STUDIES ON MELT RHEOLOGICAL CHARACTERISTICS OF LINEAR POLYOLEFINS USING UHMW-PE AS AN ADDITIVE

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT FOR THE AWARD OF DEGREE

of

B.Sc (HONS)

in

POLYMER SCIENCE

by

SHAMEEK VATS

UNDER SUPERVISION OF

Dr. Saroj Shukla   Dr. Uma Sankar Sathpathy

Associate Professor   General Manager

Bhaskaracharya College of Applied Sciences   RTG-VMD, RIL

BHASKARACHARYA COLLEGE OF APPLIED SCIENCES

JUNE-JULY 2012

ACKNOWLEDGEMENTS

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SYNOPSIS OF THE WORK

Although the polyolefins (PP/HDPE) of commerce has many desirable and beneficial properties, it is deficient in melt strength or stain hardening which basically implies an increase in resistance to stretching during elongation of the molten material. Thus it has a variety of melt processing shortcomings, including the onset of edge weave during high speed extrusion coating of paper or other substrates, sheet sag and local thinning in melt thermoforming, and flow instabilities in co extrusion of laminate structures. As a result its use has been limited in such potential applications as, for example, extrusion coating, blow moulding, profile extrusion, and thermoforming. It is expected that improving the melt strength behaviour of Polyolefins (PP/HDPE) will substantially contribute to the growth of this polymer in the plastic market.

On the other hand, Ultra High Weight Poly Ethylene (UHMWPE) is a subset of thermoplastic of polyethylene. It has a very high molecular weight. UHMWPE has the highest impact strength of any thermoplastic presently made. Besides, UHMWPE is known to be a linear grade polyethylene, as is high-density polyethylene (HDPE), but it possesses a weight average molecular mass (Mw) of at least 7.5×10^5 g/mol (according to ASTM D4020). Preferably the UHMWPE has a weight average molecular mass of at least 3×10^6 g/mol.

Because of the intrinsic properties related to high values of molecular mass, UHMWPE is widely used in several applications which include high abrasion resistance, high-modulus and high-strength tapes and fibers, biaxial films. However, it's extremely **high melt viscosity** severely affects its process-ability while processing it through conventional techniques, such as screw extrusion or injection molding. Problems that are commonly encountered in processing UHMWPEs include die blockage, melt fracture, wall slippage, and a small processing temperature window.

Processing UHMWPE, therefore, requires a proper combination of temperature, pressure, and sufficient time to achieve complete plasticization. Inadequate control of the process can lead to fusion defects stemming from the memory of the powder morphology. Currently, UHMWPE resin is consolidated mainly by compression molding or rams extrusion .Compression molding progresses slowly and involves costly equipment, whereas ram extrusion is relatively cheap. However, some unconsolidated regions in the center of the material may occur. Considerable efforts have been devoted to developing better methods for UHMWPE processing. In addition, relevant literature

was carefully screened & compiled in this report which is quite useful for this current study.

Therefore, we find a scope to modify polyolefin matrix (PP / HDPE) USING uhmwpe as an additive where dispersion & melt compatibility of this material into polyolefin matrix (here it is HDPE) has been improved using a suitable lubricant polyethylene glycol (PEG) with an option of with or without decaline as an plasticizer. The concept has a drive to modify either HDPE or PP to a high melt strength product simply using UHMWPE as an additive in presence of effective lubricant/plasticizer under optimum extrusion conditions.

Some of the salient findings were summarized here.

- UHMWPE can be a potential additive for making niche grade polyolefin (HDPE /PP) products which has been successfully demonstrated in current study.
- Conceptually open up outlets for oriented products via melt processing
- Observed significant reduction in MFI (>10 folds) after modification of HDPE & consequently melt viscosity enhanced significantly (>10 folds)
- Melt Rheological properties namely, melt viscosity, G' & G", Tan delta etc. after modification distinctly differentiates from plain HDPE.
- Broadening in MWD was quite distinct after modification of HDPE
- Exhibited improvement in dispersion & melt compatibility of UHMWPE in HDPE matrix
- Closite in presence of UHMWPE facilitates nucleation & thereby crystallization temp (Tc) increased to4-5 0C as compared to plain HDPE.
- Compressed molded sheet showed improvement in mechanical properties.

INTRODUCTION:-

Polypropylene (PP) has very attractive properties such as high modulus, tensile strength, rigidity, excellent heat resistance, and low cost when compared to other thermoplastic. In 2011 the global market for polypropylene had a volume of 60.7 million tons, which led to a turnover of $80 billion. Although PP has many useful advantages, commercial PP when produced by Ziegler-Natta or metallocene catalyst results in highly linear chains and relatively narrow molecular weight distribution. Its linear structure leads to poor processing ability, such as for extrusion coating, foam extrusion and film blowing. It is expected that improving the melt strength behavior of PP will substantially contribute to the growth of this polymer in the plastic market.

Ultra High molecular Weight Poly Ethylene is a subset of thermoplastic of polyethylene. It has very high molecular weight. UHMWPE has the highest impact strength of any thermoplastic presently made. It is highly resistant to corrosive chemicals with exception of oxidizing acids; has extremely low moisture absorption and a very low coefficient of friction; is self lubricating and is highly resistant to abrasion.

So the idea is to disperse the properties of UHMWPE in the polypropylene matrix. As PP is a low cost polymer, a modified PP with UHMWPE will have improved mechanical and flow properties. Keeping the goal in mind here we had use the reactive extrusion process to disperse UHMWPE in PP polymer chains. The extrudated process is tested for properties. We are trying to find out optimum conditions for maximum dispersion of UHMWPE in PP and conceptualize it.

CHAPTER-1 : GENERAL LITERATURE SURVEY

1.1: Polypropylene (PP) as a polymer matrix:

$$\left(\!\!\begin{array}{c} CH - CH_2 \\ | \\ CH_3 \end{array}\!\!\right)_n$$
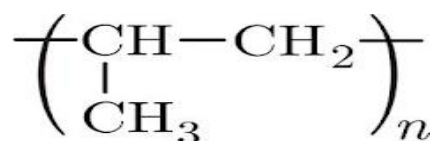
Polypropylene is a versatile thermoplastic offering a useful balance of heat (160 °C) and chemical resistance, good mechanical strength, electrical properties, processing. Besides PE and PVC, PP is the third largest commodity polymer produced and applied in large quantities. Polypropylene is synthesized by the polymerization of propylene, a monomer derived from petroleum using potential initiator reported in literature in Table 1.1

Table 1.1 Catalyst use in polymerization of polypropylene

Catalyst system	Catalyst performance		Industrial Process
	Yield (gm/gm)	Isotactic	
TiCl4+AlEt3(only historical interest	500	40%	Nil
First generation catalyst TiCl3+AlEt2Cl	3500-5000	89%	Slurry in solvent ,slurry in liquid Monomer gas phase process
Second generation catalyst TiCl3+Al-alkyl	5000-15000	94%	Slurry in solvent ,slurry in liquid Monomer gas phase process/solution process

Third generation Catalyst Ti compound Supported by Mg-Halide in active Form	>300000	>95%	Slurry in solvent ,slurry in liquid Monomer gas phase process

The range of molecular weight for PP is Mn = 38,000 to 60,000 Mw = 220,000 to 700,000. The molecular weight distribution (Mn/Mw) an range from 2 to 11. Polypropylene is less resistant to degradation (particularly to high temperature oxidation) than polyethylene, but it has better environmental stress cracking resistance. The decreased degradation resistance of PP is due to the tertiary carbon in PP, allowing for easier hydrogen abstraction compared with PE. Polypropylene is one of the lightest plastics, with a relative density of ~0.905. The non polar nature, low surface energy makes it difficult to bond, join or coat due to the difficulty of wetting the surface thus PP does not absorbs moisture.

