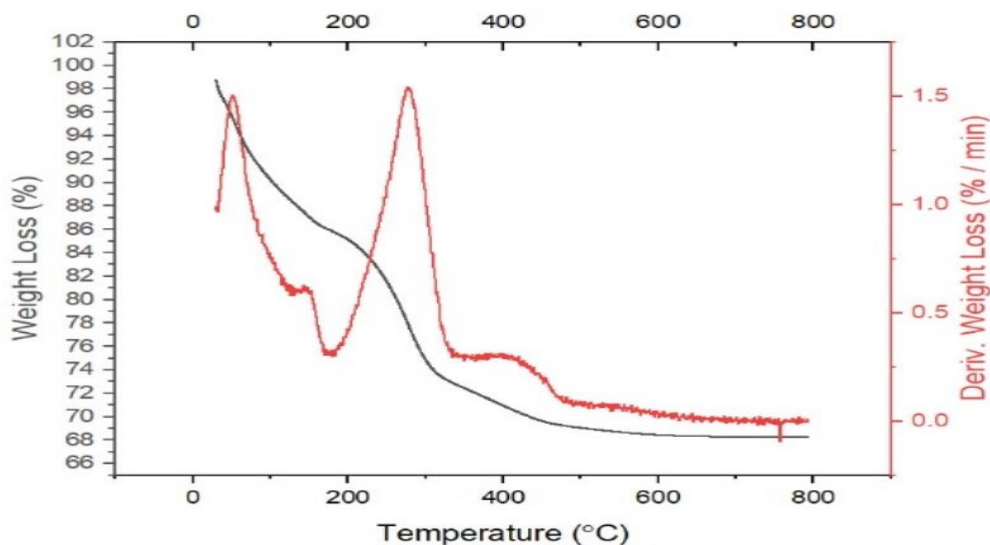


Figure 30: NiFe LDH TGA Results

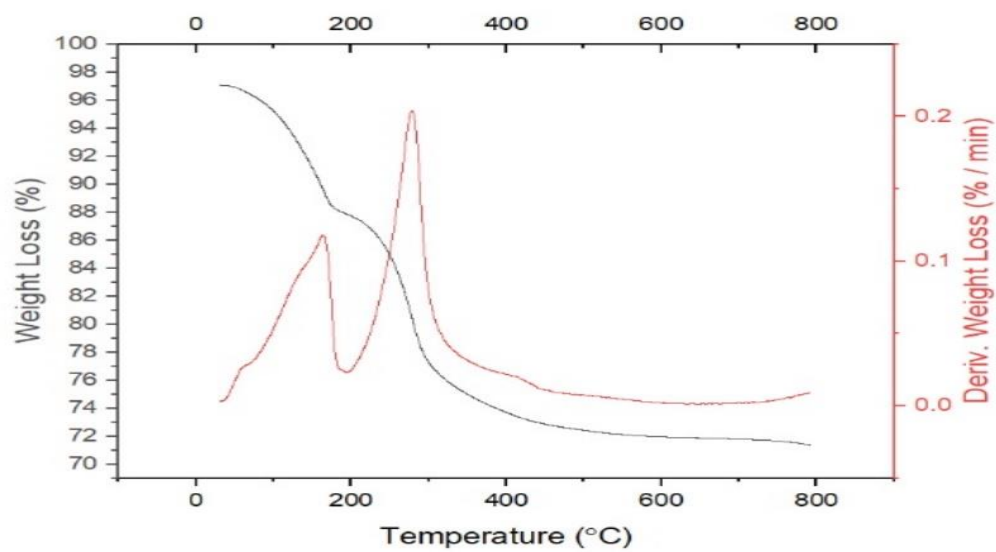


Figure 31: NiFe-Gr LDH TGA Results

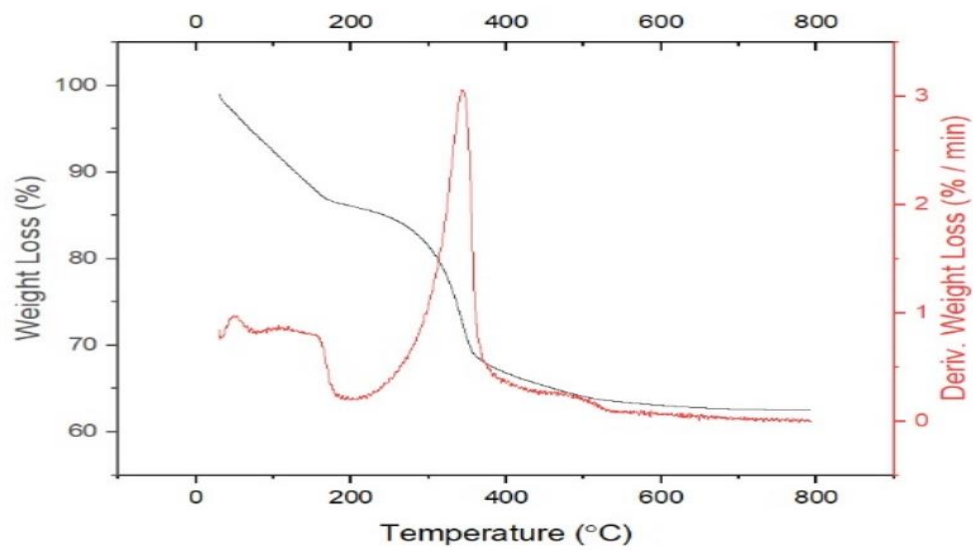


Figure 32: MgFe LDH TGA Results

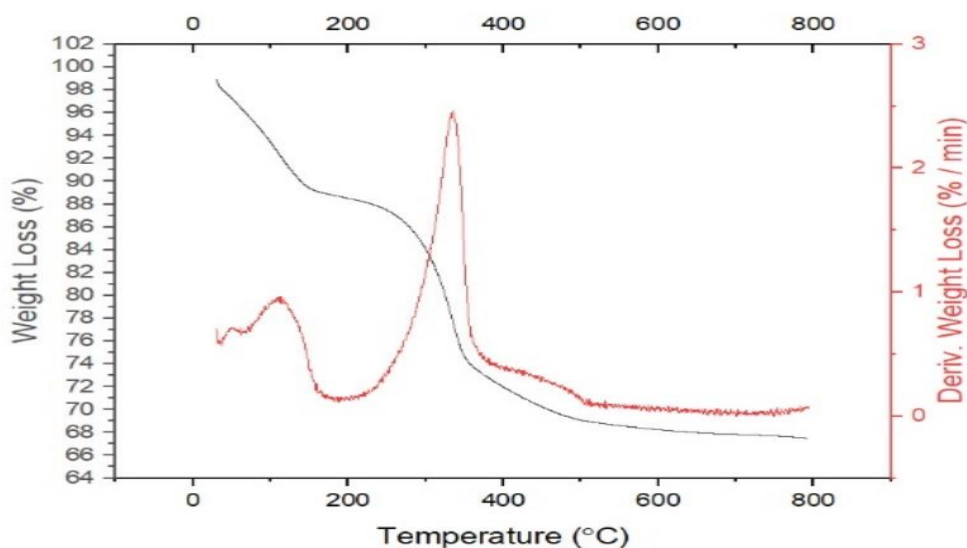


Figure 33: MgFe-Gr LDH TGA Results

The TGA curves of LDHs as shown in figures 30, 31, 32 & 33 show three weight loss zones. Approximately, the first weight loss zone starts from 30 to 200 °C for MgFe (/-Gr) LDH and from 30 to 195°C for NiFe (/-Gr) LDH which is due the loss of the absorbed NO_3^{2-} on the surface and the loss of the adsorbed interlayer water. The second weight loss zone stars from 200 to 400 °C for MgFe (/-Gr) LDH and from 195 to 337 °C for NiFe (/-Gr) LDH attributed to the partial loss of NO_3^{2-} and the de-hydroxylation. The last weight loss zone starts from 400 to 512 °C for MgFe (/-Gr) LDH and from 337 to 482 °C for for NiFe (/-Gr) LDH. The last zone occurred due to the complete loss of interlayer anions. Consequently, the layered double oxide will form.

4.2 PE/LDHs nanocomposites Characteristics

LLDPE/LDHs nanocomposites were characterized by SEM, XRD, DSC, and TGA. The former two methods were used to study the dispersion of each LDH type in LLDPE. While the later two methods were used for the thermal stability investigations. The used amount of each LDH was 1%, 2%, and 3% by weight of the total except that for LDHB 5% by weight were used in addition to the previous amounts.

4.2.1 DSC Nanocomposites Results

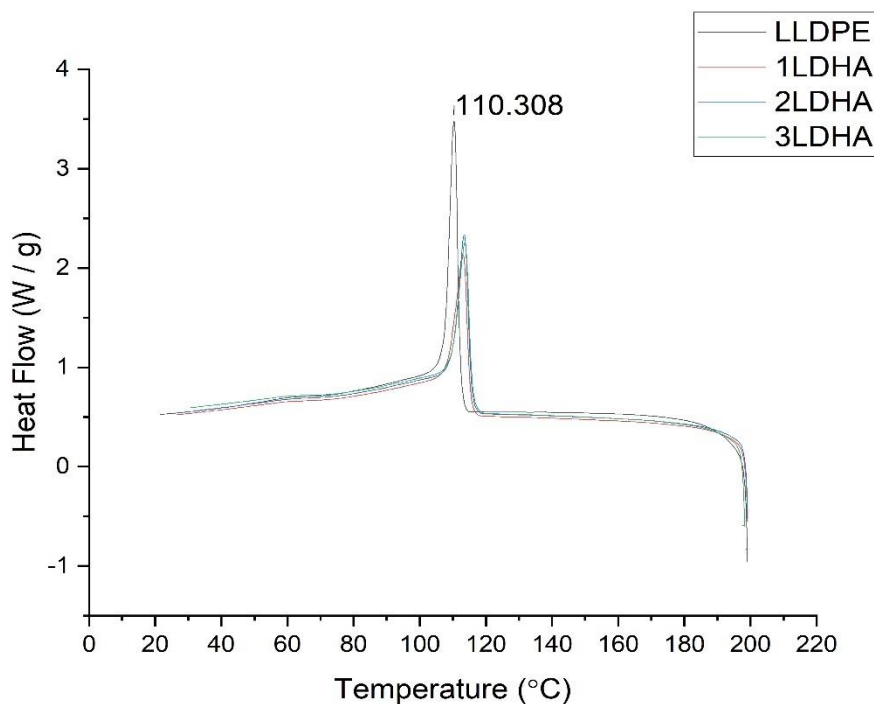


Figure 34: Effect of LDHA on LLDPE (first cooling scan)

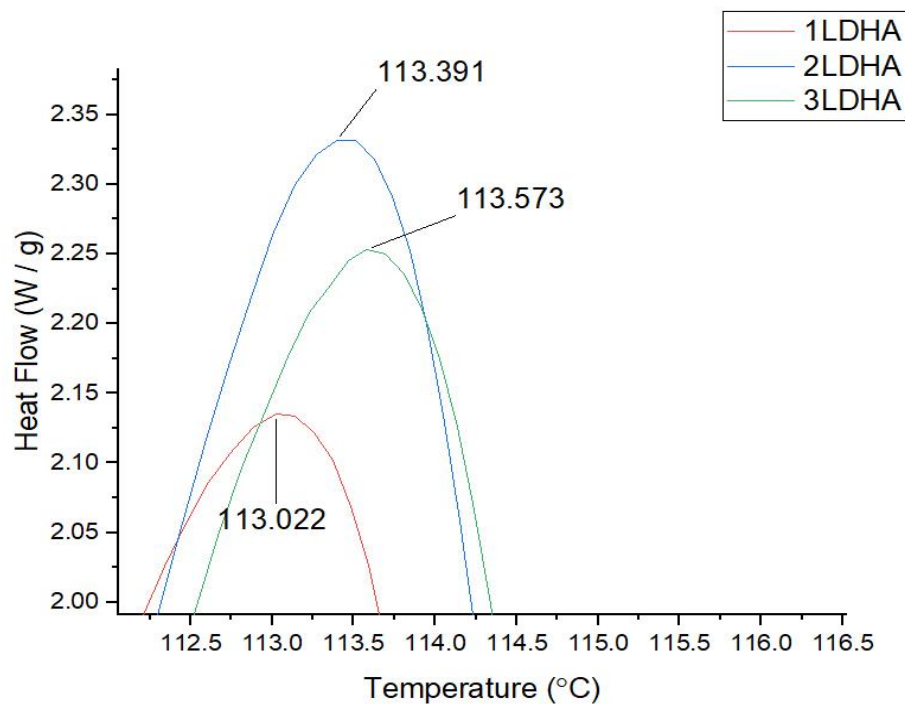


Figure 35: Effect of LDHA on LLDPE (first cooling scan) - Zoomed

The achieved crystallinity caused by the addition of LDHA to LLDPE can be shown by the first cooling scan which is illustrated by figure 34. It is noticed that all LDHA nanocomposites show a peak shift toward the right which indicates that the crystallinity is increased due to the nucleation as shown in figure 34. The crystallization enthalpy increases as LDHA concentration increases as shown in table 6, this is because the crystallization process is becoming slower.² The crystalline peak temperature slightly increases as the LDHA concentration increases as shown in figure 35 and table 6. LDHA slightly increased the Onset and crystalline peak temperature of LLDPE by 2.73 %

Table 6: DSC data for LLDPE and LDHA nanocomposites (first cooling scan)

Material	Onset Temperature, °C	Crystallization peak, °C	Crystallization enthalpy (J/g)
LLDPE	112.38	110.31	- 93.75
1LDHA	115.16	113.02	- 85.72
2LDHA	115.5	113.39	- 84.98
3LDHA	115.67	113.57	- 82.71

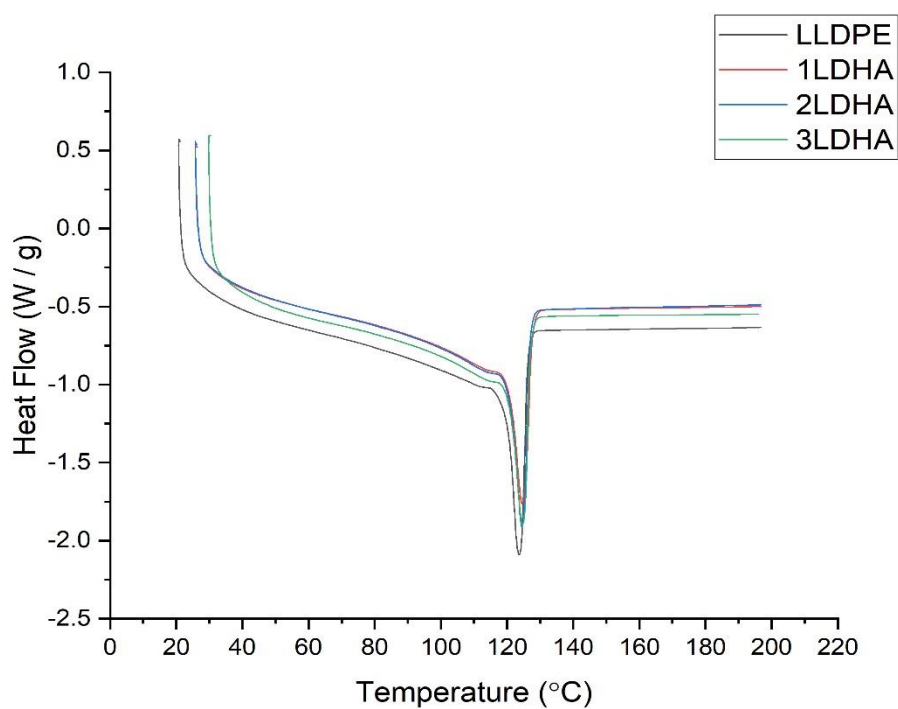


Figure 36: Effect of LDHA on LLDPE (Second Heating Scan)

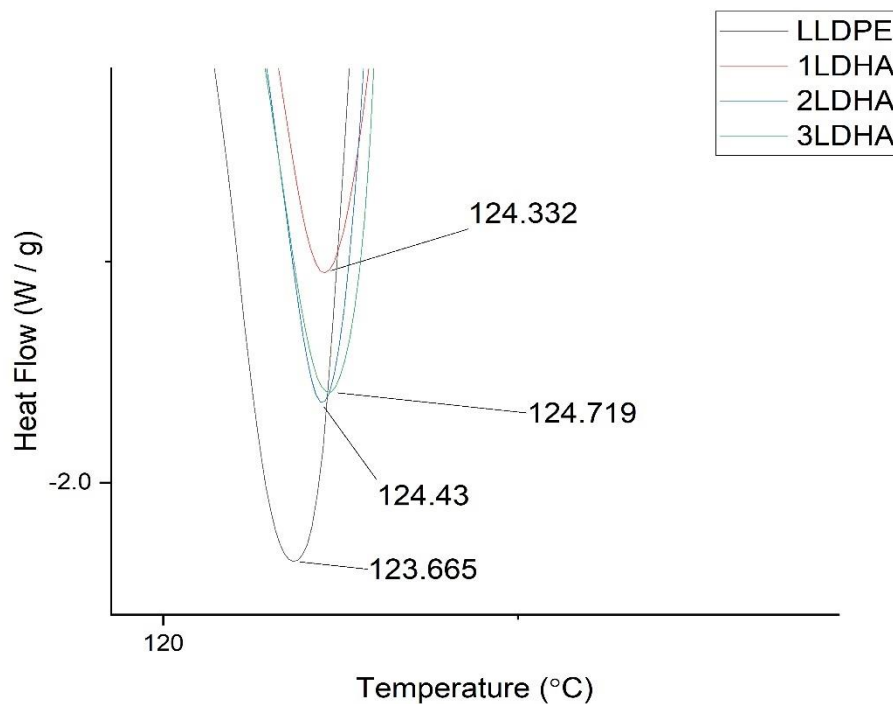


Figure 37: Effect of LDHA on LLDPE (Second Heating Scan) – Zoomed

Figure 36 illustrates the second heating scan which shows the effect of LDHA on LLDPE melting temperature. All LDHA show a decreased peak width and a peak shift toward the right. 2LDHA shows the maximum shift as shown in figure 37. The melting peak temperature slightly increases as the LDHA concentration increases as shown in table 7. LDHA slightly increased the maximum melting temperature of LLDPE by 0.67 % while the onset temperature slightly increased by 0.31 %.

Table 7: DSC data for LLDPE and LDHA nanocomposites (Second Heating scan)

Material	Onset Temperature, °C	Melting peak, °C	Enthalpy of fusion (J/g)	Crystallinity %
LLDPE	119.02	123.67	102.97	35.84
1LDHA	119.46	124.33	105.37	37.05
2LDHA	119.44	124.43	103.67	36.82
3LDHA	119.48	124.72	101.49	36.42

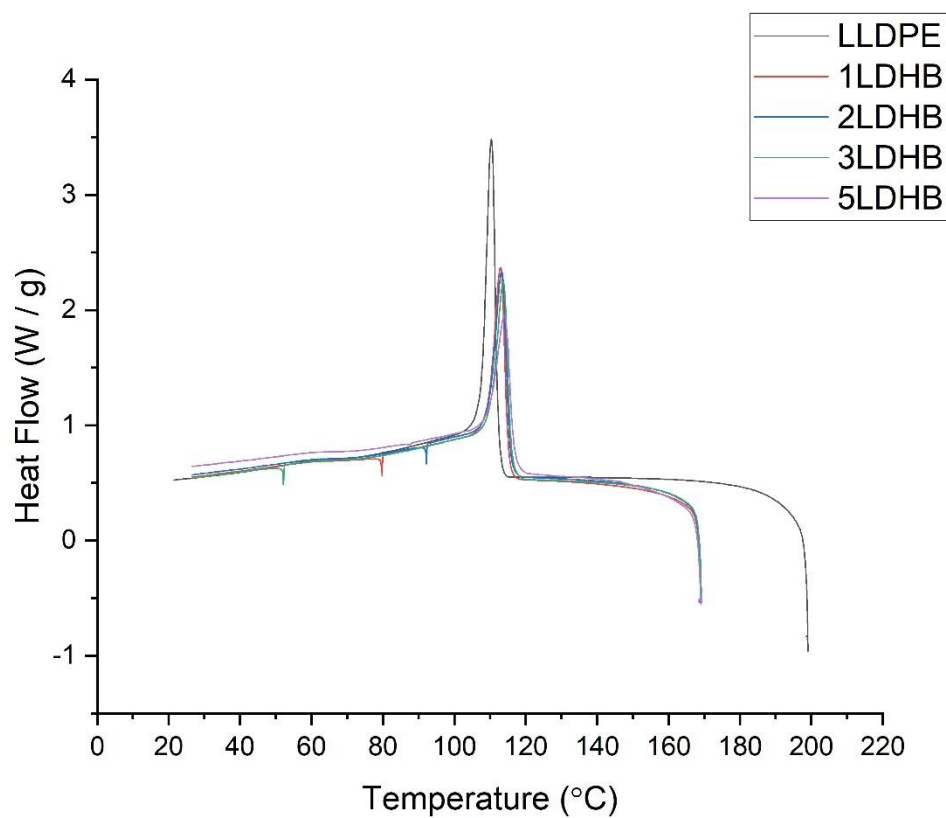


Figure 38: Effect of LDHB on LLDPE (first cooling scan) - Zoomed

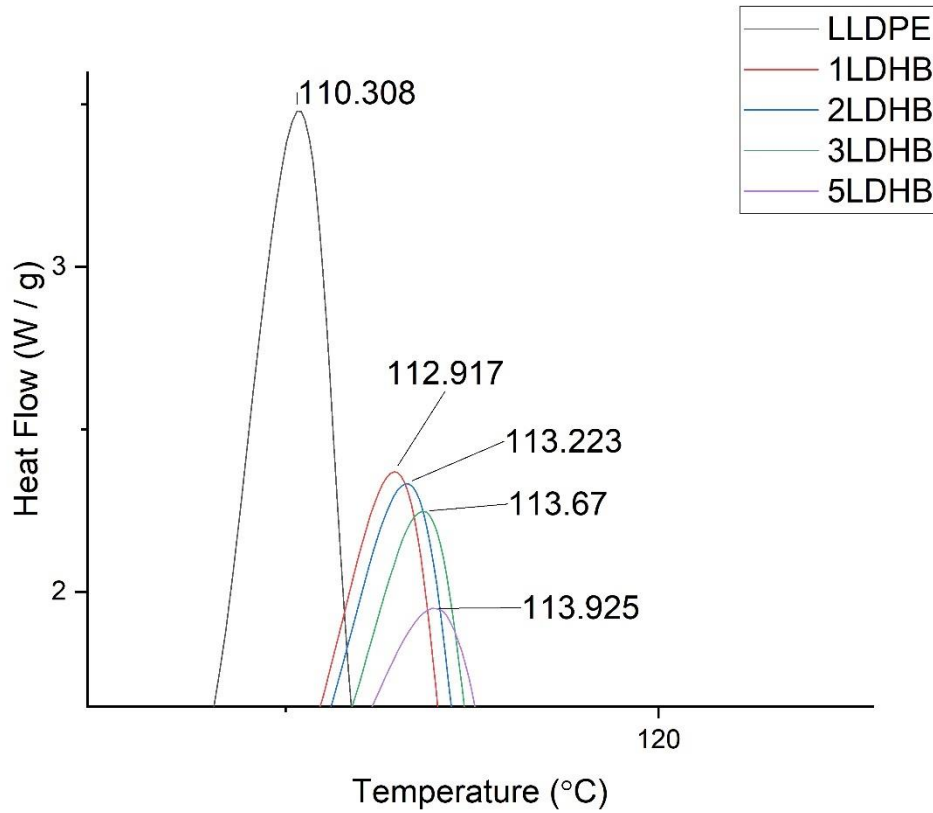


Figure 39: Effect of LDHB on LLDPE (first cooling scan) – Zoomed

The achieved crystallinity caused by the addition of LDHB to LLDPE can be shown by the first cooling scan which is illustrated by figure 38. It is noticed that all LDHA nanocomposites show a peak shift toward the right which indicates that the crystallinity is increased due to the nucleation as shown in figure 38. The crystalline peak temperature slightly increases as the LDHB percentage increases as shown in figure 39 and table 8. The crystallization enthalpy increases as LDHB concentration increases as shown in table 8, this is because the crystallization process is becoming slower.² LDHB slightly increased

the minimum crystalline temperature of LLDPE by 2.83 % while the onset temperature slightly increased by 3.06 %.

Table 8: DSC data for LLDPE and LDHB nanocomposites (first cooling scan)

Material	Onset Temperature, °C	Crystallization peak, °C	Crystallization enthalpy (J/g)
LLDPE	112.38	110.31	- 93.75
1LDHB	115.08	112.92	- 94.46
2LDHB	115.53	113.22	- 90.01
3LDHB	115.96	113.67	- 89.99
5LDHB	116.72	113.93	- 78.61

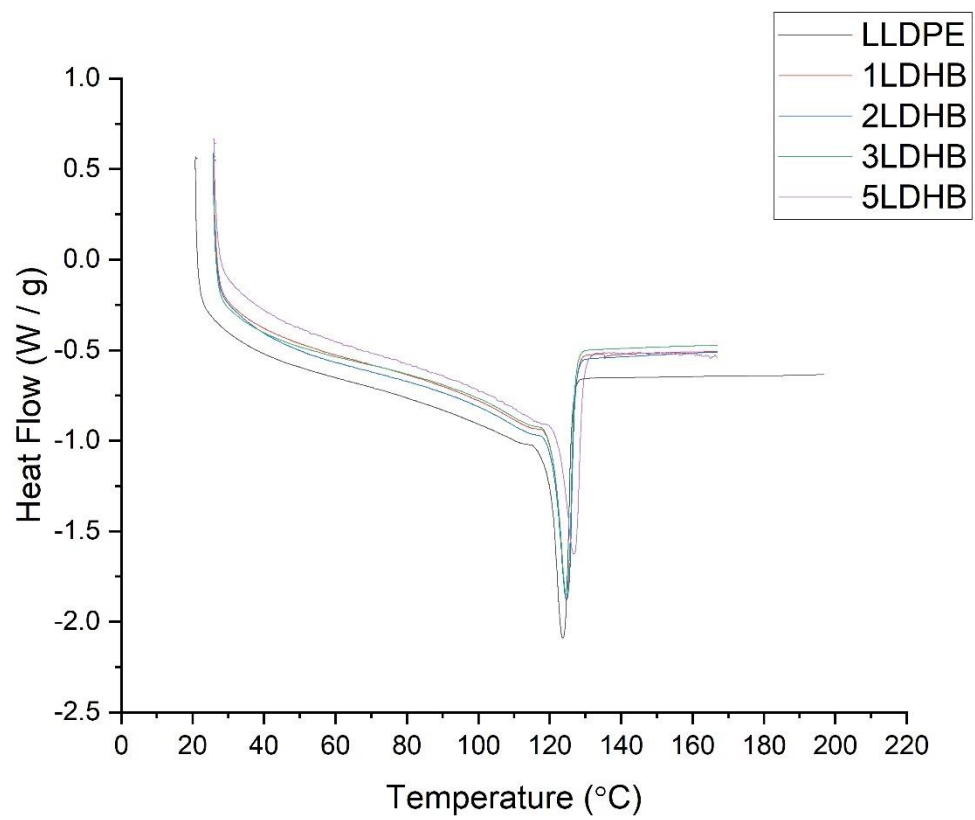


Figure 40: Effect of LDHB on LLDPE (Second Heating Scan)

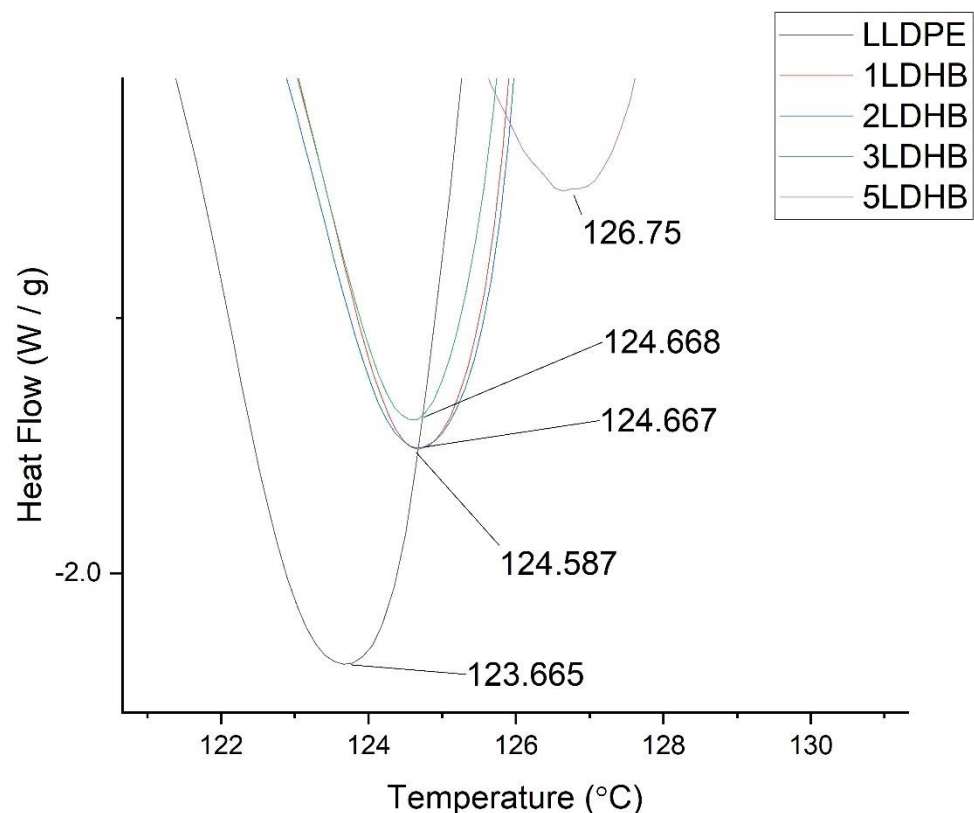


Figure 41: Effect of LDHB on LLDPE (Second Heating Scan) – Zoomed

Figure 40 illustrates the second heating scan which shows the effect of LDHB on LLDPE melting temperature. All LDHB nanocomposites show a decreased peak width and a peak shift toward the right. 1LDHB and 2LDHB show the maximum shift as shown in figure 41. The melting peak temperature slightly increases as the LDHA concentration increases as shown in table 9. 1LDHB, 2LDHB, and 3LDHB show comparable melting temperature enhancement but not as much as in the case of 5LDHB which is the highest. LDHB slightly increased the melting peak temperature of LLDPE by 0.78 % while the onset temperature slightly increased by 0.36 %.

Table 9: DSC data for LLDPE and LDHA nanocomposites (Second Heating scan)

Material	Onset Temperature, °C	Melting peak, °C	Enthalpy of fusion (J/g)	Crystallinity %
LLDPE	119.02	123.67	102.97	35.84
1LDHB	119.54	124.59	110.75	38.89
2LDHB	119.48	124.667	111.9	39.74
3LDHB	119.34	124.668	110.5	39.65
5LDHB	120.02	126.75	108.85	39.88

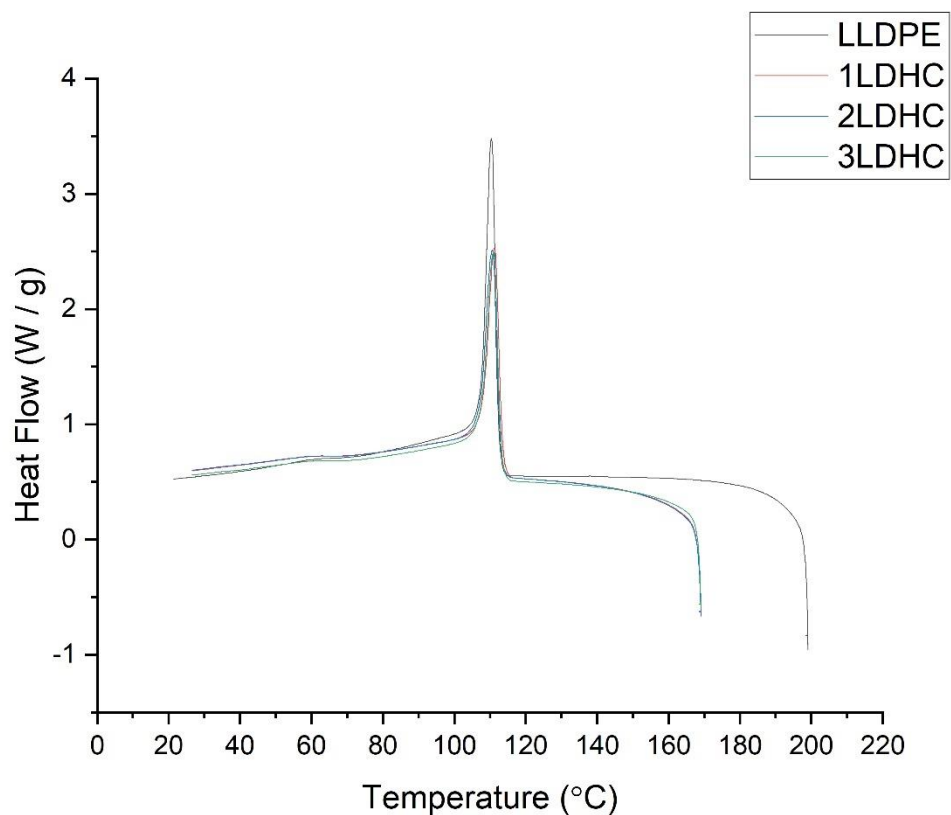


Figure 42: Effect of LDHC on LLDPE (first cooling scan)

Table 10: DSC data for LLDPE and LDHC nanocomposites (first cooling scan)

Material	Onset Temperature, °C	Crystallization Peak, °C	Crystallization enthalpy (J/g)
LLDPE	112.38	110.31	- 93.75
1LDHC	113.21	110.94	- 80.57
2LDHC	113.11	110.79	- 80.13
3LDHC	113.22	111.06	- 79.16

The achieved crystallinity caused by the addition of LDHC to LLDPE can be shown by the first cooling scan which is illustrated by figure 42. It is noticed that all LDHC nanocomposites show a peak shift toward the right which indicates that the crystallinity is increased due to the nucleation as shown in figure 42 and table 10. The crystallization enthalpy increases as LDHC concentration increases as shown in table 10, this is because the crystallization process is becoming slower.² LDHC slightly increased the crystalline peak temperature of LLDPE by 0.56 % while the onset temperature slightly increased by 0.71 %.