Boor, J et al. Newyork press (1979) G. Natta (1954) first described crystalline polymers of propylene in the literature and his associates at the Chemical Industrial Del Politechico di Milano. Earlier efforts to initiates propylene polymerization had only results in non crystalline polymers of little or no importance. With the introduction of heterogeneous, stereo specific catalyst discovered by K. Ziegler for the low pressure polymerization of ethylene, the scene suddenly changed. These reactions are product of transition of metal compounds with selected organo metallic compounds contains active sites for polymerization, such that each new propylene molecule was incorporated in the polymer chain in a regular, geometric manner identical to all preceding methyl groups. Stereo regular crystalline polymers, chain can be obtained first by Natta and co-worker. Three geometric forms of the polymer chain can be obtained as shown below Fig-1.1.

Natta classified them as.

1. Isotactic - All methyl groups aligned on one side of the chain

2. Syndotactic - Methyl groups alternating

3. Atactic - Methyl groups randomly positioned

Structure of different forms was summarized below. Modification of PP/PP-ICP/PPCP matrix is known to be influenced by type & quantity of tacticity of polymer matrix. Therefore, it always remained a research topic in Polyolefin modification.
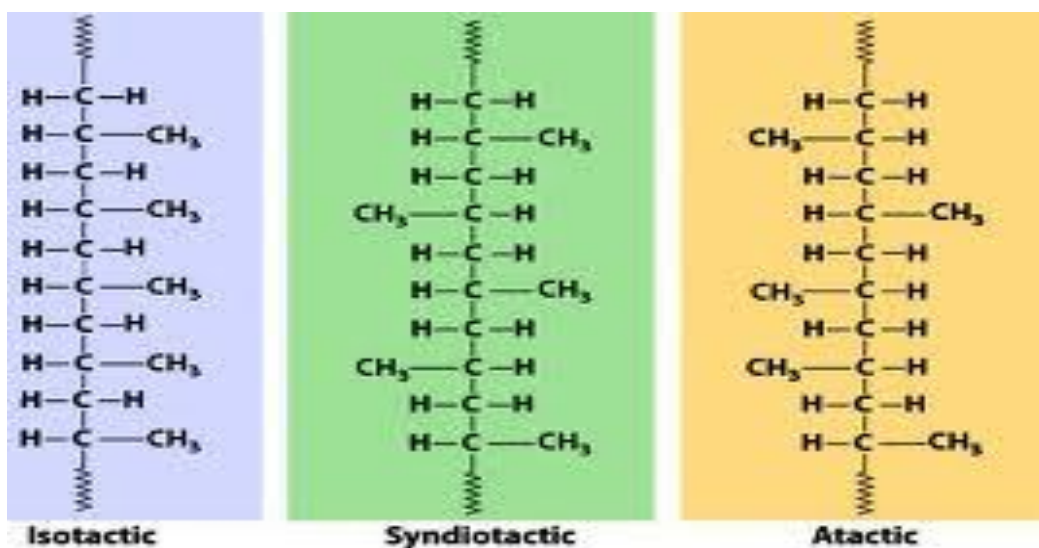
1.1 Types of polypropylene on basis of geometry.

Both isotactic and syndotactic forms will crystallize when they are cooled from molten states. PP was the first stereo regular plastic and the resulting crystalline produces a stiff polymer chain and exceptional properties.

Homopolymer: Homopolymer means that only propylene will take part in polymerization to synthesize PP. The choice of catalyst allows the production of isotactic, syndotactic or atactic varieties of homopolymer PP and all having varying properties. It is therefore difficult to characterize PP by one set of statements regarding the properties.

Random Copolymers: These are a type of where basic structure of the polymer chain has been modified by the incorporation of a different polymer molecule. Ethylene is the most commonly used molecule and this is inserted randomly along the polymer backbone at about 1-7% concentration. The random copolymers give increased clarity and impact strength.

Commercial injection moulding and extrusion grade PP are generally 94 to 97% isotactic. Fabricated parts are typically 60% crystalline, with a range of polyhedral spherulite forms and sizes, depending on the mode of crystallization form the melt. Atactic PP though is not suited to structural plastic uses, have been doveloped as modifires in hot melt adhesives, roofing compounds, and communications cable- filler gel.

PP can be made in to a multidimensional range of product with properties and characteristics dependent on the

- Type of polymer: homopolymer, random,or block polymer.
- Molecular weight and molecular weight distribution.
- Morphology and crystalline structure.
- Additives.
- Fillers and reinforcing materials.
- Fabrication technique.

Homopolymer have resistance to deformation at elevated temperature, while high stiffness, tensile strength surface hardness and good toughness can be observed at ambient temperatures. Random ethylene-propylene copolymers are characterized by higher melt strengths. They have good clarity and resistance to impact at low temperature, gained at some sacrifice in stiffness, tensile strength and hardness. Block polymer, preferably with ethylene, classified as having medium, high or extra-high impact strength with particular respect to sub-zero temperature. Some properties that are usually considered inherent advantages of PP are:

- Low specific gravity & excellent chemical resistance.
- High melting point & Good stiffness/toughness balance.

- Adaptability to many converting.

- Great range of special purpose grades.

- Excellent dielectric properties.

- Low cost (per unit volume).

Properties usually considered being disadvantages of PP are:

- Flammability & Low temperature brittleness

- Moderate stiffness

- Difficult printing, painting and gluing

- Low UV resistance

- Reduce extruder output

- Haziness

1.2 Degradation:

Polypropylene is liable to chain degradation from exposure to heat and UV radiation such as that present in sunlight. Oxidation usually occurs at the tertiary carbon atom present in every repeat unit. A free radical is formed here, and then reacts further with oxygen, followed by chain scission to yield aldehydes and carboxylic acids. In external applications, it shows up as a network of fine cracks and crazes that become deeper and more severe with time of exposure. For external applications, UV-absorbing additives must be used. Carbon black also provides some protection from UV attack. The polymer can also be oxidized at high temperatures, a common problem during moulding operations. Anti-oxidants are normally added to prevent polymer degradation.

1.3 Applications:

Since polypropylene is resistant to fatigue, most plastic living hinges, such as those on flip-top bottles, are made from this material. However, it is important to ensure that chain molecules are oriented across the hinge to maximize strength.

1. Very thin sheets of polypropylene are used as a dielectric within certain high-performance pulse and low-loss RF capacitors.

2. Polypropylene is used in the manufacturing piping systems; both ones concerned with high-purity and ones designed for strength and rigidity.

3. Many plastic items for medical or laboratory use can be made from polypropylene because it can withstand the heat in an autoclave.

4. A common application for polypropylene is as biaxial oriented polypropylene (BOPP). These BOPP sheets are used to make a wide variety of materials including clear bags. When polypropylene is biaxial oriented, it becomes crystal clear and serves as an excellent packaging material for artistic and retail products.

5. Polypropylene, highly colourfast, is widely used in manufacturing carpets, rugs and mats to be used at home.

6. Polypropylene is widely used in ropes, distinctive because they are light enough to float in water.

7. Polypropylene is also used as an alternative to polyvinyl chloride (PVC) as insulation for electrical cables for low-ventilation environments, primarily tunnels.

8. Expanded polypropylene EPP is extensively used in model aircraft and other radio controlled vehicles by hobbyists.

9. Polypropylene fibres are used as a concrete additive to increase strength and reduce cracking.

1.4 Post reactor Modification of polymer with additives:

Most of the macromolecule substances, especially solid polymer that are received from manufacturing processes cannot be used as received. Almost every time, small amount of additives have to be mixed as processing aid or to improve the properties of polymer before moulding or granulating these compounds. The lists of most commonly used ones and the most beneficial to processing:

- Lubricants are used to enhance the rheological properties during manufacture and ease processing.
- Stabilizers are added in melt to prevent thermo oxidative degradation.
- Antioxidant and light stabilizers are used as anti ageing additives to protect against oxygen and light usage.
- Plasticizers increase process ability, flexibility and impact strength.
- Fillers and reinforcing materials for selectively modifying certain predominant mechanical properties.

1.5 Antioxidant used in PP :

The performance of polyolefin is adversely affected by the various stage of their life cycle involving polymer manufacture, storage, processing/fabrication and the environment. Polyolefin like other hydrocarbon polymer are highly susceptible to attack by molecular oxygen, and auto oxidation is the major cause to loss of useful properties and ultimate mechanical failure of the polymer aircrafts. The resistant to oxidation, depending on their chemical structure and their physical and morphological characteristics. Increasing chain branching lead to more rapid oxidation and polypropylene is the most oxidizable polymer out f the major commercial polyolefin.

The oxidative degradation process of PP, however are normally accelerated under the influence of temperature, UV light and other factors, such as mechanical stress, atmospheric pollutants, but temp. and UV light parameter is most important.

Both thermal and photo oxidation process are responsible for the ageing and properties of polypropylene. The adverse effect of oxidation can be minimized by use of oxidation inhibitors (Antioxidants).

1.5.1Thermal antioxidants

Thermal antioxidants are the chemical agents which stabilized the polymer against the high temperature. Inhibition of thermal oxidants can be achieved by use of low levels (0.05- o.25 wt%) of antioxidants which are incorporated during fabrication process.

On the basic of their mode of action antioxidant are of following type

(A) **Chain breaking anti-oxidants or primary anti-oxidants:** Primary antioxidant act by removing the propagating radicals.

(B) **Preventive antioxidant:** Preventing antioxidants preventing on inhibiting the generation of free radical in auto oxidation cycle.
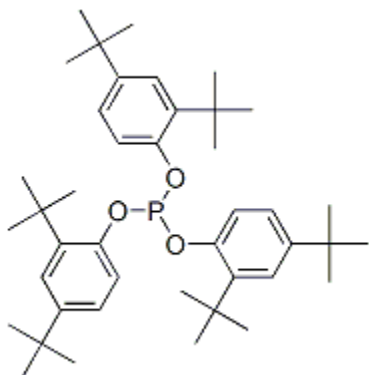
Figure 1.2 Chemical structure of Irgafos 168
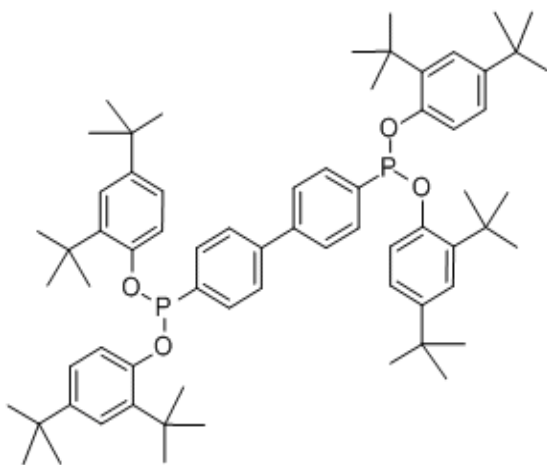
Figure 1.3 Chemical structure of Irgafos Pepq
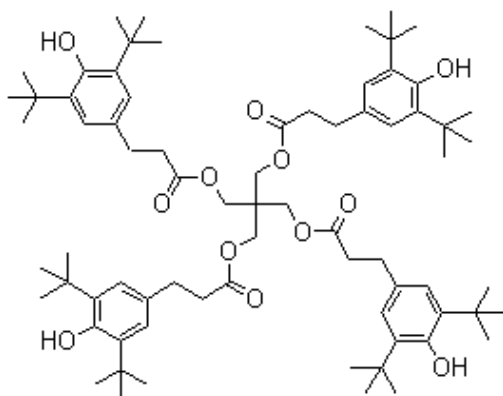
Figure 1.4 Chemical structure of Irganox 1010

CHAPTER 2: RELEVANT LITERATURE WITH RESPECT TO PROJECT WORK

2.1 Polyolefins:-

Polyolefins, which include large volume materials such as polyethylene (PE) and Polypropylene (PP) and specialty materials such as elastomers, have become established as commodity plastics due to their cost/performance balance and economical and environmentally friendly production. During the last 50 years, polyolefins have undergone a tremendous growth and still have further growth potential due to their versatility in properties and applications, low cost and easily available raw materials.

Because of their combination of product performance and low cost, polyethylene (PE) films have become the most popular flexible packaging material. Key product performance attributes for packaging applications often include:

1. Processing/converting characteristics

- Machinability
- Sealing Properties
- Shrink Properties (where applicable)

2. Physical Properties

- Toughness (tear / impact strength)
- Optics (clarity/gloss)
- Stiffness (or flexibility)
- Barrier (especially for food packaging)

LDPE-based films are used in numerous packaging applications due to their excellent sealing, shrink and optical properties. Many applications, however, require machinability, stiffness, toughness and/or barrier properties that LDPE alone cannot provide. To enhance the properties of LDPE films in these areas, various HDPE resins are commonly used as a minority blend component in LDPE-based films. Key film properties are affected by HDPE level, as well as by the type of HDPE resin used in the LDPE/HDPE film blend. Unfortunately, there is little published information[1,2] on the effect of HDPE resin choice and content on the physical properties of LDPE/HDPE film blends. This report presents information on the different types of HDPE resins available for blending and on the impact of these different HDPE resins on key packaging film properties.

2.1.1 Background on HDPE Resins:-

Commercially-available HDPE film resins can be grouped into three general technology categories:

1. Chromium-based catalyst resins

2. Single-reactor Ziegler-Natta (Z-N) catalyst resins

3. Multi-reactor/bimodal Z-N catalyst resins

These resins differ in basic composition, processing and performance characteristics, as discussed below.