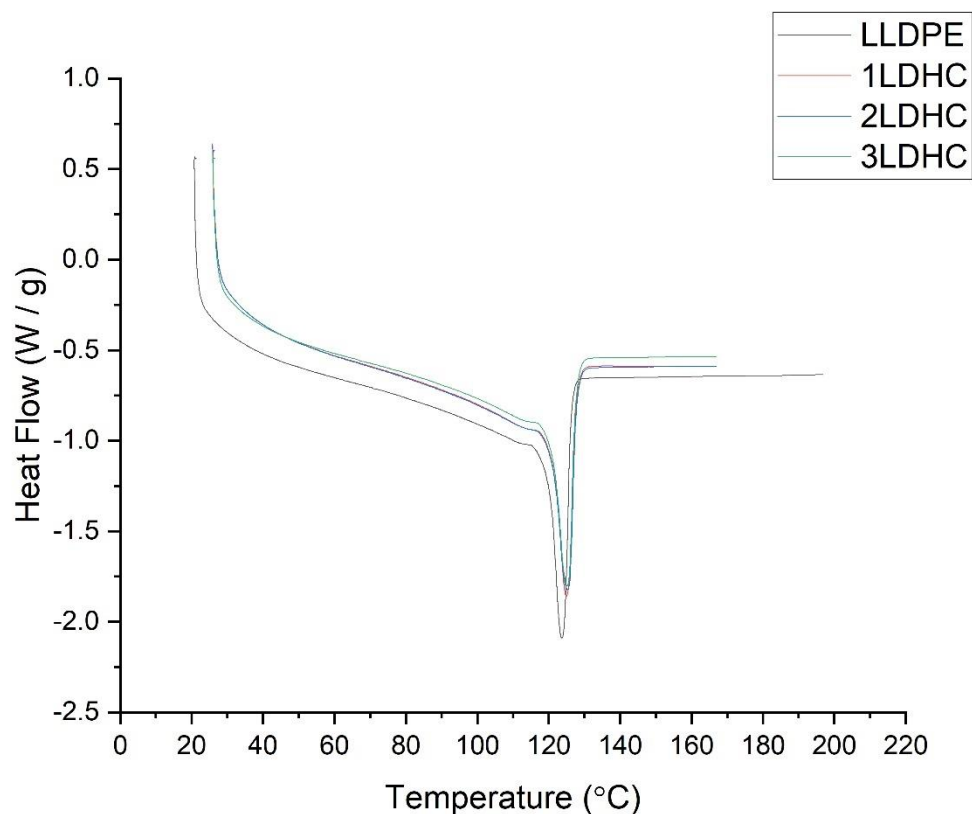


Figure 43: Effect of LDHC on LLDPE (Second Heating Scan)

Table 11: DSC data for LLDPE and LDHC nanocomposites (Second Heating scan)

Material	Onset Temperature, °C	Melting peak, °C	Enthalpy of fusion (J/g)	Crystallinity %
LLDPE	119.02	123.67	102.97	35.84
1LDHC	119.90	124.92	109.04	38.33
2LDHC	119.67	125.23	110.40	39.21
3LDHC	119.85	125.05	107.20	38.47

Figure 43 represents the second heating scan which shows the effect of LDHC on LLDPE melting temperature. All LDHC nanocomposites show a decreased peak width and a peak shift toward the right. LDHC slightly increased the maximum melting temperature of LLDPE by 1.13 % while the onset temperature slightly increased by 0.66 %.

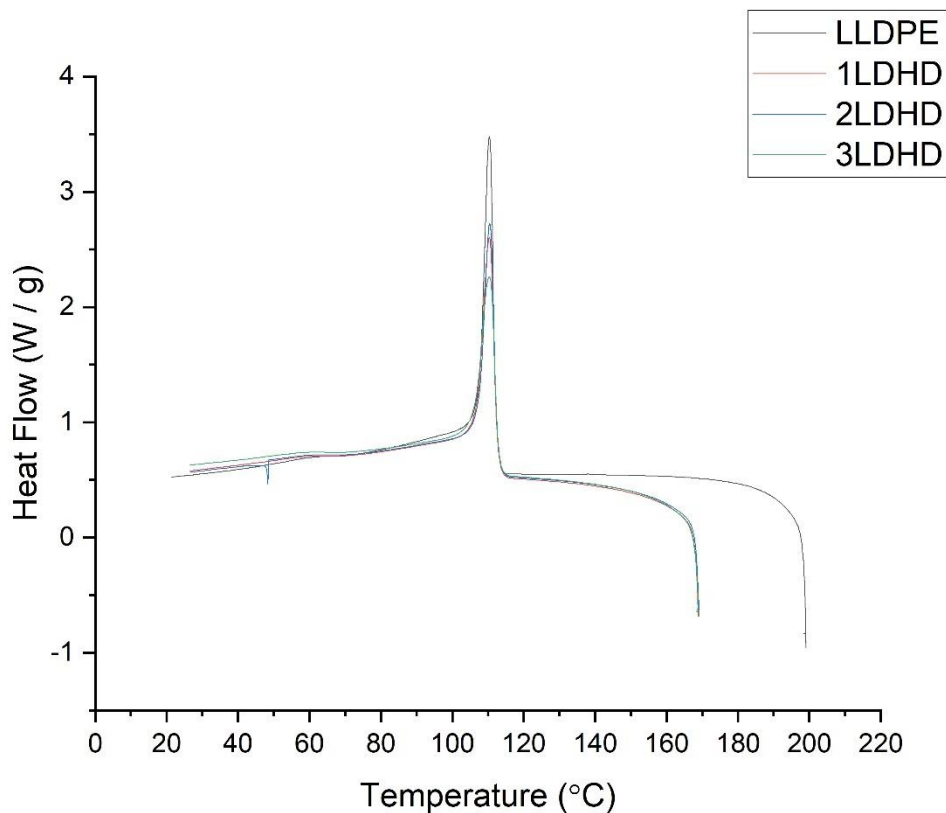


Figure 44: Effect of LDHD on LLDPE (first cooling scan)

The achieved crystallinity caused by the addition of LDHD to LLDPE can be shown by the first cooling scan which is illustrated by figure 44. It is noticed that all LDHC nanocomposites show a slight peak shift toward the right which indicates that the crystallinity is increased slightly due to the nucleation as shown in figure 44 and table 11. LDHD increased the crystalline peak temperature of LLDPE by 0.38 % while the onset temperature increased slightly by 0.61 %.

Table 12: DSC data for LLDPE and LDHD nanocomposites (first cooling scan)

Material	Onset Temperature, °C	Crystallization peak, °C	Crystallization enthalpy (J/g)
LLDPE	112.38	110.31	- 93.75
1LDHD	113.40	111.03	- 79.83
2LDHD	112.85	110.63	- 80.49
3LDHD	112.92	110.53	- 78.23

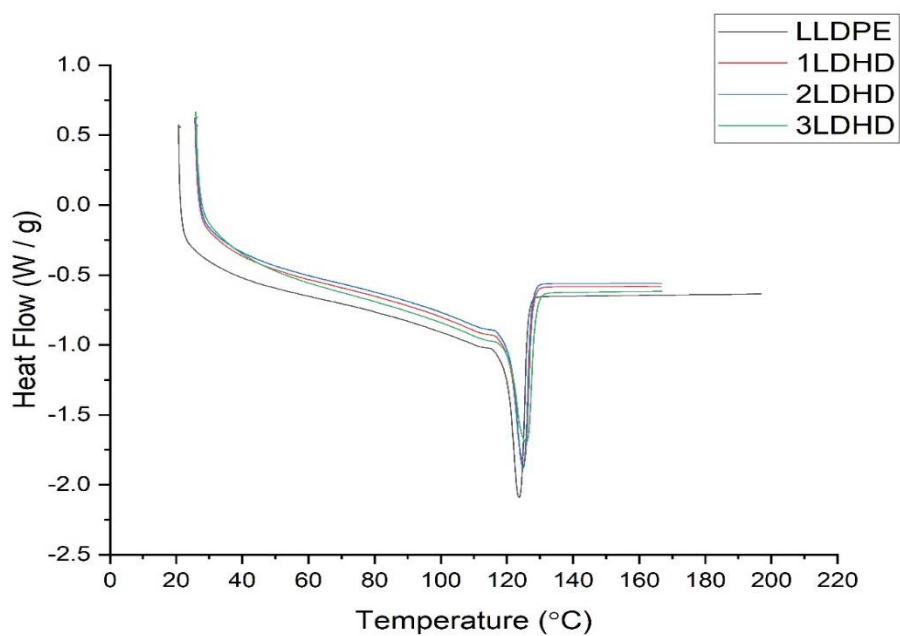


Figure 45: Effect of LDHD on LLDPE (Second Heating Scan)

Table 13: DSC data for LLDPE and LDHD nanocomposites (Second Heating scan)

Material	Onset Temperature, °C	Melting peak, °C	Enthalpy of fusion (J/g)	Crystallinity %
LLDPE	119.02	123.67	102.97	35.84
1LDHD	119.61	124.13	111.20	39.09
2LDHD	119.67	124.91	109.25	38.80
3LDHD	119.16	125.37	112.60	40.40

Figure 45 represents the second heating scan which shows the effect of LDHD on LLDPE melting temperature. All LDHD nanocomposites show a decreased peak width and a peak shift toward the right. LDHD slightly increased the maximum melting temperature of LLDPE by 0.92 % while the onset temperature increased slightly by 0.39 %.

Generally, the increment in the nucleation rate can be observed by the slight increase in the onset temperature of crystallization which is the beginning of crystallization. Also, it could be observed by the curve shifts toward higher temperatures. The previous enhancement is attributing to the short chain structure of LLDPE.² Also, tables 6, 8, and 10 show an increment in the crystallization enthalpy with the incorporation of LDHs, this is due to the crystallinity enhancement in which the crystallization rate is becoming slower allowing the molecules to adopt arrangements that is suitable to the formation of crystallites. Sometime the crystallization and melting peak are not increasing in a clear trend, instead of that they

fluctuate. This is because the lamellar size depends on both the crystallization conditions and the macro-structure.

4.2.2 TGA Nanocomposites Results

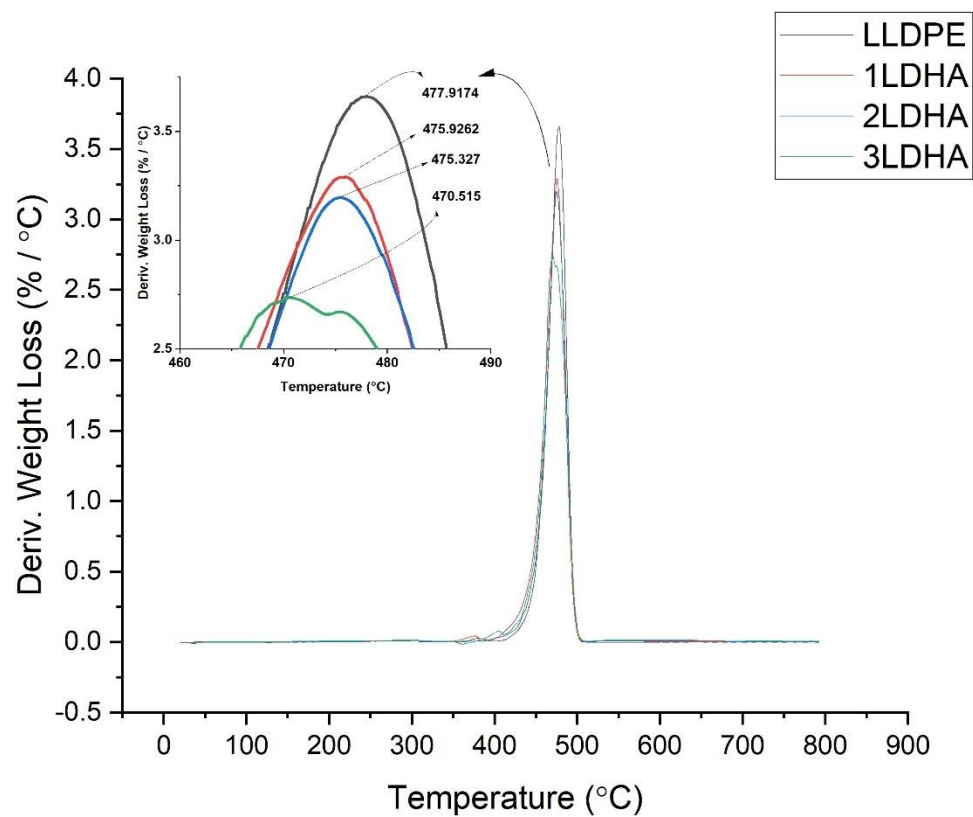


Figure 46: TGA curves of pure PE & LDHA nanocomposites

The thermal stability of LLDPE/LDHA nanocomposites slightly decreases with the increase of LDHA concentration as shown in figure 46. The peak of the graph is representing the degradation temperature at which the rate of degradation is maximum. The addition of LDHA shifted the degradation temperature towards lower values, which is an indication for the thermal stability decrement. When comparing the thermal stability at a weight loss of 50% for the three concentrations, 1LDHA showed 2.64^oC decrement, 2LDHA showed 2.23^oC decrement, and 3 LDHA recorded 4.07^oC decrease from the pure LLDPE as shown in table 14.

Table 14: TGA data for PE and LDHA nanocomposites

Material	Onset Temperature, ^o C	Max rate of decomposition, %/ ^o C	Temperature at 50% Weight Loss, degC	Residue, %	Residue, mg	Area under curve
LLDPE	452.00	3.59	475.07	0.85	0.05	98.80
1LDHA	447.96	3.28	472.43	2.00	0.11	98.48
2LDHA	448.33	3.17	472.84	2.81	0.17	97.44
3LDHA	446.83	2.78	471.00	2.12	0.12	97.87

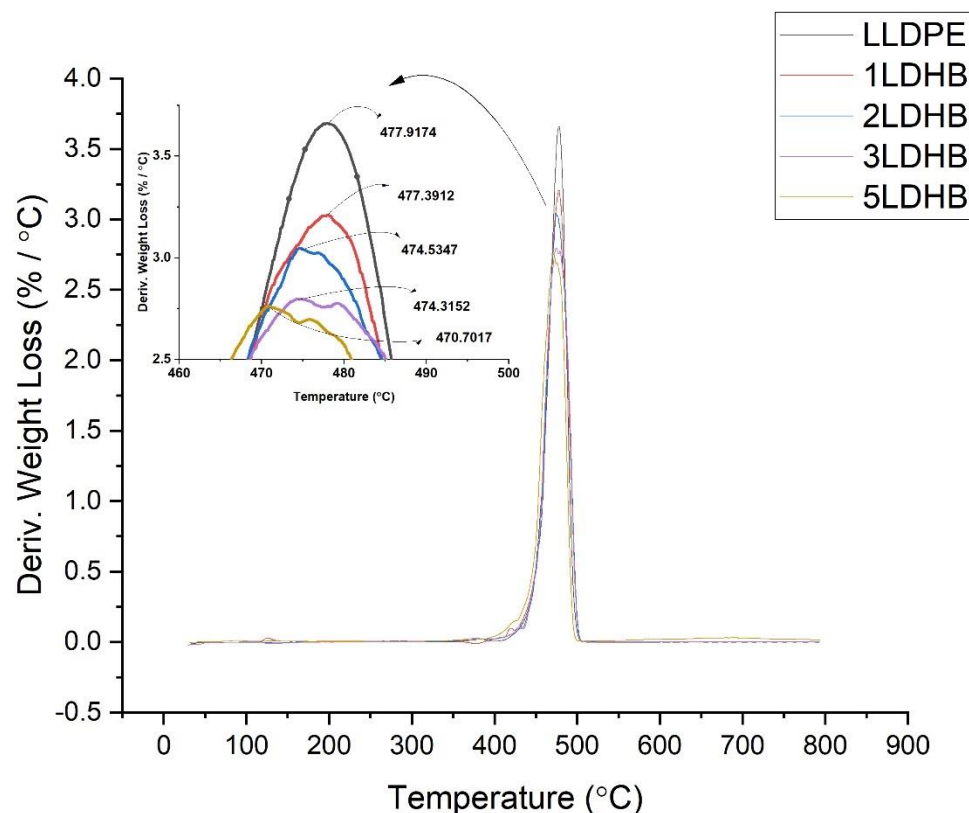


Figure 47: TGA curves of pure PE & LDHB nanocomposites

The thermal stability of LLDPE/LDHB nanocomposites slightly decreases with the increase of LDHB concentration as shown in figure 47. The peak of the graph is representing the degradation temperature at which the rate of degradation is maximum. The addition of LDHB shifted the degradation temperature towards lower values, which is an indication for the thermal stability enhancement. However, when comparing the thermal stability at a weight loss of 50% for the three concentrations, 1LDHB showed 0.4°C increment, 2LDHB showed 0.31°C increment, 3LDHB showed 0.19°C increment and 5LDHB recorded 4.04°C decrease from the pure LLDPE as shown in table 15.

Table 15: TGA data for PE and LDHB nanocomposites

Material	Onset Temperature, °C	Max rate of decomposition, %/°C	Temperature at 50% Weight Loss, degC	Residue, %	Residue, mg	Area under curve
LLDPE	452.00	3.59	475.07	0.85	0.05	98.80
1LDHB	450.96	3.23	475.47	1.78	0.26	98.35
2LDHB	450.40	3.09	475.38	2.15	0.36	98.72
3LDHB	449.66	2.86	475.26	3.67	0.57	97.35
5LDHB	449.10	2.79	471.03	1.53	0.23	95.88

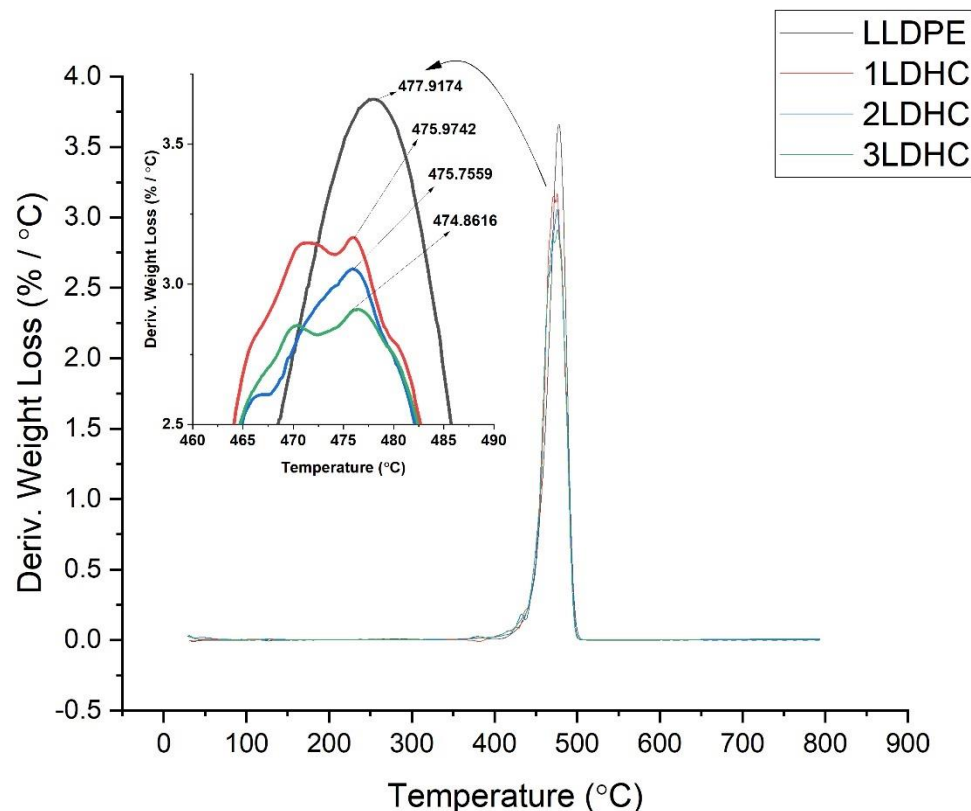


Figure 48: TGA curves of pure PE & LDHC nanocomposites

The thermal stability of LLDPE/LDHC nanocomposites slightly decreases with the increase of LDHC concentration as shown in figure 48. The peak of the graph is representing the degradation temperature at which the rate of degradation is maximum. The addition of LDHC shifted the degradation temperature towards lower values, which is an indication for the thermal stability decrement. When comparing the thermal stability at a weight loss of 50% for the three concentrations, 1LDHC showed 3.43^oC decrement, 2LDHC showed 3.24^oC decrement and 3LDHC recorded 4.09^oC decrease from the pure LLDPE as shown in table 16.