2.1.1.1 Chromium-based resins

One distinguishing feature of chromium-based-catalyst HDPE resins is their high level of long-chain branching (LCB). LCB is also the distinguishing characteristic of LDPE resins and significantly affects PE resin processing and property performance in the following manner:

1. Processing – Resins with LCB exhibit higher melt strength (better bubble stability) and lower back pressure than resins with no LCB. This is probably the most positive feature of chromium-based (and LDPE) resins and is a key reason for their popularity in blow molding, sheet, pipe and many film applications.

2. Properties – Many film strength properties (tear, impact) are negatively affected by LCB content. Film barrier properties are also negatively affected by LCB.

LCB content cannot be detected using standard resin analytical methods such as melt index (MI) and melt flow ratio (MFR). More sophisticated analytical methods have been used to determine LCB level, including techniques reported by Lai et al 3 and Shroff et al4. In Shroff's method, a measure denoted as Elastic Response

(ER) characterizes the LCB content of PE resins - resins having higher levels of LCB exhibit higher ERs. (Note: Very broad, bimodal MWD resins can also exhibit high ERs.)

2.1.1.2 Single-reactor Z-N resins

Single-reactor Z-N resins are characterized by their narrow molecular weight distribution (MWD), as Indicated by low MFRs, and minimal LCB-content. Single-reactor Z-N resins exhibit higher back pressure and lower melt strength compared to chromium-based and multi-reactor resins with similar average molecular weights (MIs). As a result of these processing drawbacks, there is minimal use and few commercial offerings of single reactor Z-N resins for HDPE blown film applications, although these resins are commonly used in cast film applications. None of the resins evaluated in this study are produced using Z-N catalysts in a single-reactor process.

2.1.1.2 Multi-reactor/bimodal z-n resins

Over the last 15 years, multi-reactor Z-N HDPE blown film resins have enjoyed significant growth due to their combination of good processing characteristics and excellent physical properties. For example, dual reactor/bimodal HMW-HDPE blown film resins have displaced LLDPE and become the industry standard in plastic grocery sacks and commercial/institutional trash can liners. Likewise, multi-reactor MMW-HDPE blown film resins have displaced chromium-based HDPE resins in becoming the industry standard in cereal and cracker packaging. Multiple reactors can produce broader MWD resins having improved processing characteristics versus narrow MWD resins. In addition, the lower LCB-content occurring with Z-N catalyst (versus chromium-based resins) results in superior film physical properties. This combination of processing and property performance has resulted in the above average growth rate occurring with multi-reactor, Z-N, HDPE blown film resins. The Z-N resins evaluated in this study are all produced using multi-reactor technologies.

2.2 Carbon Nano tube & HDPE composite:

Carbon nanotubes (CNTs) have been widely applied for their specific electrical, thermal, and mechanical properties (1). Structural reinforcement of polymer matrices formed by carbon nanotubes has been broadly applied where significant improvement of mechanical properties was achieved at a very low carbon nanotube loading rate.

However, because of the expenditure, single-wall carbon nanotubes (SWCNTs) are not prevalently adopted in structural reinforcement. Multi-wall carbon nanotubes (MWCNTs), on the other hand, are not only cheaper and easier to produce but also generate surprising mechanical properties compare to that of SWCNTs. The average strain modulus of MWCNTs estimated is over 1.8 TPa (2,3).

Studies have proved that increasing polymer matrices by carbon nanotubes to form structural reinforcement and electrical conductivity have significantly improved mechanical and electrical properties at very low carbon nanotubes loading. In other words, increasing polymer matrices by carbon nanotubes to form structural reinforcement can reduce friction coefficient and enhance anti-wear property. However, producing traditional MWCNTs in polymeric matrix is an extremely complicated process. Using melt-mixing process or in situ polymerization leads to better dispersion effect on composite materials. In this study, therefore, to simplify MWCNTs /HDPE composite process and increase dispersion, powder was used directly to replace pellet to mix and sinter with MWCNTs. The composite bulks with 0, 0.5, 1, 2 and 4% nanotube content by weight was analyzed under SEM to observe nanotubes dispersion. At this rate, a MWCNTs/HDPE composite bulk with uniformly dispersed MWCNTs was achieved, and through the wear bench (Pinon-Disk), the wear experiment has accomplished. Accordingly, the result suggests the sintered MWCNTs/HDPE composites amplify the hardness and wear-resist property.

Although the simplified melting extruder process is simple and compatible with existing polymer processing techniques, the process is difficult to manipulate dispersion in high viscosity with high nanotube concentration. To improve the dispersion of high nanotubes concentration in melting polymer, the reduplicate melt processing has to break nanotube aggregates or prevent such formation. Tang et al produced MCNTs-HDPE composites film in three steps. The first step is blending, heating and compressing to carry out the MWCNTs-HDPE sheet.

The MWCNTs=HDPE sheet is then chopped into smaller pieces. However, this approach is not strong enough to break nanotube aggregates. To improve the dispersion of carbon nanotubes in polymer matrix, the prepared MWCNTs=HDPE composite pieces are fed into a twin-screw extruder to blend through the shearing by the rotating screws. Finally, the extrusive composite strip is compressed again to form a thin film. Although a good dispersion of carbon nanotubes in polymer matrix is achieved by reduplicating melt process, it is extremely complicated and expensive.

2.2.1 Fabrication: MWCNT-HDPE Composite:

The traditional approach to from MWCNTs in polymeric matrix is an extremely complicated process. The two melt mixing process or in situ polymerization can result in better dispersion effect on composite materials. This study replaces pellet with powder directly to blend and sinter with MWCNTs in order to simplify the process and increase dispersion. Fabrication of MWCNTs=HDPE bulk samples for wear bench test can be described in two steps. The first step is the preparation of a precursor material in the

form of MWCNTs=HDPE composite powder. Carbon nanotubes are mechanically dispersed into a HDPE powder by isopropyl alcohol (IPA) to blend in a hopper. The central idea is to use low-viscosity liquid and to stable the solution with well-dispersed nanotubes obtained by mixing. The IPA solvent in mixer is evaporated in vacuum heating system and then is recycled via cooling distillation system. The procedure used to prepare the composite powder is shown schematically in Figures. As shown in this figure, powder of neat HDPE, correct weight percentage of MWCNT powder and IPA solvent are blended in a hopper, heated in a vacuum oven at 60C for 10 minutes to fully evaporate the dispersing solvent. The second step is to feed the prepared composite powder into a hot compact mold to sinter, as shown in Figure 2.1. In the sintering process, the temperature is maintained at 180C for 2 hours to melt and sinter the composite powder to form a bulk MWCNT=HDPE composite. On the purpose of performing a standard wear test, the bulks are compressed and sintered to 5mm in thickness. After the bulk is cooled down to the room temperature and washed, thin cylindrical test specimens of diameter 15 mm and thickness 5 mm are polished for the wear test

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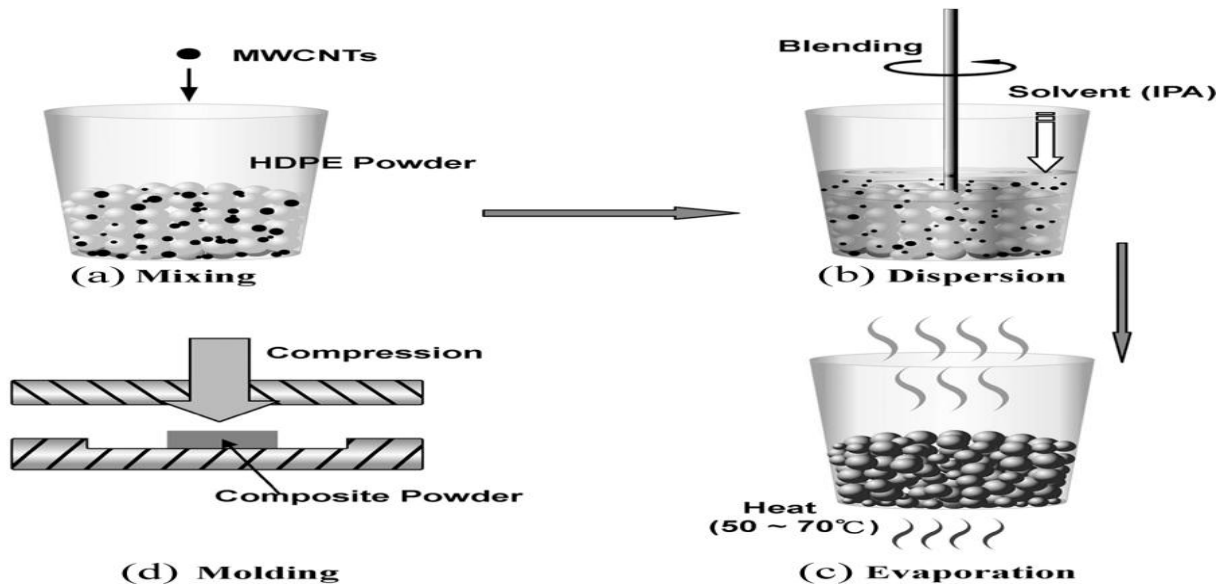
Fig. 2.1 : Procedures for preparing MWCNTs=HDPE bulk composite.

Further, SEM picture as shown in fig-2.2 exhibited dispersion of MWCNT in HDPE
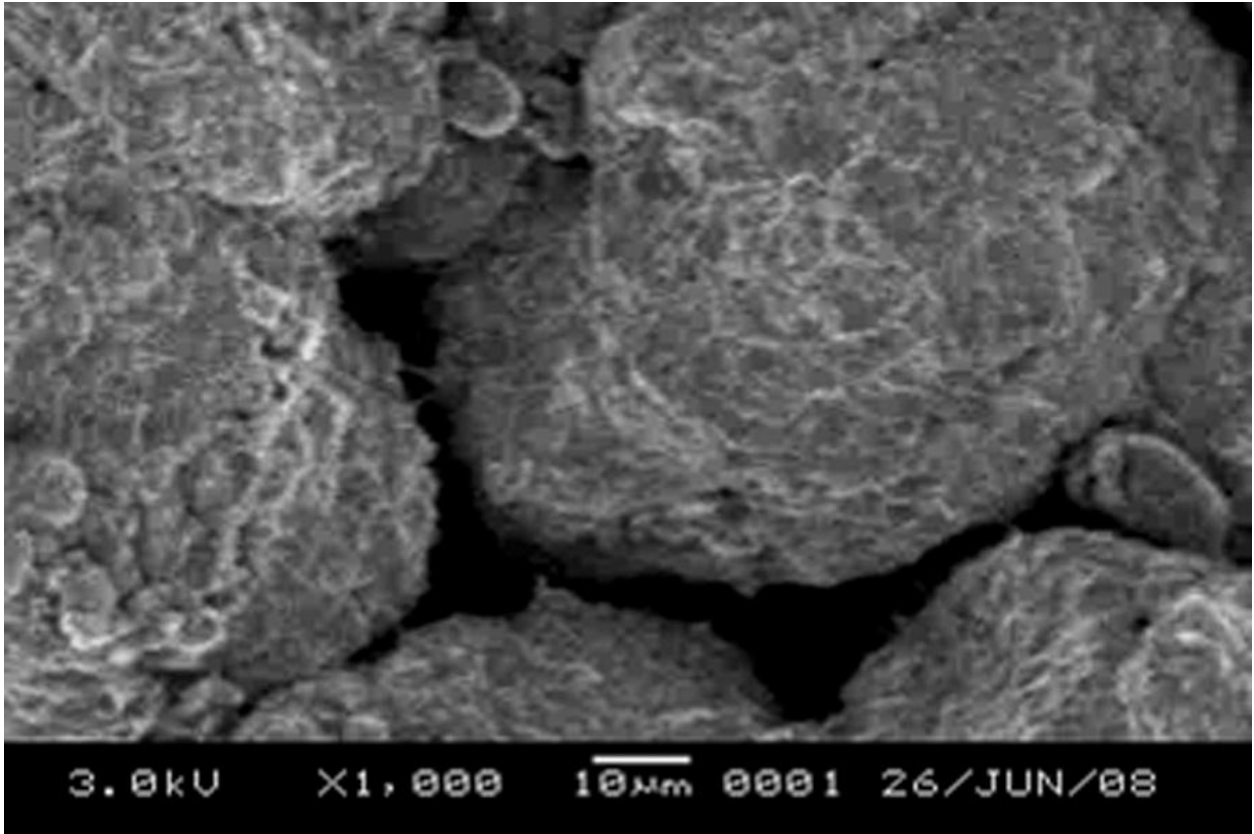
Fig. 2.2: SEM image of carbon nanotubes were uniformly dispersed and implanted within HDPE powder.

It has been already demonstrated that the MWCNTs=HDPE bulk composite with homogeneously dispersed carbon nanotubes within HDPE matrix can be fabricated directly by polymer powder to blend and sinter. The hardness and wear resistance property of fabricated MWCNTs=HDPE composite were significantly increased by increasing the weight fraction of carbon nanotubes. The remarkable enhancement of hardness is originated from the homogeneously distributed carbon nanotubes in HDPE matrix, excellent interfacial strength at MWCNTs=HDPE interfaces and high relative density of nano composites. The dispersed carbon nanotubes in HDPE-matrix composite provides considerably enhanced wear resistance by retarding the peeling of HDPE matrix during sliding wear process. It is concluded that the homogeneous distribution of carbon nanotubes with interface in matrix is an important technology issue to enhance

the hardness and wear resistance property of MWCNTs=polymer composite.

High Density Polyethylene (AVPE)

Processing HDPE Natural Virgin (20 Melt)

Convert Imperial		
Mold		20 – 60 Deg. C
Melt		180 – 250 Deg. C
Max Temp		280 Deg. C
Drying		80 Rarely
Injection Speed		Medium to High
Purge		HDPE

Physical Characteristics

Structure		Crystalline
Opacity		Translucent to Opaque
Physical		Tough, Waxy Surface
Specific Gravity		0.97
Shrinkage		1.0 to 2.0%
Melting Point		100 Deg. C
HDT		60 – 90 Deg. C
Service Temp		84 Deg. C

HDPE is generally easy to process, with higher molecular weight grades having stiffer flow properties.