Table 16: TGA data for PE and LDHC nanocomposites

Material	Onset Temperature, °C	Max rate of decomposition, %/°C	Temperature at 50% Weight Loss, degC	Residue, %	Residue, mg	Area under curve
LLDPE	452.00	3.59	475.07	0.85	0.05	98.80
1LDHC	450.38	3.21	471.64	0.56	0.08	99.13
2LDHC	448.99	3.10	471.83	0.91	0.14	97.54
3LDHC	444.88	2.93	470.98	0.59	0.09	96.76

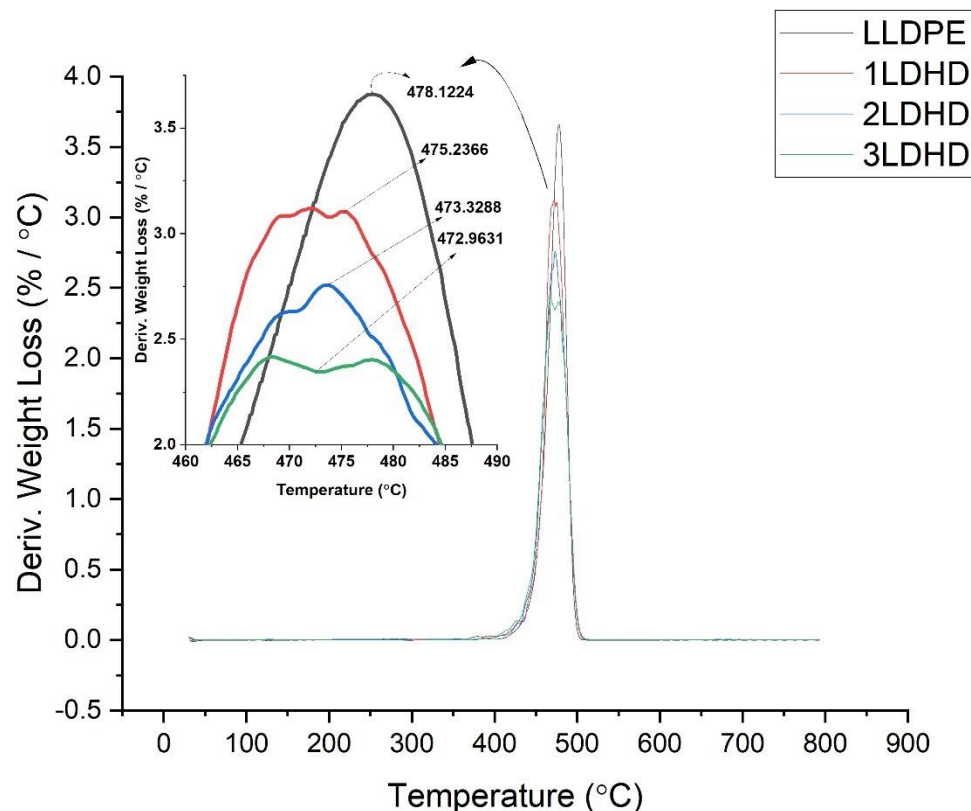


Figure 49: TGA curves of pure PE & LDHD nanocomposites

The thermal stability of LLDPE/LDHD nanocomposites slightly decreases with the increase of LDHD concentration as shown in figure 49. The peak of the graph is representing the degradation temperature at which the rate of degradation is maximum. The addition of LDHD shifted the degradation temperature towards lower values, which is an indication for the thermal stability decrement. When comparing the thermal stability at a weight loss of 50% for the three concentrations, 1LDHD showed 2.27^oC decrement, 2LDHD showed 3.115^oC decrement and 3LDHD recorded 3.11^oC decrease from the pure LLDPE as shown in table 17.

Table 17: TGA data for PE and LDHD nanocomposites

Material	Onset Temperature, °C	Max rate of decomposition, %/°C	Temperature at 50% Weight Loss, degC	Residue, %	Residue, mg	Area under curve
LLDPE	452.00	3.59	475.07	0.85	0.05	98.80
1LDHD	454.26	3.13	472.8050	1.22	0.18	98.19
2LDHD	445.67	2.75	471.9550	2.63	0.40	96.60
3LDHD	444.33	2.41	471.9600	4.08	0.45	94.85

The thermal stability is decreasing with LDHA, LDHC, and LDHD as indicated by the decomposition peak temperature in figures 46, 48 and 49. This decrement in thermal stability can be noticed when the comparison of the thermal stability at 50% weight loss is conducted for LDHA, LDHC, and LDHD as shown in tables 14, 16, and 17. This is possible for some cases when the material increases the thermal conductivity of LLDPE. Also, it could be from the used mixing method as mentioned by Mochane et al.⁸² when he reviewed the thermal stability of polymer/LDH nanocomposites. Such decrease or the usual increase in the thermal stability of polymers by the addition of LDHs were recorded in previous studies depending on the system of polymer/LDH nanocomposites.^{83,84}

4.2.3 XRD Nanocomposites Results

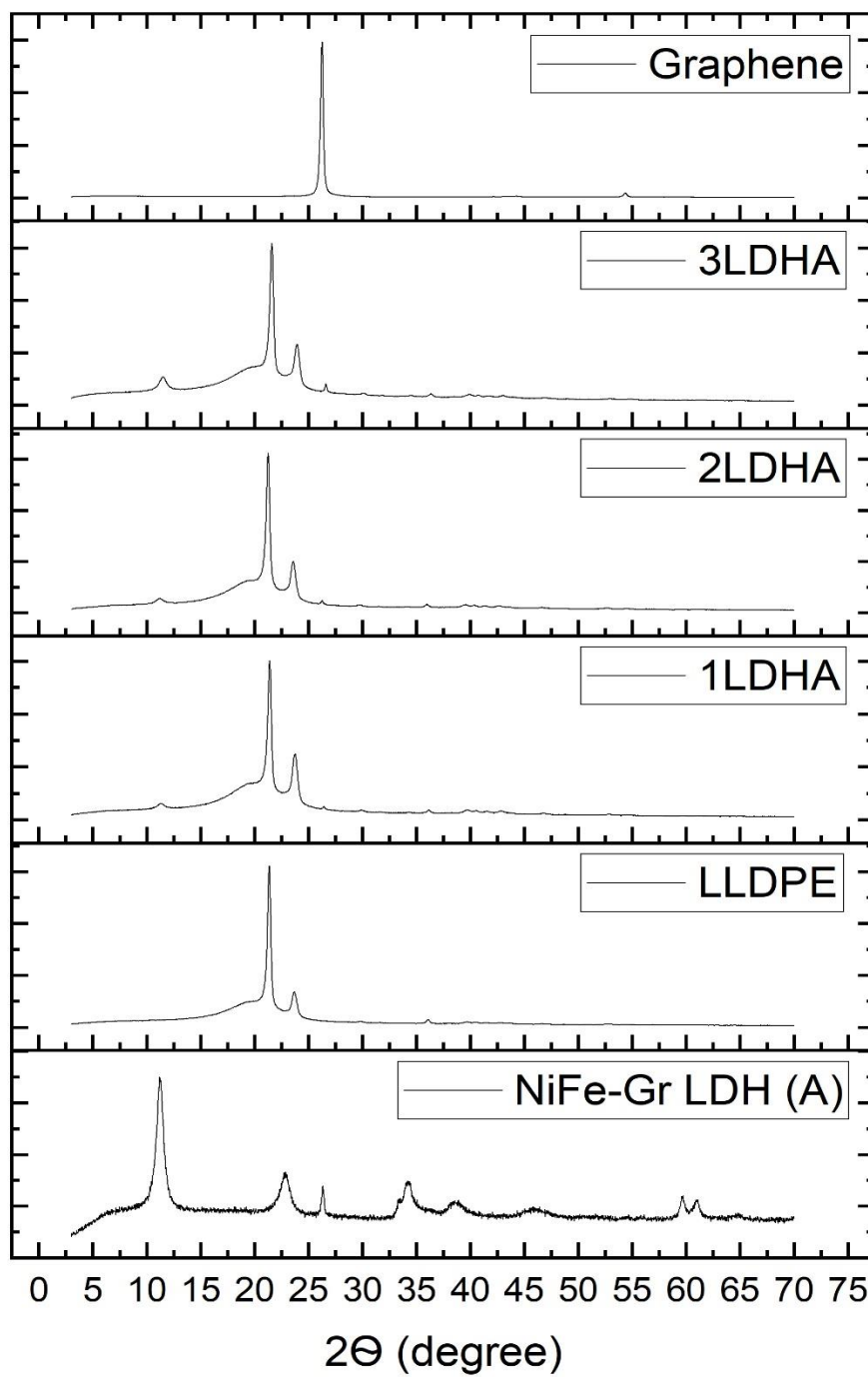


Figure 50: XRD pattern for Graphene, LLDPE, LDHA and the nanocomposites

Table 18: XRD patterns of LDHA and the nanocomposites: Effect of LLDPE addition on the (003) peak of LDHA

Material	2 Θ (degree)	d (Å)	FWHM (degree)
LDHA	11.238	7.867	0.790
1LDHA	11.312	7.816	0.780
2LDHA	11.214	7.884	0.865
3LDHA	11.480	7.702	0.914

Table 19: XRD patterns of LDHA and the nanocomposites: Effect of LDHA addition on the (004) peak of LLDPE

Material	2 Θ (degree)	d (Å)	FWHM (degree)
LLDPE	21.322	4.1638	0.356
1LDHA	21.392	4.1504	0.387
2LDHA	21.227	4.1822	0.382
3LDHA	21.580	4.1146	0.385

Pure LLDPE shows two peaks at 2 Θ around 21 $^{\circ}$ and 24 $^{\circ}$ while LDHA is showing a major peak at 2 Θ around 11 $^{\circ}$ as shown in figure 50. In this study the former two peaks which belong to LLDPE are designated as (004) and (005), respectively. The later peak which belongs to LDHA is known as (003) peak. LLDPE concentration effect in LDHA nanocomposites can be observed in (003) peak as shown in table 18. 1LDHA shifted the peak (003) toward the right, decreased the d spacing, and decreased the FWHM. 3LDHA has the highest peak (003) shift toward the right, decreased d spacing, increased d spacing. 2LDHA shifted peak (003) toward the left but increased both the d spacing and FWHM.

LDHA concentration effect in LLDPE nanocomposites can be observed in peak (004) as shown in table 19. Both 1LDHA and 3LDHA shifted peak (004) toward the right,

decreased the d spacing and increased FWHM. However, 3LDHA shifted peak (004) toward the left, increased both d spacing and FWHM. Based on Scherrer's equation the crystalline lamella decreases as the FWHM increases. It can be concluded from the obtained results that LDHA layered structure is retained in the nanocomposites. The decrement in d spacing could be from the collapse of the surfactant in LDHA galleries.

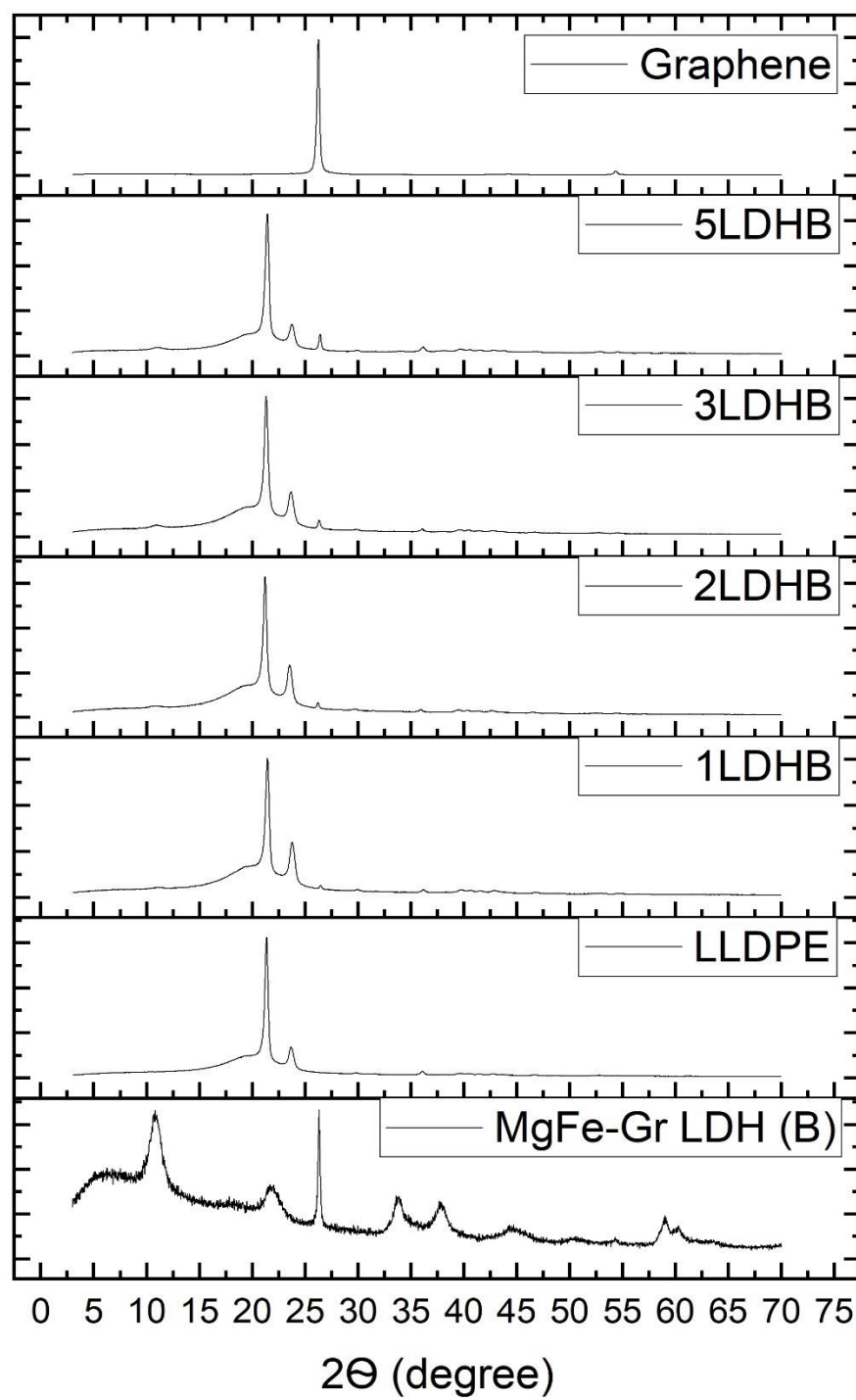


Figure 51: XRD pattern for Graphene, LLDPE, LDHB and the nanocomposites

Table 20: XRD patterns of LDHB and the nanocomposites: Effect of LLDPE addition on the (003) peak of LDHB

Material	2 Θ (degree)	d (Å)	FWHM (degree)
LDHB	10.825	8.167	1.336
1LDHB	11.01	8.03	1.26
2LDHB	10.82	8.17	4.08
3LDHB	10.88	8.129	1.18
5LDHB	10.99	8.044	1.21

Table 21: XRD patterns of LDHB and the nanocomposites: Effect of LDHB addition on the (004) peak of LLDPE

Material	2 Θ (degree)	d (Å)	FWHM (degree)
LLDPE	21.322	4.1638	0.356
1LDHB	21.433	4.1426	0.399
2LDHB	21.196	4.1884	0.389
3LDHB	21.285	4.1709	0.417
5LDHB	21.4245	4.1441	0.399

LLDPE shows two peaks at 2 Θ around 21 $^{\circ}$ and 24 $^{\circ}$ while LDHB is showing a major peak at 2 Θ around 11 $^{\circ}$ as shown in figure 51. The former two peaks which belong to LLDPE are designated as (004) and (005), respectively. The later peak which belongs to LDHB is designated as (003) peak. LLDPE concentration effect in LDHB nanocomposites can be observed in (003) peak as shown in table 20. 1LDHB shifted peak (003) toward the right, decreased d spacing, and decreased the FWHM. 2LDHB has the highest FWHM, shifted (003) peak slightly toward the left, and increased d spacing. Both 3LDHB and 5LDHB shifted peak (003) toward the right, decreased d spacing and decreased FWHM.