Applications include: Containers, Storage, seals & closures.

Table 2.1: Characteristics of Polyolefins

2.3 Melt Strength

Sterigenics employs their extensive knowledge and capability of radiation processing to modifying the rheological properties of linear polyolefins like high density polyethylene (HDPE) and linear low density polyethylene (LLDPE). While the physical properties of HDPE and LLDPE are highly desirable for many applications, they exhibit poor melt processability due to shear thinning. Shear thinning is the typical rheological behavior exhibited when stress is applied to linear Polyolefins while in the melt phase. It can be compared roughly to the behavior of salt water taffy. When pulled apart, it will thin and

elongate from a single point and offers decreasing resistance to elongation. In terms of polymer melt processability, the shear thinning polymer will yield poor gauge uniformity in films and thermoforming, high neck-in and low maximum draw ratios in extrusion coating and cell collapse in low density foams.

It is important to view melt strength over a broad shear rate and extensional rate range as various melt processes require different melt performance levels at low shear rates (profile extrusion) or high extensional rates (extrusion coating). In some processes like melt phase thermoforming, the polymer sheet is required to exhibit high melt strength at low shear rates as the sheet is being heated: sag resistance. After the sheet is heated, the material is plugged, the molds close and the part is formed using vacuum at higher extensional rates and the material is required to resist thinning: strain hardening.

At Sterigenics, utilizing our highly controlled radiation processes, we are able to induce long chain branching in linear polyolefins to create a network of entanglements. The result is Raprex® HDPE and LLDPE grades that exhibit extraordinary melt strength. They are not cross-linked. Gel content, if measurable, is less than 0.4% so the materials are 100% reprocess able.

2.3.1 Sag Resistance (high melt strength at low shear rates).

The shear VS viscosity curves in Figure 3, clearly show the dramatic increase in viscosity of the radiation processed HDPE VS their unprocessed, linear precursors. They exhibit the behavior of resins with a much broader molecular weight distribution. When a large, heavy extruded sheet is being heated to above its melting point in preparation for thermoforming, this is the type of behavior that allows the material to support its own weight and not sag into the heating bank. When blow molding produces large parts, the hanging parison will resist sagging.
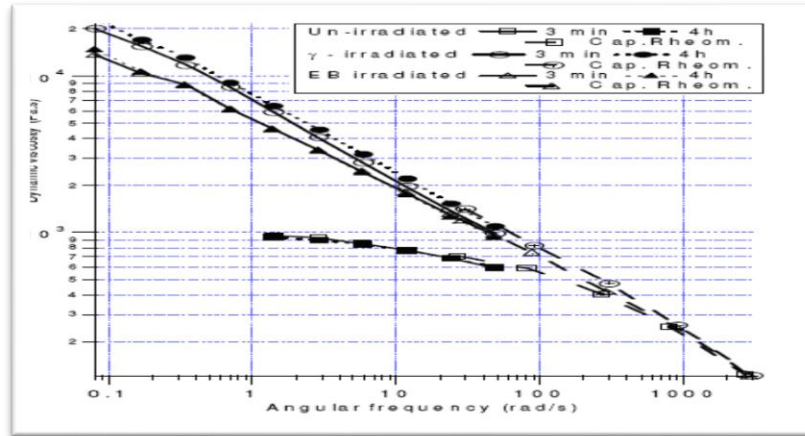
Fig-3 : Shear rate VS Viscosity

2.3.2 Strain Hardening (High Melt Strength at High Extensional Rates)

Many melt processes require the melt to resist thinning at high extensional rates. In extrusion Coating, the melt curtain is pulled from the die onto the substrate at draw ratios greater than 100:1 and at line speeds greater than 1000 feet / minute. Linear polymers exhibit necking and Melt resonance at draw ratios and extensional rates far below the process requirements for economic production rates. Melt resonance is an oscillating, thick / thinning effect caused by the unstable melt curtain. In thermoforming and blow molding, after the mold closes and forming pressure is applied, extensional rates are accelerated and the polymer must resist thinning as material is distributed into the far corners of the part. Polymers exhibiting strain hardening or high extensional viscosity *deform uniformly* as stress is applied to the melt.

2.3.3 Extensibility

In melt processing, equally important as melt strength, is the ability for the polymer to exhibit high melt strength while being extended, at high rates, to form the finished product: coating, film, fiber, formed part. This extensibility requirement for each process must be considered when designing the higher performing polymers. The Gottfort Extensional Rheometer (Rheotens, Fig. 2.3) is a device that measures both melt strength and extensibility simultaneously by combining the capillary rheometer with a device that pulls the melt away from the die at increasing rates and draw ratios. The throughput from the die remains constant. It is a relatively simple, fast but elegant way to relate rheological properties to melt processability.

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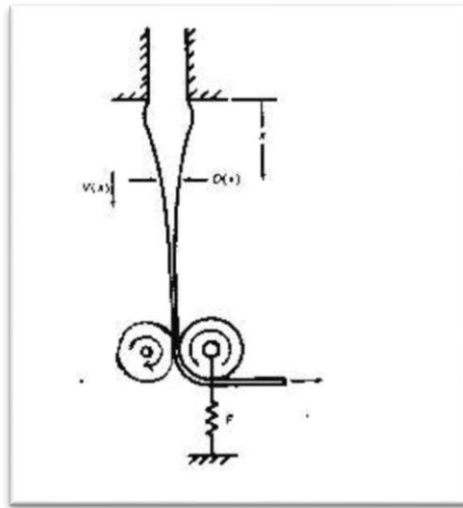
Fig. 2.3: Gottfert Rheotens Melt Tension (cN) Velocity at Break (mm/sec)

In Figure 5, Raprex® R100, a radiation processed HDPE, is compared to its linear precursor. As the linear HDPE is extended, it exhibits an apparent increase in extensional viscosity as the polymer chains are strained. However, the polymer chains begin to slide over one another and the polymer begins to shear-thin at about 65mm/sec. The branched R100 exhibits a dramatic increase in melt tension that continues to increase as the melt is extended. The melt strength Of Raprex® R100 at break (at the same extensibility) is two times that of the melt strength of its linear precursor.
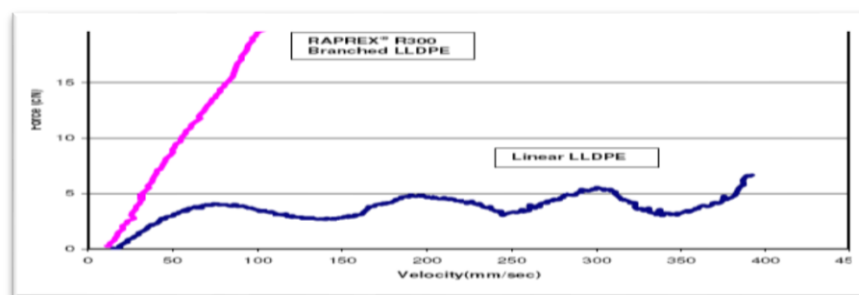
Fig. 2.4: Melt tension VS extensibility

2.4 Structure Property Relationship

Nowadays polymers, ranging from the large volume commodity plastics to the small volume specialty polymers, have replaced metals and other natural products in many applications and therefore properties such as strength and long life of a polymer become a requisite in such applications. Ultimate polymer properties are dependent on several aspects, starting from the chemical and physical structure of polymer chains to the mode and conditions of their processing. The intrinsic properties of a polymer (for a given microstructure) are governed to an important extent by its molecular weight; the higher the molecular weight (MW), the better is the physical properties of a polymer. High MW is essential for better mechanical properties, fatigue resistance and wear properties. However, high MW polymers, due to their high melt viscosity, become intractable and difficult to process using conventional processing techniques. Up to the critical molecular weight (M_c, typically twice the average molecular weight between entanglements) of a polymer, the viscosity increases linearly with molecular weight, but above M_c the viscosity of the polymer increases with the 3.4th power of the molecular weight. Intractability of a high MW polymer limits the means of its processing and its applications. Therefore the finished products become expensive due to the high cost involved in specially designed processing techniques.