LDHB concentration effect in LLDPE nanocomposites can be observed in peak (004) as shown in table 21. Both 1LDHB and 5LDHB shifted peak (004) toward the right, decreased d spacing and increased FWHM. 2LDHB and 3LDHB shifted peak (004) toward the left, decreased d spacing and increased FWHM. Based on Scherrer's equation the crystalline lamella increases as the FWHM decreases. It can be concluded from the obtained results that LDHB layered structure is retained in the nanocomposites. The decrement in d spacing could be from the collapse of the surfactant in LDHB galleries.

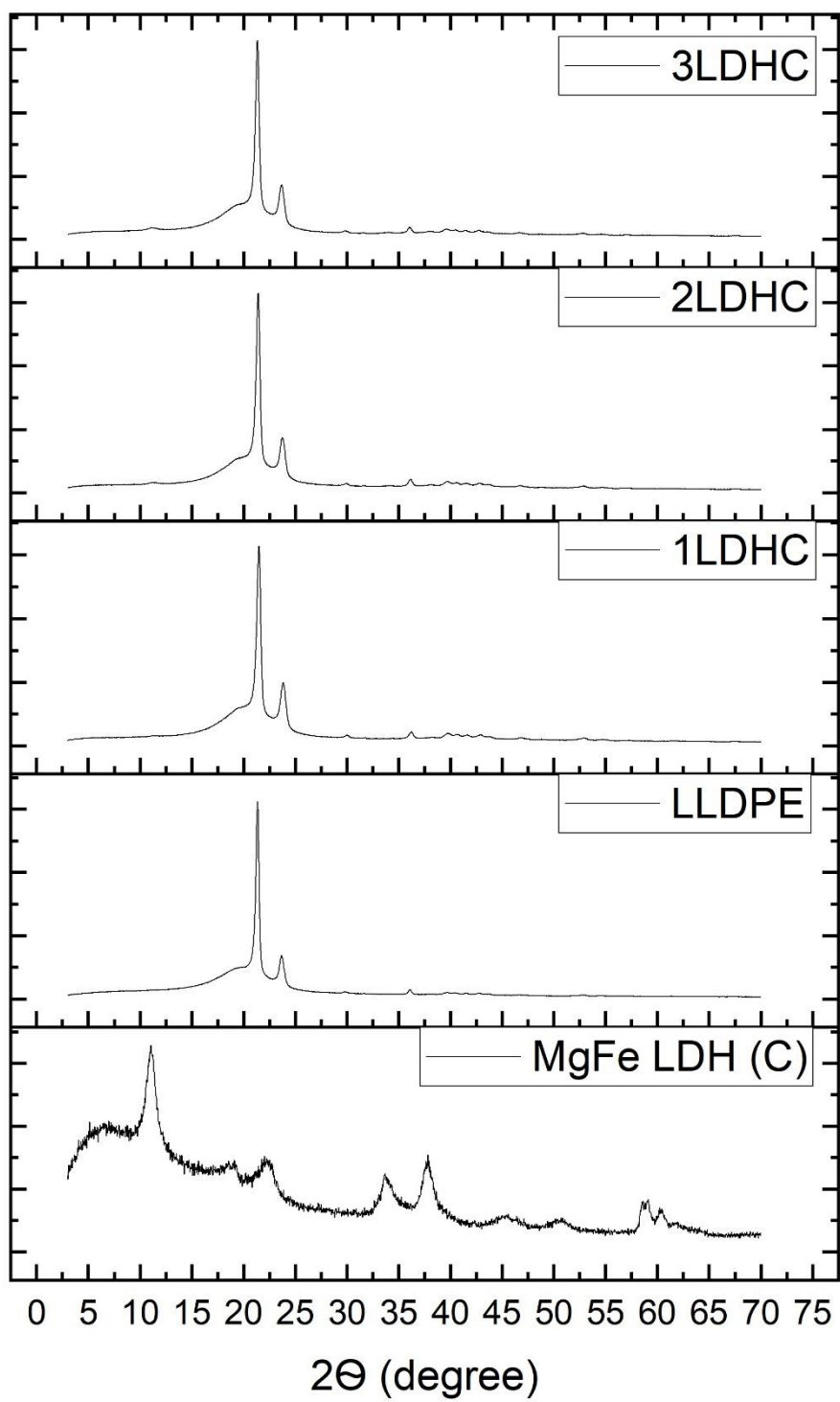


Figure 52: XRD pattern for LLDPE, LDHC and the nanocomposites

Table 22: XRD patterns of LDHC and the nanocomposites: Effect of LLDPE addition on the (003) peak of LDHC

Material	2 Θ (degree)	d (Å)	FWHM (degree)
LDHC	11.02	8.019	1.37
1LDHC	11.18	7.91	1.43
2LDHC	11.62	7.61	1.43
3LDHC	11.14	7.93	1.01

Table 23: XRD patterns of LDHC and the nanocomposites: Effect of LDHC addition on the (004) peak of LLDPE

Material	2 Θ (degree)	d (Å)	FWHM (degree)
LLDPE	21.322	4.1638	0.356
1LDHC	21.4828	4.1330	0.4409
2LDHC	21.401	4.1486	0.423
3LDHC	21.3334	4.1616	0.4103

LLDPE shows two major peaks at 2 Θ around 21 $^{\circ}$ and 24 $^{\circ}$ while LDHC is showing a major peak at 2 Θ around 11 $^{\circ}$ as shown in figure 52. The former two peaks which belong to LLDPE are designated as (004) and (005), respectively. The later peak which belongs to LDHC is designated as (003) peak. LLDPE concentration effect in LDHC nanocomposites can be observed in (003) peak as shown in table 22. 1LDHC shifted peak (003) toward the right, decreased d spacing, and increased the FWHM. 2LDHC increased FWHM, shifted (003) peak toward the right, and decreased d spacing. 3LDHC shifted peak (003) toward the right, decreased d spacing and decreased FWHM.

LDHC concentration effect in LLDPE nanocomposites can be observed in peak (004) as shown in table 23. All 1LDHC, 2LDHC and 3LDHC shifted peak (004) toward the right,

decreased d spacing and increased FWHM. Based on Scherrer's equation the crystalline lamella increases as the FWHM decreases. It can be concluded from the obtained results that LDHC layered structure is retained in the nanocomposites. The decrement in d spacing could be from the collapse of the surfactant in LDHC galleries.

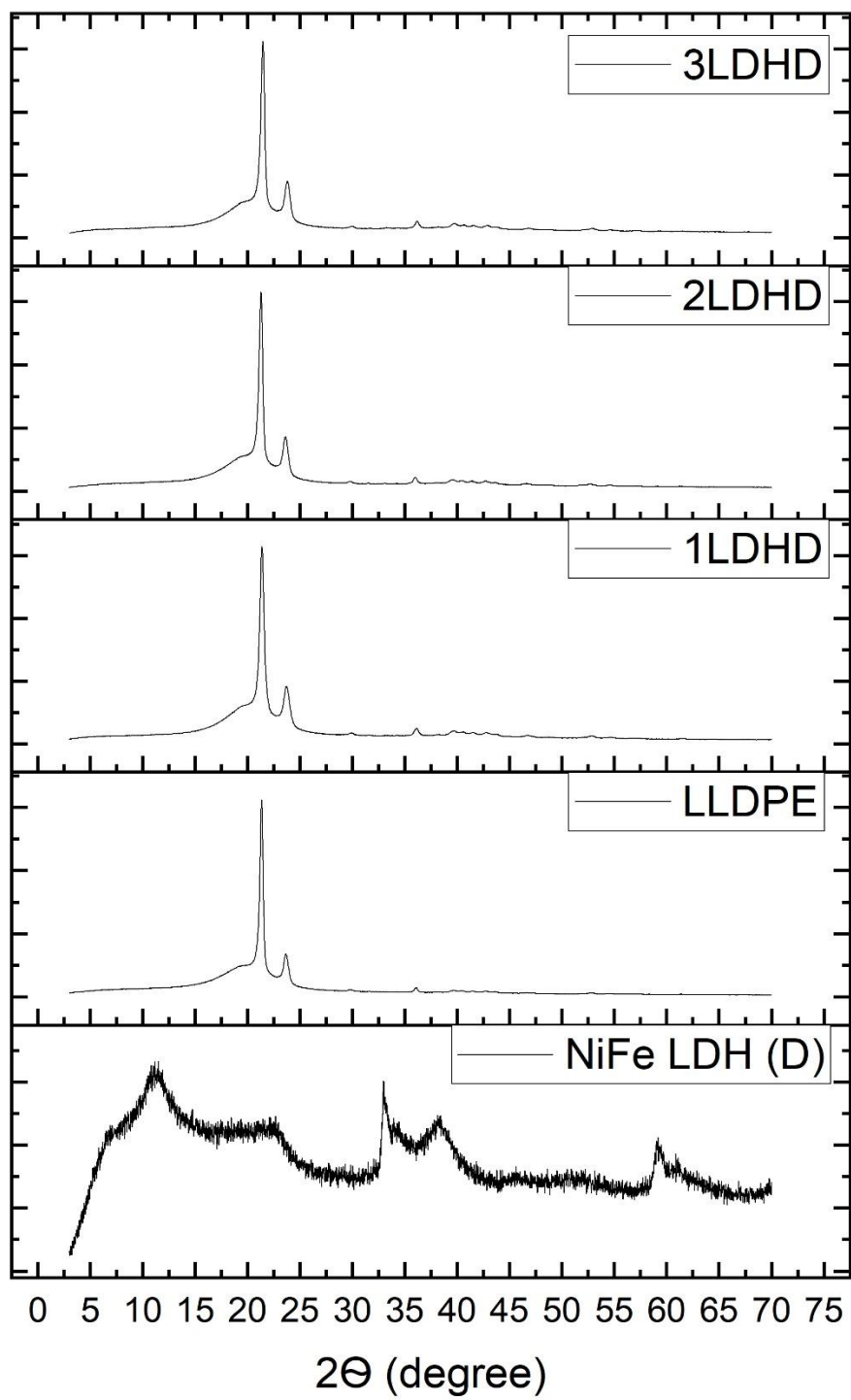


Figure 53: XRD pattern for LLDPE, LDHD and the nanocomposites

Table 24: XRD patterns of LDHD and the nanocomposites: Effect of LLDPE addition on the (003) peak of LDHD

Material	2 Θ (degree)	d (Å)	FWHM (degree)
LDHD	11.50	7.69	5.12
1LDHD	12.59	7.03	2.5
2LDHD	11.64	7.59	2.48
3LDHD	-	-	-

Table 25: XRD patterns of LDHD and the nanocomposites: Effect of LDHD addition on the (004) peak of LLDPE

Material	2 Θ (degree)	d (Å)	FWHM (degree)
LLDPE	21.322	4.1638	0.356
1LDHD	21.336	4.1553	0.470
2LDHD	21.2921	4.1696	0.3971
3LDHD	21.477	4.1342	0.416

LLDPE shows two major peaks at 2 Θ around 21 $^{\circ}$ and 24 $^{\circ}$ while LDHD is showing a major peak at 2 Θ around 11 $^{\circ}$ as shown in figure 53. The former two peaks which belong to LLDPE are designated as (004) and (005), respectively. The later peak which belongs to LDHD is designated as (003) peak. LLDPE concentration effect in LDHC nanocomposites can be observed in (003) peak as shown in table 24. 1LDHD shifted peak (003) toward the right, decreased d spacing, and decreased the FWHM. 2LDHD decreased FWHM, shifted (003) peak toward the right, and decreased d spacing. Peak (003) was not shown with 3LDHD due to the high dispersion in LLDPE.

LDHD concentration effect in LLDPE nanocomposites can be observed in peak (004) as shown in table 25. Both 1LDHD and 3LDHD shifted the peak (004) toward the right,

decreased d spacing and increased FWHM. 2LDHD shifted the peak (004) toward the left, increased d spacing and increased FWHM. According to Scherrer's equation as the crystalline lamella increases the FWHM decreases. It can be concluded from the obtained results that LDHD layered structure is retained in the nanocomposites. The decrement in d spacing could be from the collapse of the surfactant in LDHD galleries. In all LDHs results sometimes the absence of the diffraction peak is a good indication of the high dispersion which is clearly shown with LDHD.

4.2.4 SEM Nanocomposites Results

The distribution of LDHs platelets in the LLDPE matrix can be shown by the SEM images. Figures 54 – 69, shows SEM images of the fractured cross sections at different magnifications. When comparing pure LLDPE SEM figure 54 with that for nanocomposites SEM figures 55 – 69, multiple changes could be noticed. First, noticed that the agglomerate formation increases, as the concentration of the nano-clay (LDHs) increases. Second, it is observed that some of the particles are evenly distributed in LLDPE. Third, a clear image for the nano-tube formation can be seen in figure 65, knowing that nanotubes are present in all LDHs nanocomposites but this is the best image. Fourth, magnification size from 100 to 200 μm was not much useful compared with 1 – 50 μm . The later shows the fancy structure that caused by the LDHs as shown in figures 61 – 69 . Finally, the elastic fracture can be seen as well using the later magnification size. Thus, choosing the magnification size is important.

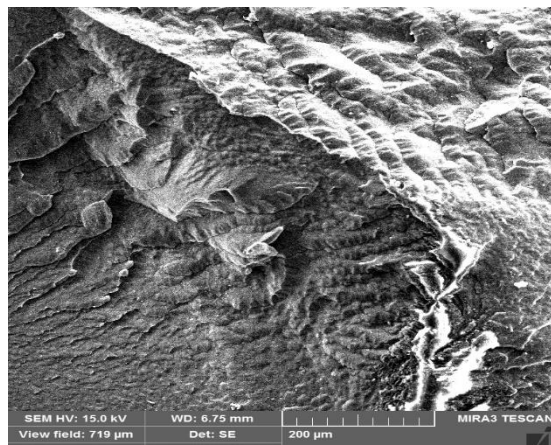
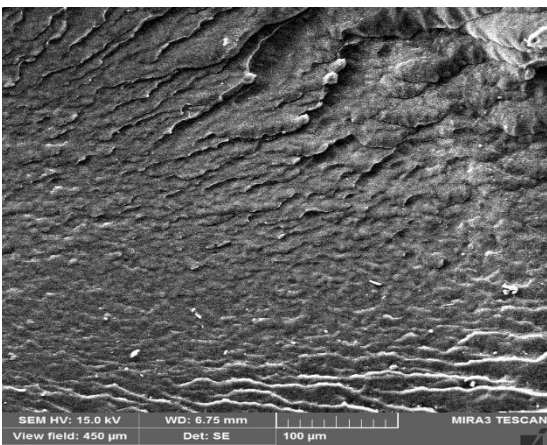
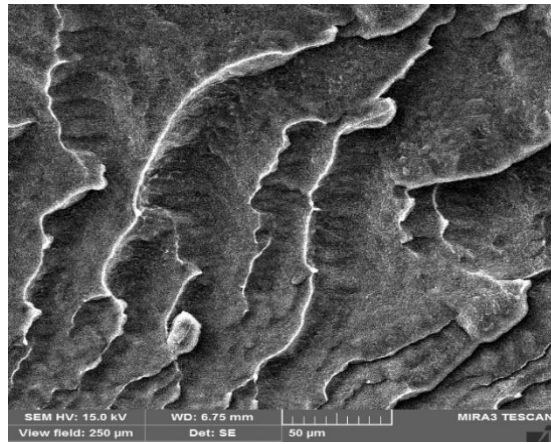
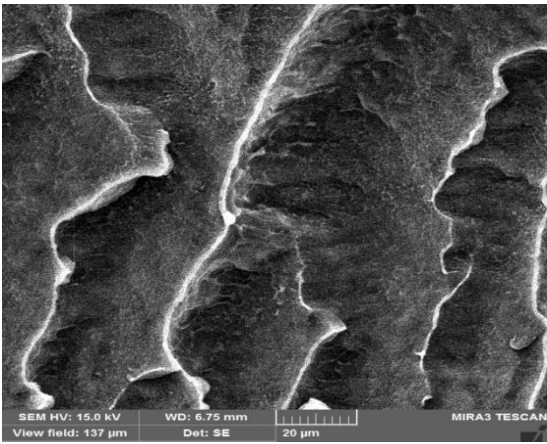


Figure 54: SEM – fractured cross section of LLDPE at different magnification (20 – 200 μm)

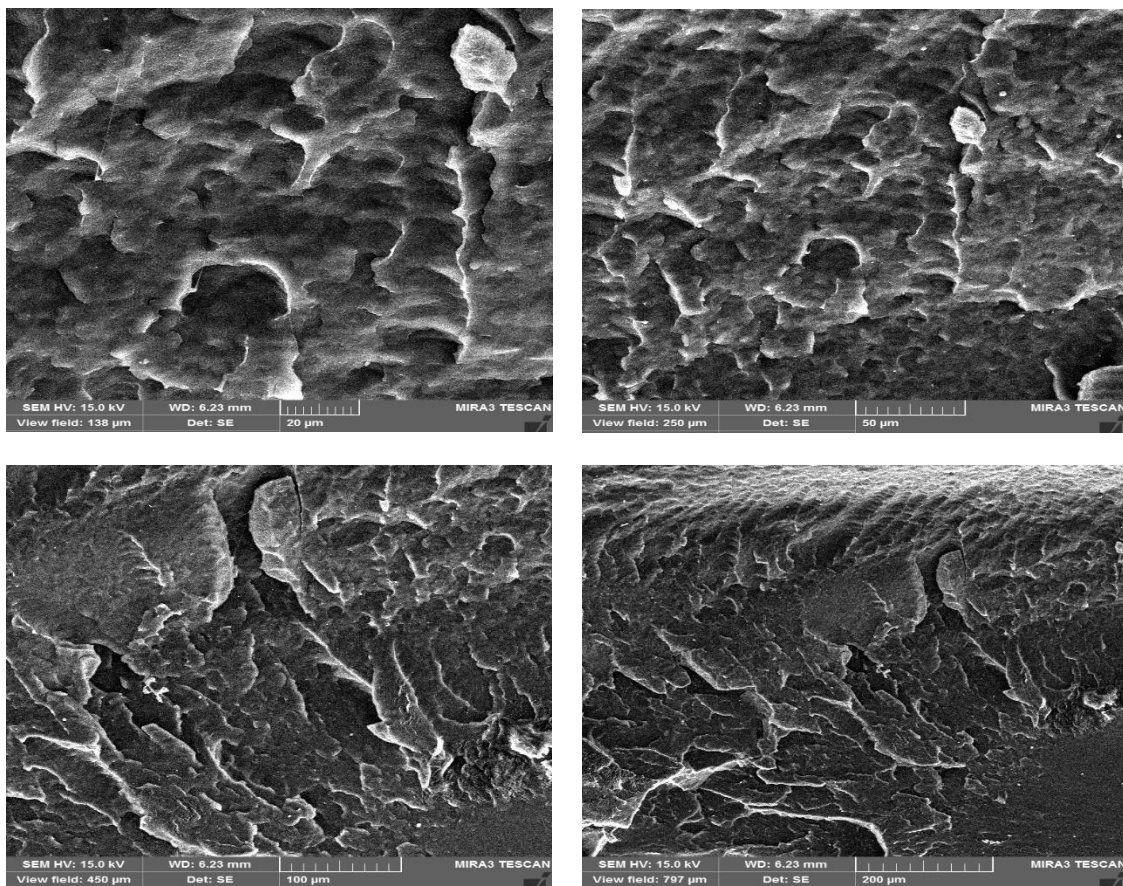


Figure 55: SEM – fractured cross section of 1LDHA nanocomposite at different magnification (20 – 200 μm)

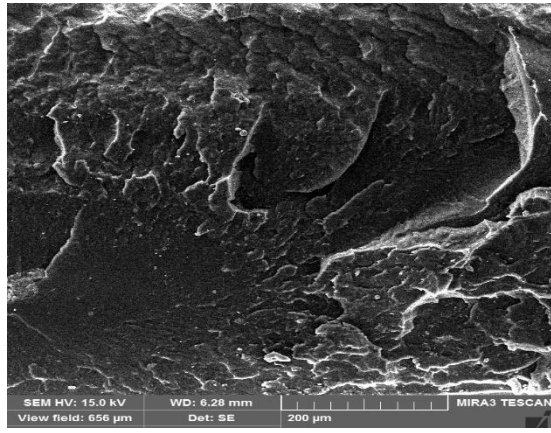
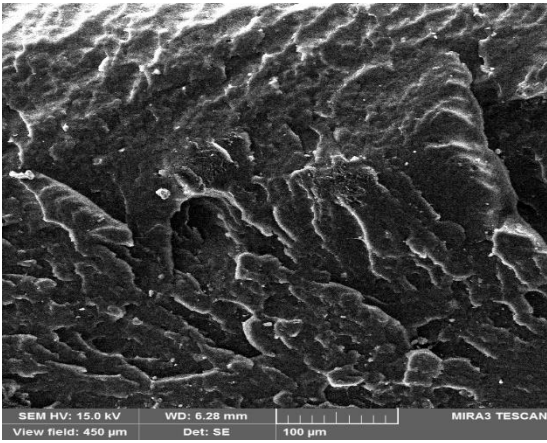
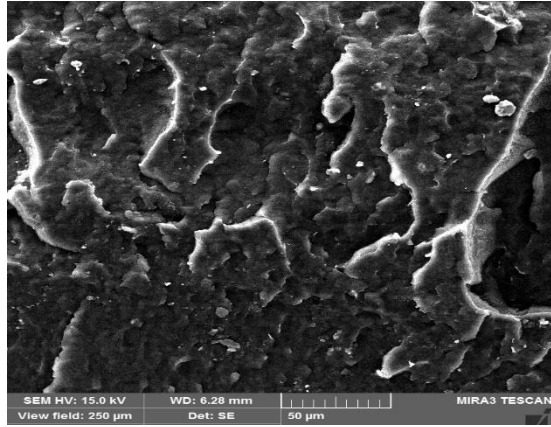
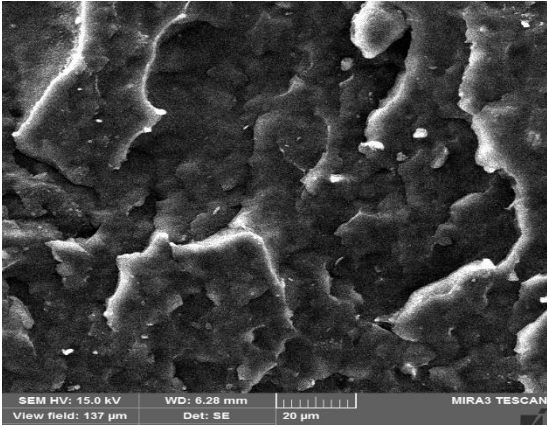


Figure 56: SEM – fractured cross section of 2LDHA nanocomposite at different magnification (20 – 200 μ m)

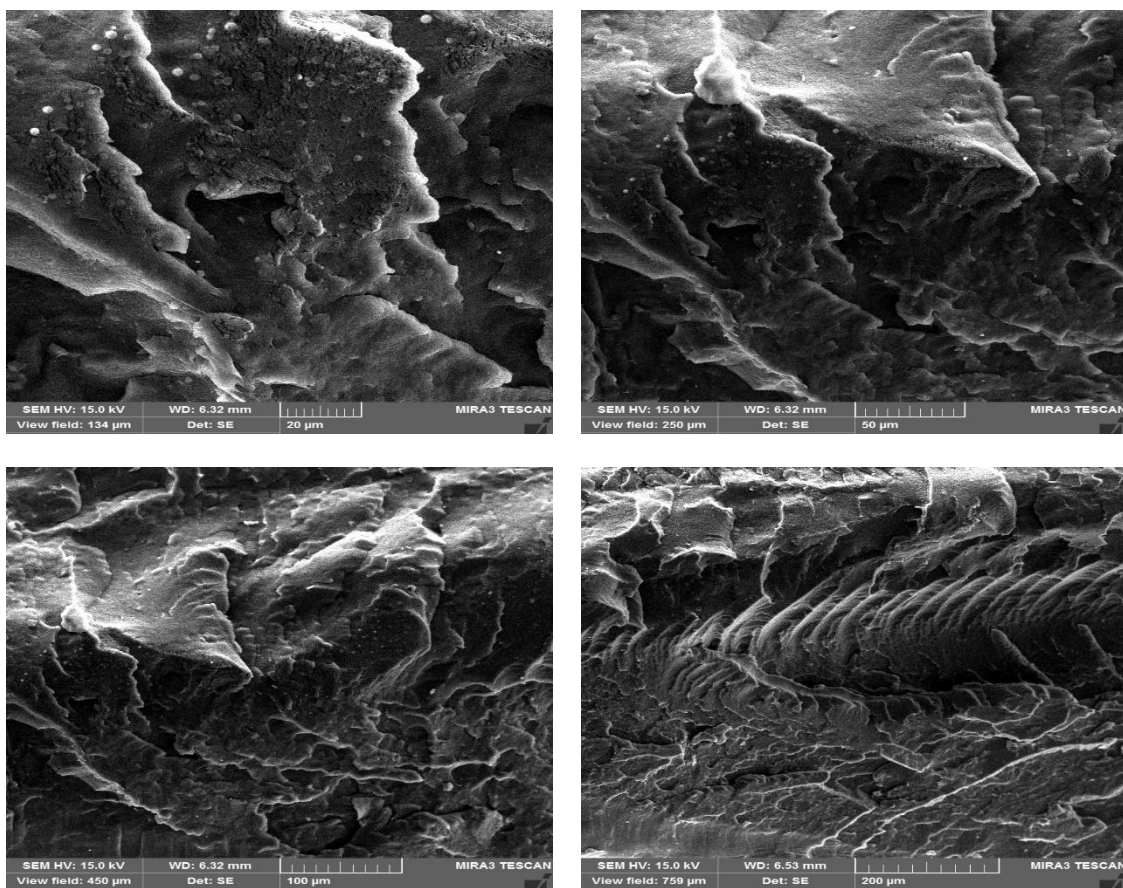


Figure 57: SEM – fractured cross section of 3LDHA nanocomposite at different magnification (20 – 200 μm)

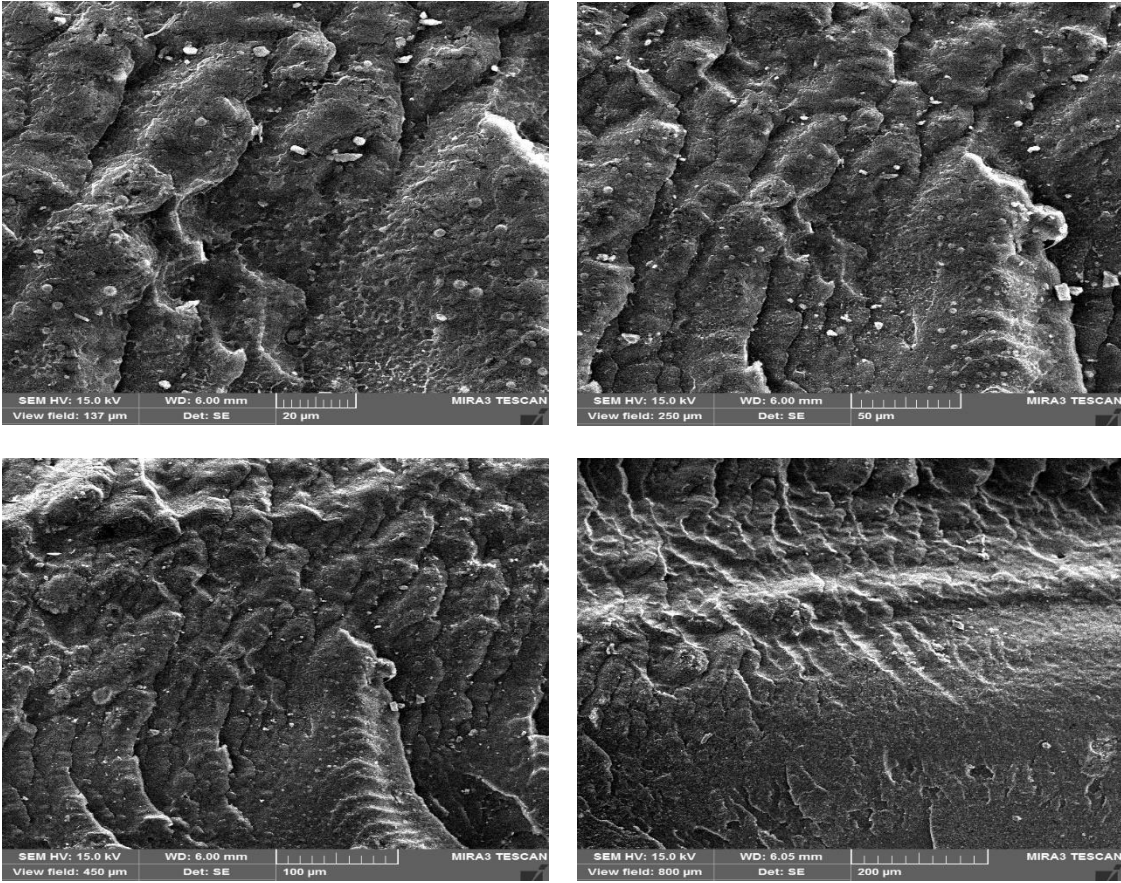


Figure 58: SEM – fractured cross section of 1LDHB nanocomposite at different magnification (20 – 200 μm)

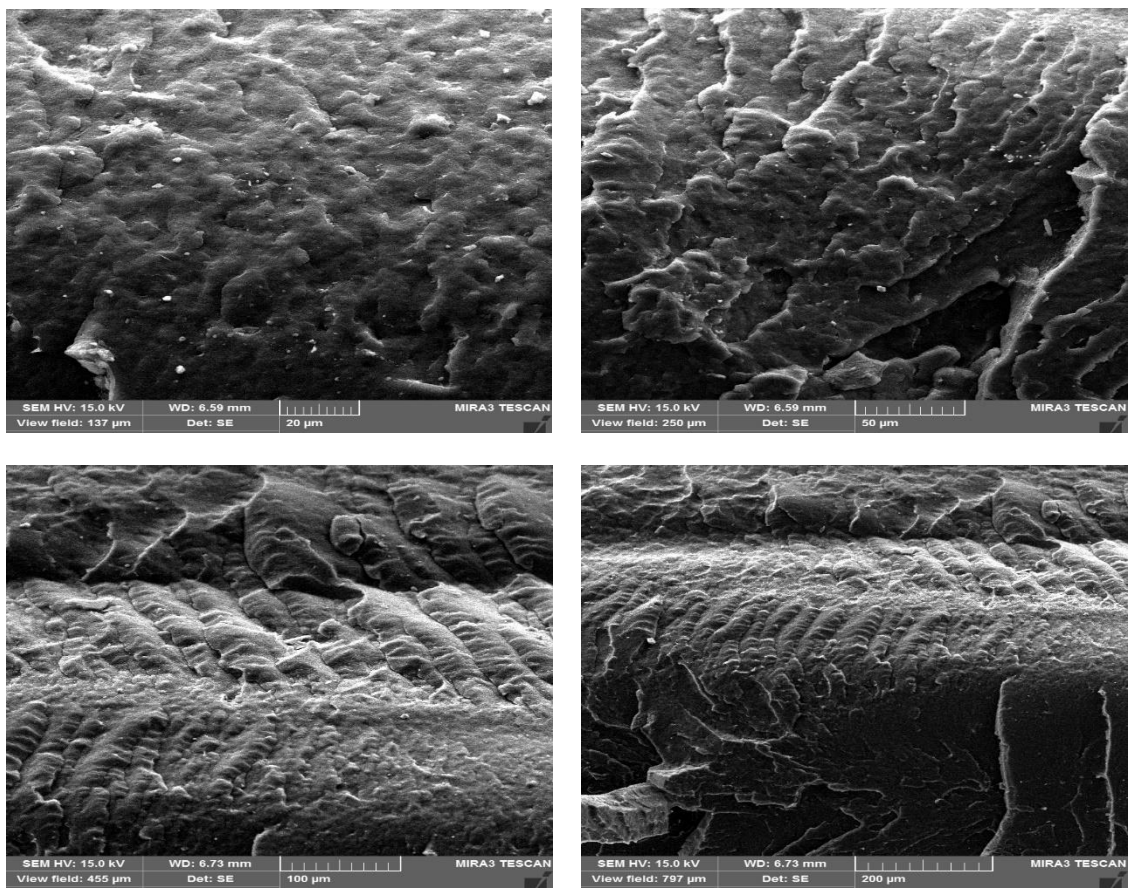


Figure 59: SEM – fractured cross section of 2LDHB nanocomposite at different magnification (20 – 200 μm)

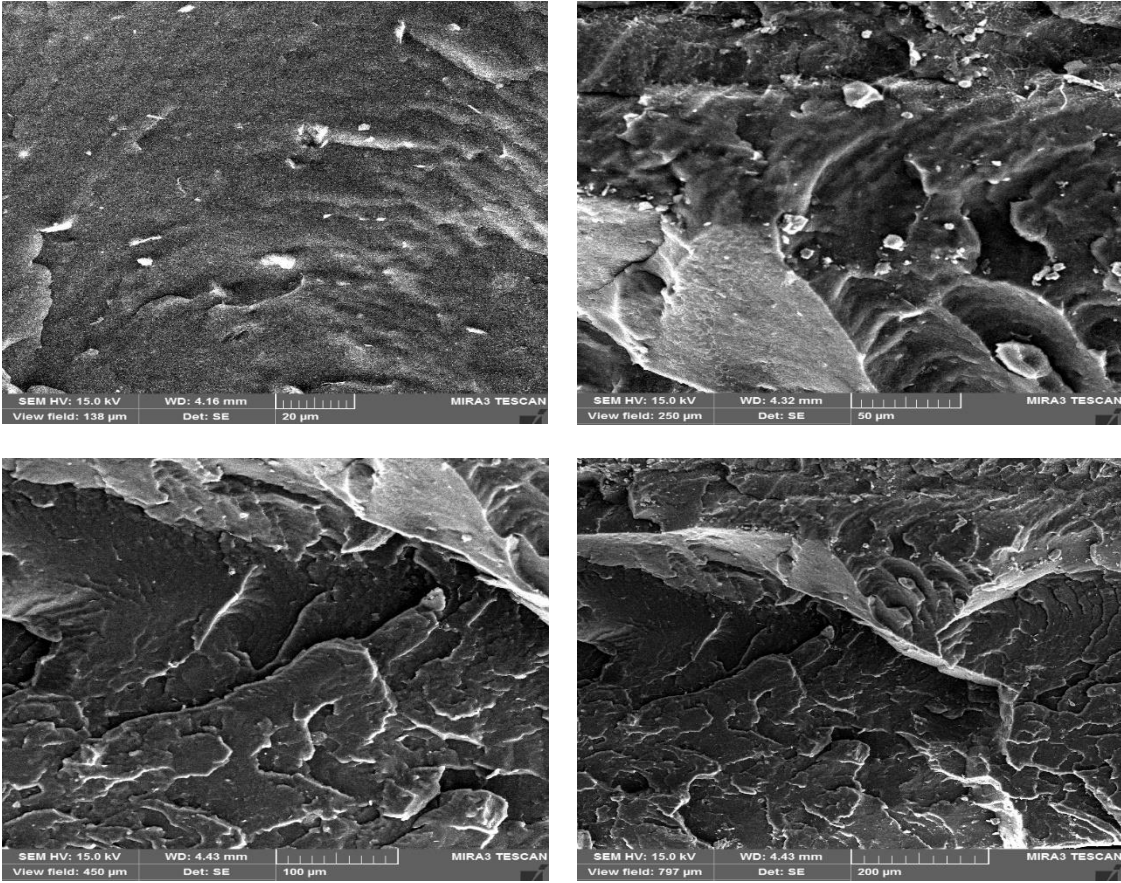


Figure 60: SEM – fractured cross section of 3LDHB nanocomposite at different magnification (20 – 200 μm)