The problem of intractability of high MW polymer melts can be overcome by techniques involving solution routes. The discovery of solution spinning of ultra high molecular weight polyethylene (UHMW-PE, $M_w >$ 106 g/mol) led to the production of high-modulus, high-strength fibres used in highly demanding applications.[1] These strong fibres are generated by spinning a semi-dilute solution of UHMW-PE in Decaline or paraffin oil; subsequent extraction of solvent from gel filament and hot drawing leads to a strong fibre at the maximum draw ratio. The strength of industrially produced Dyneema ® fibre exceeds 3 GPa, with a modulus of around 120 GPa.

High-strength, high-modulus fibres are used in several applications such as lightweight ropes, nets and textiles. However, as-spun fibres cannot be used efficiently in other applications where the strength is required not only in the fibre direction but also in the transverse direction. For such applications, fibre composites are prepared by reinforcing or gluing the fibers together with other resins (7) or with a low molecular weight material similar in chemical composition to that of the fibres (8). The fibres can possess high strength and high modulus, approaching the theoretical limits of the material; however, the overall properties of the composite are lowered due to the lower modulus

and strength of the adhesive material. In practice, even for highly demanding applications, the strength of fibres is not always required and oriented tapes or wires are sufficient for many applications. These oriented products can be prepared using conventional processing techniques such as melt processing and solid state drawing. However, for convenient processing the polymer composition has to be tailored without compromising much on the properties. In this thesis, in order to achieve a golden mean between the ease of processing and ultimate properties, an attempt is made to combine engineering with polymer chemistry and physics.

2.5 Synthesis route to overcome processability problem and achieve ultimate properties

Broad molecular weight distribution (MWD) is essential for the ease of processing. However, there is a possibility of a loss of desired mechanical properties by broadening the MWD. In such a situation, it is desirable to have a bimodal molecular weight distribution, wherein the composition of a polymer can be altered by tailoring the proportions of high and low molecular weight components. A schematic representation of molecular weight distribution is shown in Fig. 2.5.

Bimodality in polymers can be achieved by two routes: modifying the polymer architecture during synthesis in one or several reactor(s), or post-synthesis blending of different polymers. Post-synthesis blending can be performed by extrusion or solution blending, but effective blending of polymers having high molecular weights is difficult. The supported catalysts give a possibility of immobilizing two catalysts capable of generating polymers differing in chemical structure, branching content and/or molecular weights. Thus the polymer architecture can be tailored in the reactor which was reported in literature (9). The bimodal polyethylenes, having a varied composition of low and high molecular weight components, are model systems for obtaining the interlocked shish-kebab morphology as shown in Fig. 2.6. There is a need for tailoring of the composition of high MW and low MW PE in the blend, in combination with the appropriate processing conditions. Appropriate composition of the high and low MW components in PE can widen the molecular weight distribution (MWD) to attain easy melt processability, and recent advances in catalysis can assist in obtaining the required miscible blends of high and low molecular weight polyethylene. Upon flow in the molten state and subsequent crystallization followed by hot drawing, oriented structures such as shish and interlocked kebabs are reported in the literature (10)
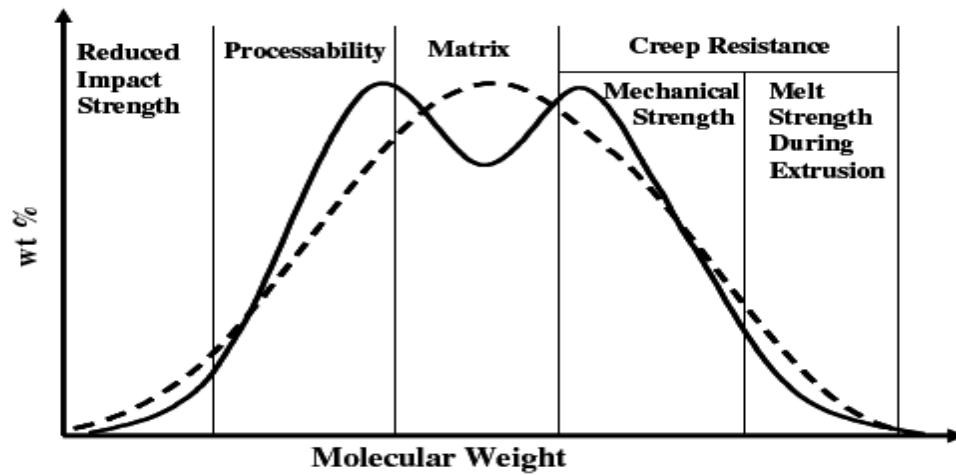
Fig. 2.5 A schematic representation of contribution of various molecular weight fractions to the property profile of polyethylene with monomodal (---) and bimodal (-) MWD
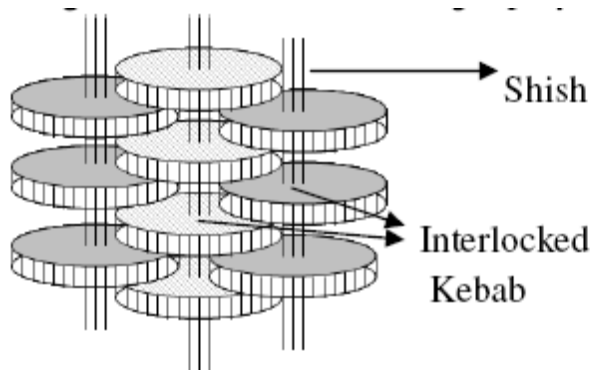
Fig. 2.6 Shish and inter-locked kebab structures. (Shading is done for differentiation)

2.6 Ultra-high-molecular- weight polyethylene(UHMWPE):

Ultra-high-molecular-weight polyethylene (UHMWPE or sometimes shortened to UHMW), also known as high-modulus polyethylene (HMPE) or high-performance polyethylene (HPPE), is a subset of the thermoplastic polyethylene. It has extremely long chains, with molecular weight numbering in the millions, usually between 2 and 6 million. The longer chain serves to transfer load more effectively to the polymer backbone by strengthening intermolecular interactions. This results in a very tough

material, with the highest impact strength of any thermoplastic presently made. It is highly resistant to corrosive chemicals with exception of oxidizing acids; has extremely low moisture absorption and a very low coefficient of friction, is self-lubricating, and is highly resistant to abrasion, in some forms being 15 times more resistant to abrasion than carbon steel. Its coefficient of friction is significantly lower than that of nylon and acetal, and is comparable to that of polytetrafluoroethylene (Teflon), but UHMWPE has better abrasion resistance than PTFE. It is odorless, tasteless, and nontoxic.