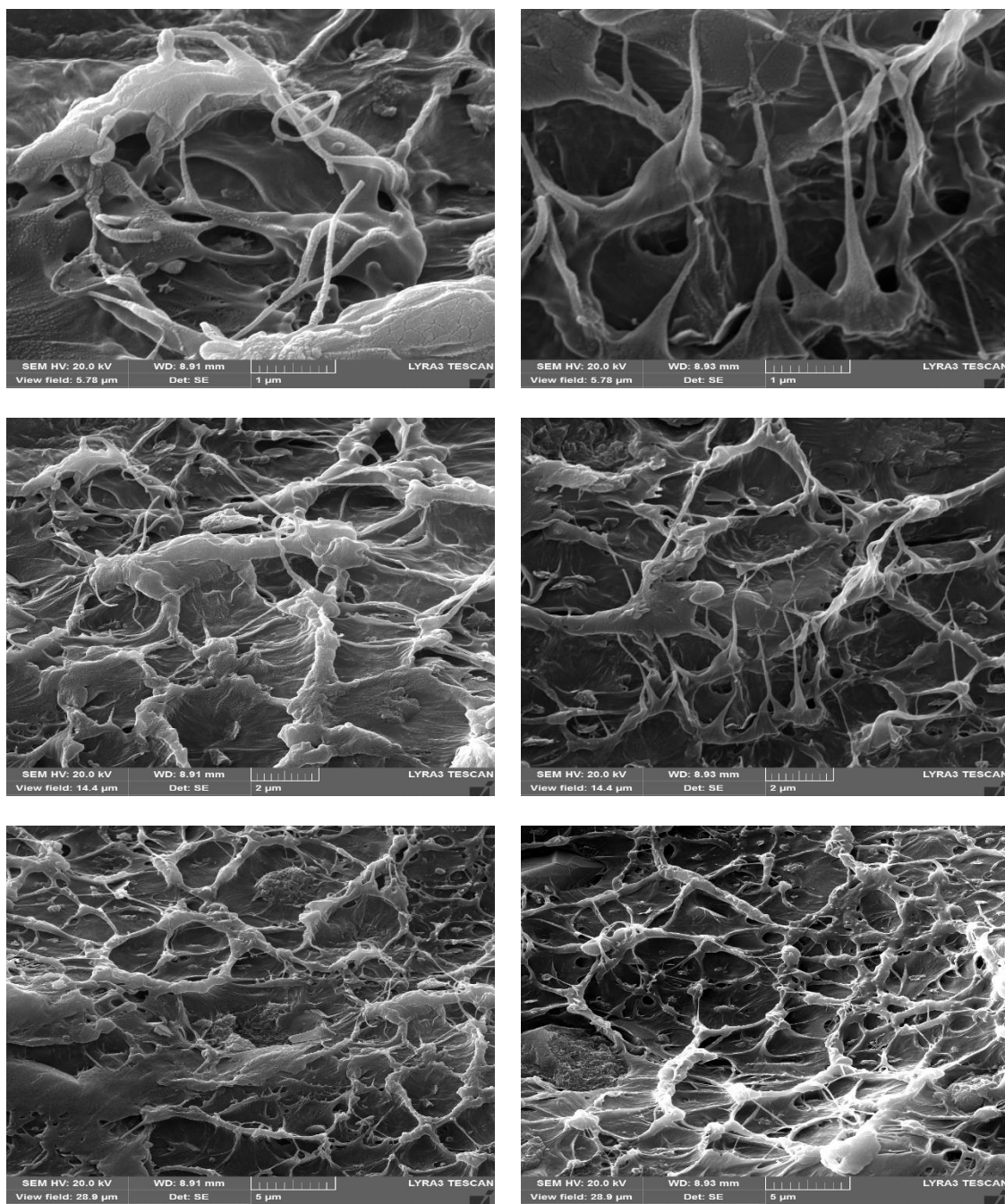


Figure 61: SEM – fractured cross section of 5LDHB nanocomposite at different magnification (1 – 5 μm)

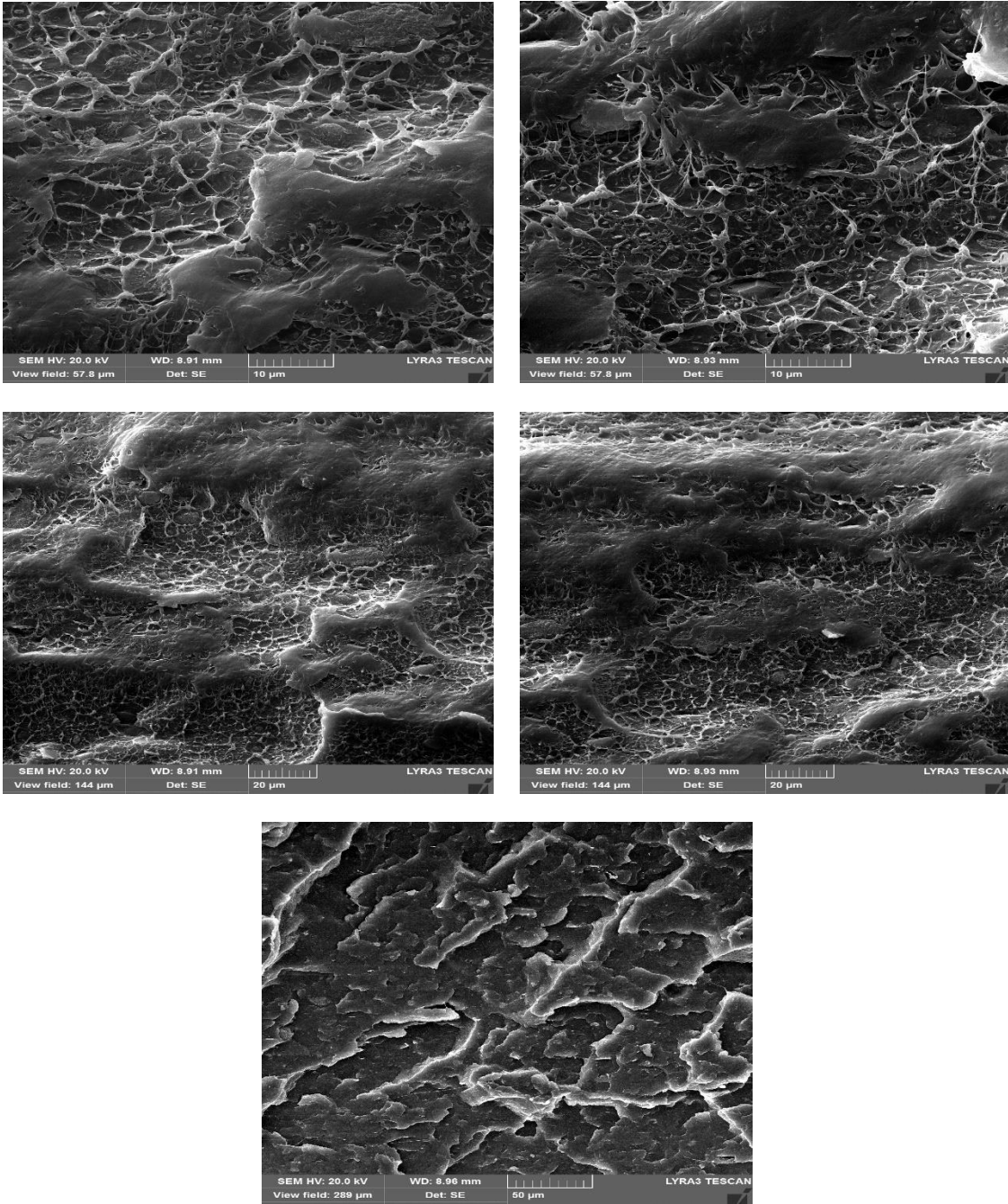


Figure 62: SEM – fractured cross section of 5LDHB nanocomposite at different magnification (10 – 50 μm)

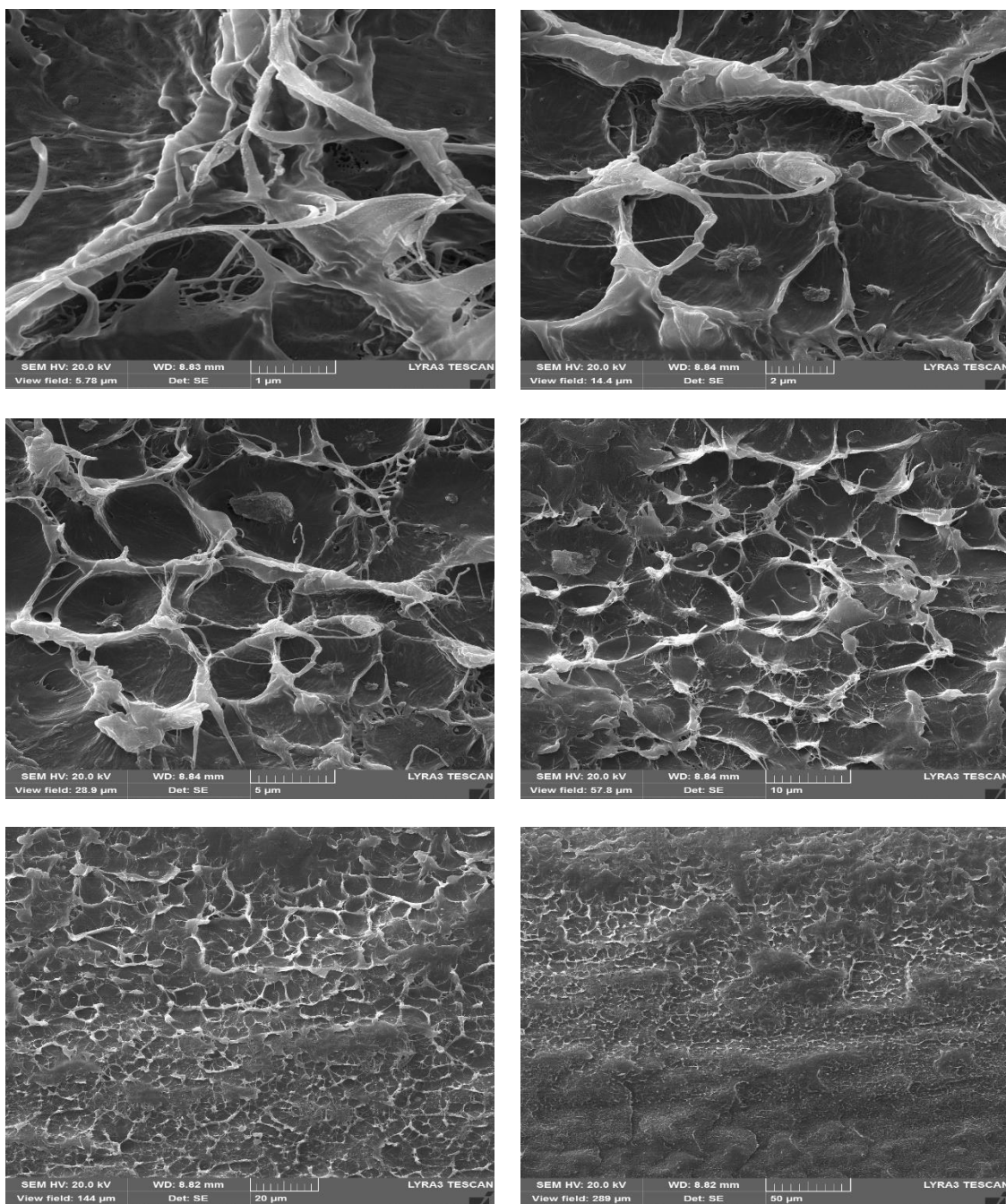


Figure 63: SEM – fractured cross section of 1LDHC nanocomposite at different magnification (1 – 50 μm)

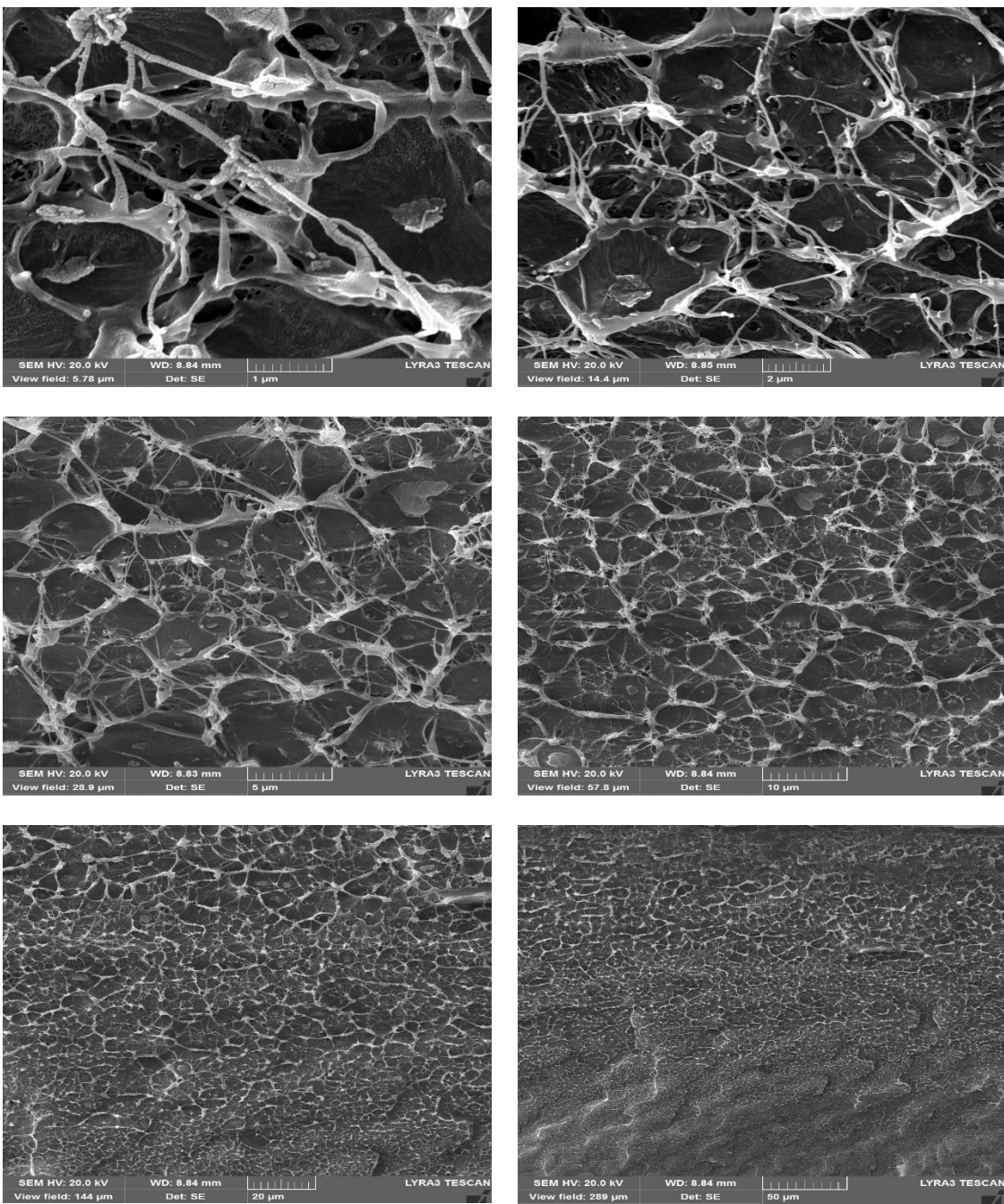


Figure 64: SEM – fractured cross section of 2LDHC nanocomposite at different magnification (1 – 50 μm)

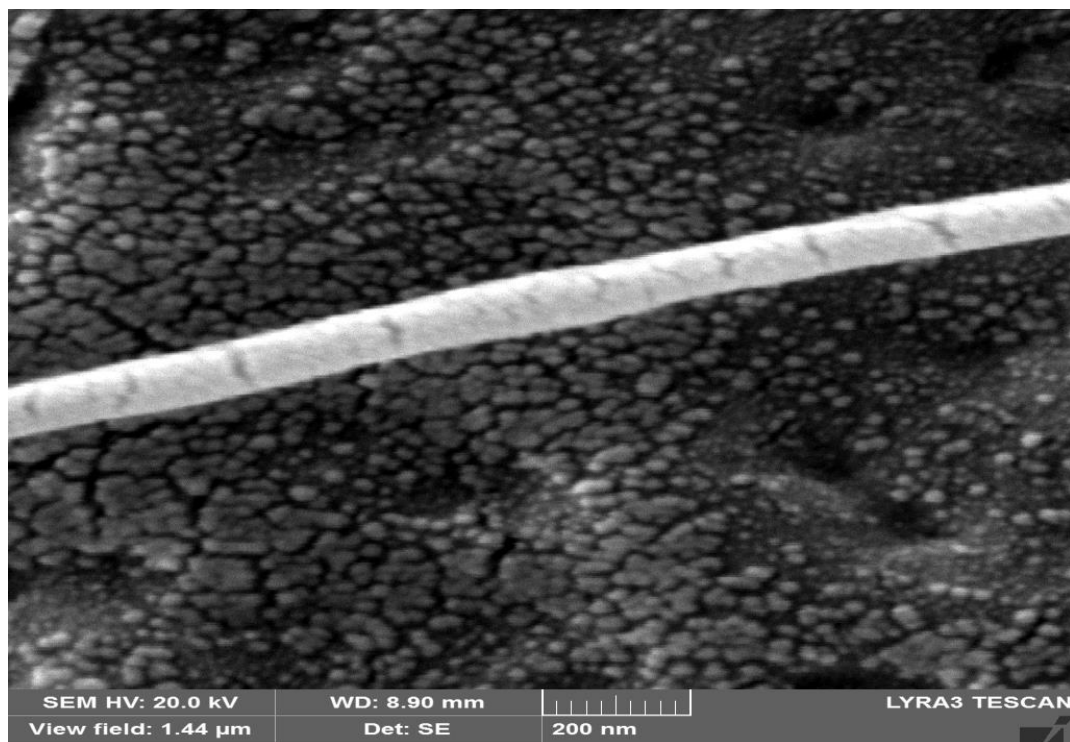


Figure 65: SEM – fractured cross section of 2LDHC nanocomposite at 200 nm magnification

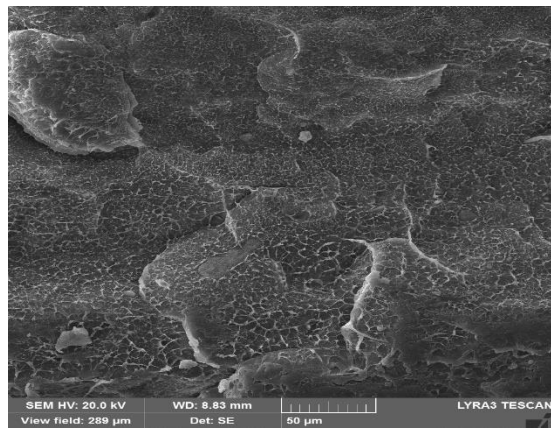
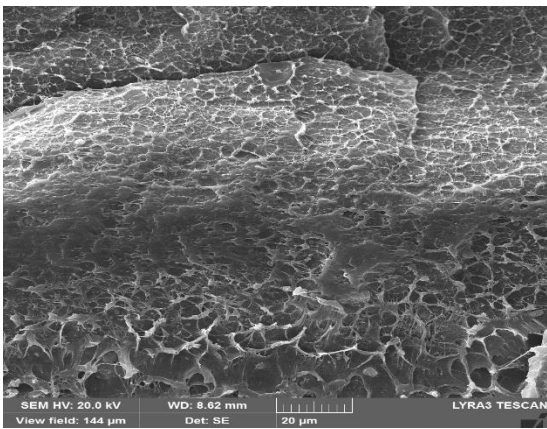
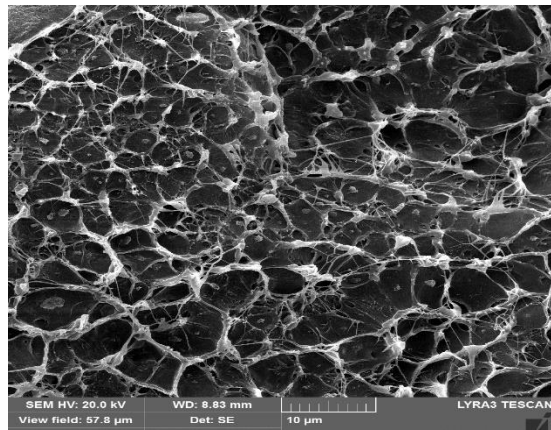
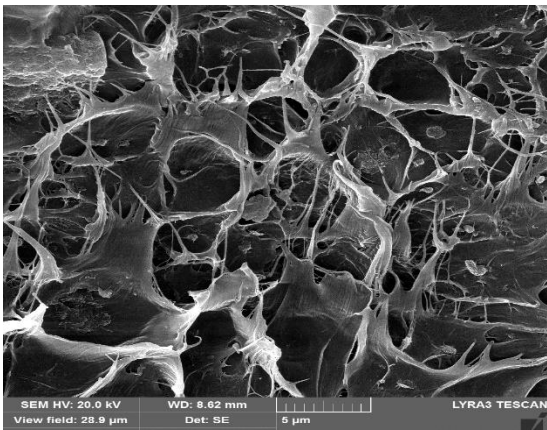
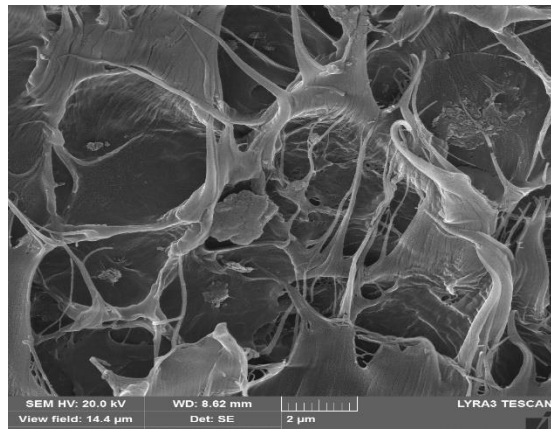
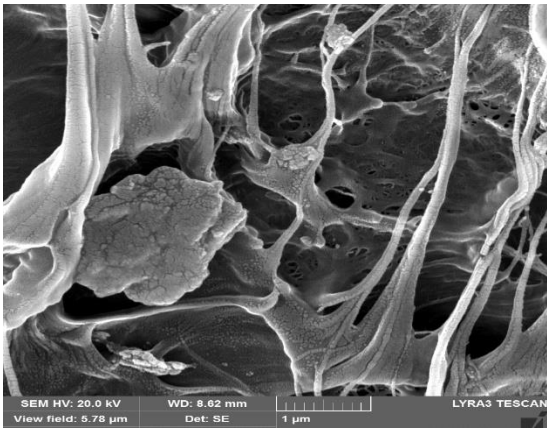


Figure 66: SEM – fractured cross section of 3LDHC nanocomposite at different magnification (1 – 50 μm)

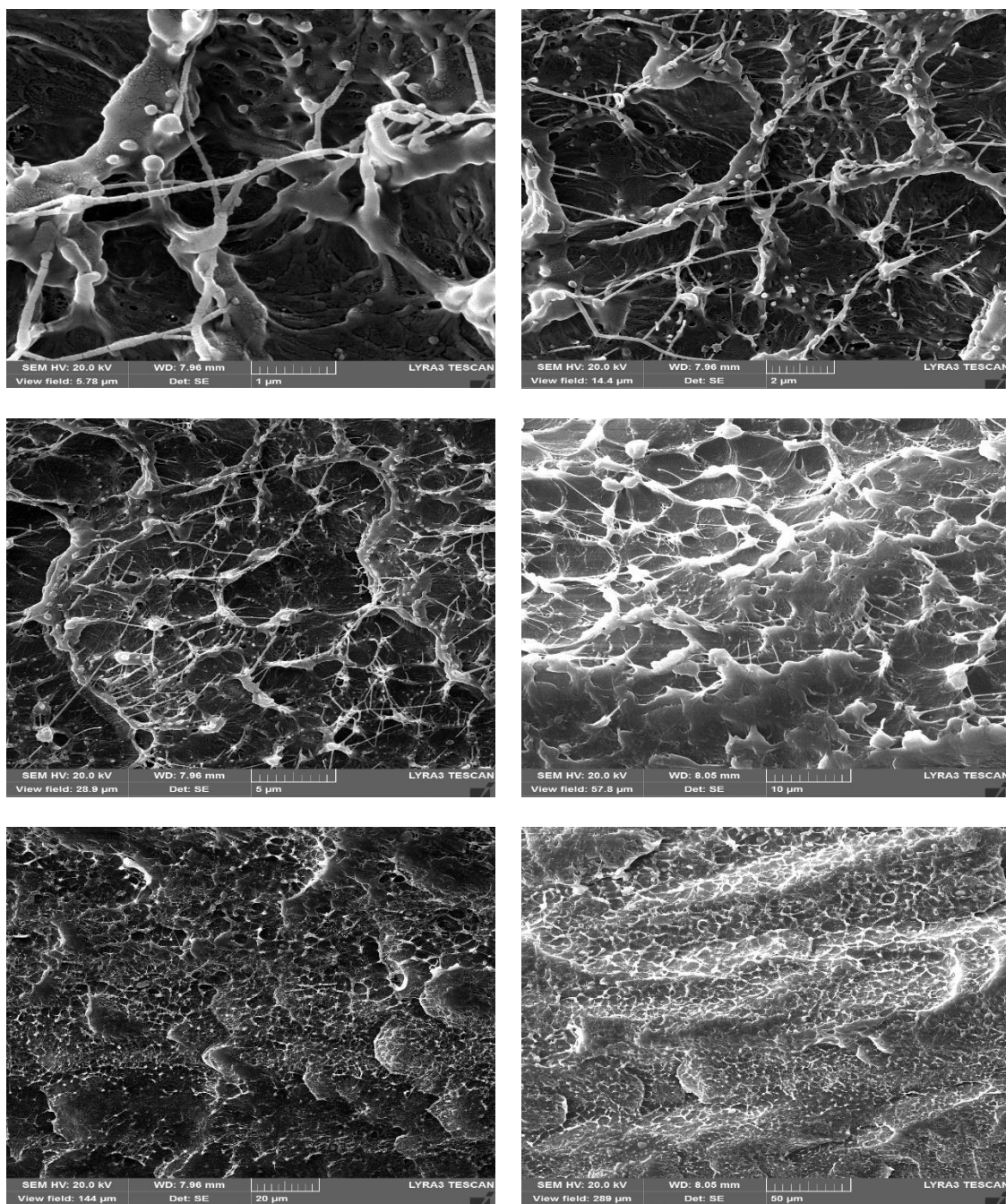


Figure 67: SEM – fractured cross section of 1LDHD nanocomposite at different magnification (1 – 50 μm)

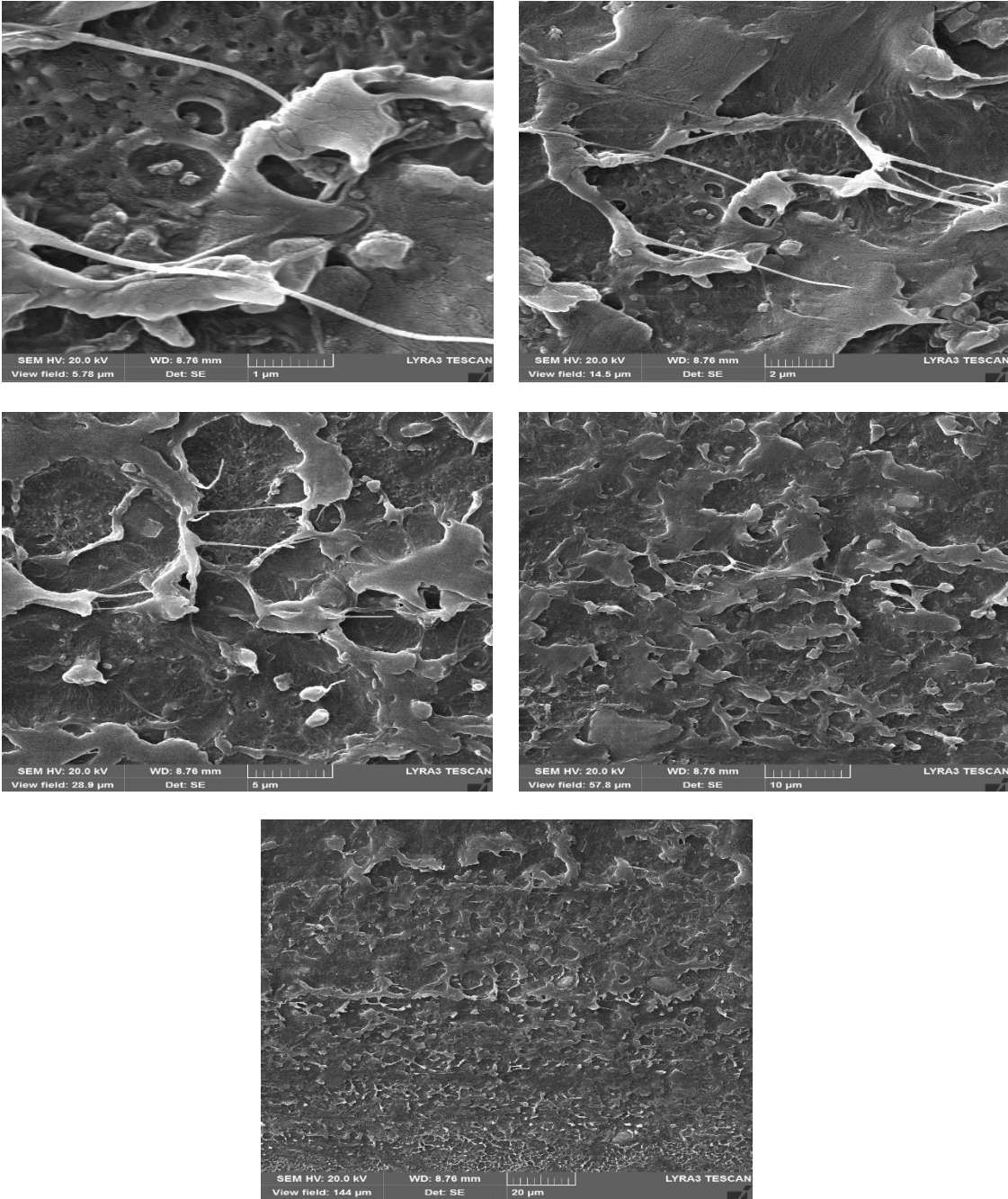


Figure 68: SEM – fractured cross section of 2LDHD nanocomposite at different magnification (1 – 20 μm)

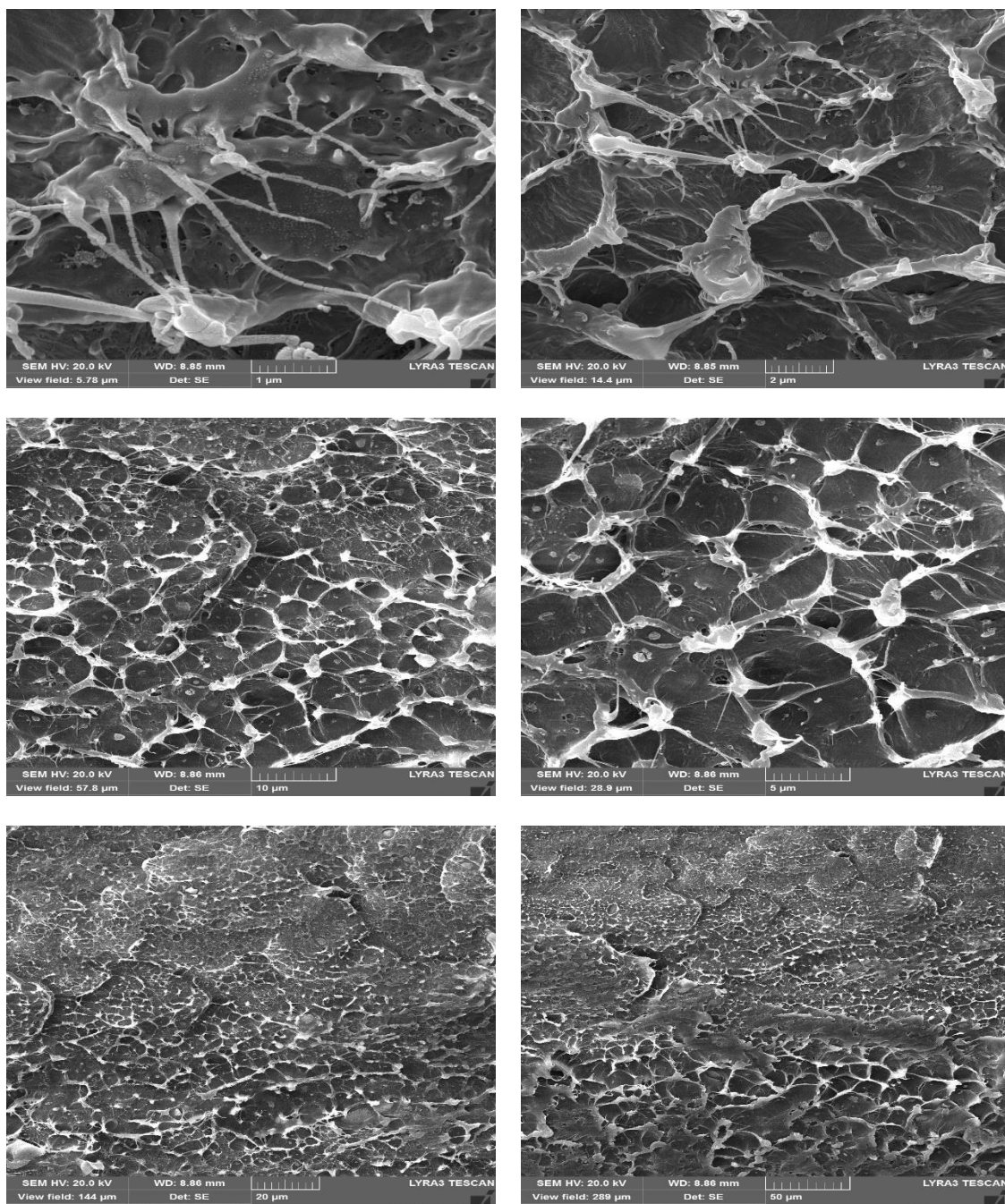


Figure 69: SEM – fractured cross section of 3LDHD nanocomposite at different magnification (1 – 50 μm)

CONCLUSION

LLDPE and LDHs (NiFe-Gr, MgFe-Gr, MgFe, and NiFe) nanocomposites were prepared. The thermal stability and the dispersion of LDHs in LLDPE were investigated and compared. Optical microscopy was used to study the dispersion. Specifically, X-ray diffraction and scanning electron microscopy were used for the dispersion study. Differential scanning calorimetry was used to study crystalline and melting behavior while thermogravimetric analysis was used to study the thermal stability. The dispersion of LDHs in LLDPE was not uniform and the agglomerates formation was observed. DSC results indicate a minor increment in the maximum melting and minimum crystalline temperatures which is noticed by the slight shift toward the right. Results obtained by TGA indicate a decrease in thermal stability for LDHA, LDHC, and LDHD nanocomposites. However, it shows an increase in thermal stability with LDHB.

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