Polymerization of UHMWPE was commercialized in the 1950s by Ruhrc emie AG, which changed names over the years; today UHMWPE powder materials are produced by Ticona, Braskem, and Mitsui. UHMWPE is available commercially either as consolidated forms, such as sheets or rods, and as fibers. UHMWPE powder may also be directly moulded into the final shape of a product. Because of its resistance to wear and impact, UHMWPE continues to find increasing industrial applications, including the automotive and bottling sectors, for example. Since the 1960s, UHMWPE has also been the material of choice for total joint arthroplasty in orthopedic and spine implants.

2.6.1 UHMWPE: Structure & Properties
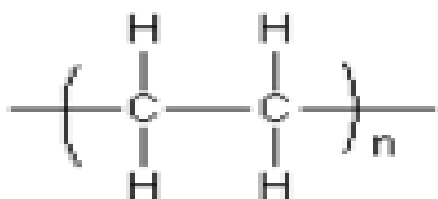
Structure of UHMWPE, with n greater than 100,000

UHMWPE is a type of polyolefin. It is made up of extremely long chains of polyethylene, which all align in the same direction. It derives its strength largely from the length of each individual molecule (chain). Van der Waals bonds between the molecules are relatively weak for each atom of overlap between the molecules, but because the molecules are very long, large overlaps can exist, adding up to the ability to carry larger shear forces from molecule to molecule. Each chain is bonded to the others with so many Van der Waals bonds that the whole of the inter-molecule strength is high. In this way, large tensile loads are not limited as much by the comparative weakness of each Van der Waals bond.

When formed to fibers, the polymer chains can attain a parallel orientation greater than 95% and a level of crystallinity of up to 85%. In contrast, Kevlar derives its strength from strong bonding between relatively short molecules. The weak bonding between olefin molecules allows local thermal excitations to disrupt the crystalline order of a given chain piece-by-piece, giving it much poorer heat resistance than other high-strength fibers. Its melting point is around 144 to 152 °C (291 to 306 °F), and, according to DSM, it is not advisable to use UHMWPE fibers at temperatures exceeding 80 to 100 °C (176 to 212 °F) for long periods of time. It becomes brittle at temperatures below −150 °C (−240 °F).

The simple structure of the molecule also gives rise to surface and chemical properties that are rare in high-performance polymers. For example, the polar groups in most polymers easily bond to water. Because olefins have no such groups, UHMWPE does not absorb water readily, nor wet easily, which makes bonding it to other polymers difficult. For the same reasons, skin does not interact with it strongly, making the UHMWPE fiber surface feel slippery. In a similar manner, aromatic polymers are often susceptible to aromatic solvents due to aromatic stacking interactions, an effect aliphatic polymers like UHMWPE are immune to. Since UHMWPE does not contain chemical groups (such as esters, amides or hydroxyl groups) that are susceptible to attack from aggressive agents, it is very resistant to water, moisture, most chemicals, UV radiation, and micro-organisms. Under tensile load, UHMWPE will deform continually as long as the stress is present - an effect called *creep.*

2.6.2 Production:

UHMWPE is synthesized from monomer of ethylene, which are bonded together to form *ultra-high-molecular-weight polyethylene* (or UHMWPE). These are molecules of polyethylene that are several orders of magnitude longer than familiar high-density polyethylene due to a synthesis process based on metallocene catalysts. In general, HDPE molecules have between 700 and 1,800 monomer units per molecule, whereas UHMWPE molecules tend to have 100,000 to 250,000 monomers each.

UHMWPE is processed using the following methods: compression moulding, ram extrusion, gel spinning, and sintering. Several European companies began compression moulding UHMW in the early 1960s. Gel-spinning arrived much later and was intended for different applications.

In gel spinning, a precisely heated gel of UHMWPE is processed by an extruder through a spinneret. The extrudate is drawn through the air and then cooled in a water bath. The

end-result is a fiber with a high degree of molecular orientation, and therefore exceptional tensile strength. Gel spinning depends on isolating individual chain molecules in the solvent so that intermolecular entanglements are minimal. Entanglements make chain orientation more difficult, and lower the strength of the final product.

2.6.3 Applications:

Synthetic fibers of UHMWPE, which have yield strengths as high as 2.4 GPa (350,000 psi) and specific gravity as low as 0.97.). High-strength steels have comparable yield strengths, and low-carbon steels have yield strengths much lower (around 0.5 GPa). Since steel has a specific gravity of roughly 7.8, this gives strength-to-weight ratios for these materials in a range from 10 to 100 times higher than steel.

- Medical applications in total joint replacement.
- UHMWPE fibers are used in armor, in particular, personal armor and on occasion as vehicle armor.
- Owing to its low density, ships' hawsers and cables can be made from the fiber, and float on sea water. "Spec Lines" as they are called in the towboat community are commonly used for face wires.
- It is also used in lifting applications for manufacturing low weight, and heavy duty lifting slings.
- The extremely low friction coefficient of UHMWPE makes it a common top sheet for boxes in terrain parks.

2.7 Rheology of Polymers

Rheology is the study of the flow of matter, primarily in the liquid state, but also as 'soft solids' or solids under conditions in which they respond with plastic flow rather than deforming elastically in response to an applied force. It applies to substances which have a complex molecular structure.

Newtonian fluids can be characterized by a single coefficient of viscosity for a specific temperature. Although this viscosity will change with temperature, it does not change with the flow rate or strain rate. Only a small group of fluids exhibit such constant viscosity, and they are known as Newtonian fluids. But for a large class of fluids, the

viscosity change with the strain rate (or relative velocity of flow) and are called non-Newtonian fluids. Rheology generally accounts for the behaviour of non-Newtonian fluids, by characterizing the minimum number of functions that are needed to relate stresses with rate of change of strains or strain rates.

2.7.1 Importance of Rheology

In the making of plastic articles, the manufacturer often starts with pellets of the plastic and ends up with the finished article, often both the starting point and the final article being in a 'solid' state. To make the finished article, we need to take the polymer into an intermediate state.

This intermediate step in the forming or shaping of plastic articles involves the passage of the polymer through either the viscous flow region or the rubbery region.

2.7.2 Melt Flow Index

Melt flow index or MFI is a measure of the ease of flow of the melt of a thermoplastic polymer. It is defined as the mass of polymer, in grams, flowing in ten minutes through a capillary of a specific diameter and length by a pressure applied via prescribed alternative gravimetric weights for alternative prescribed temperatures. The method is described in the similar standards ASTM D1238 and ISO 1133.

Melt flow rate is an indirect measure of molecular weight, with high melt flow rate corresponding to low molecular weight. At the same time, melt flow rate is a measure of the ability of the material's melt to flow under pressure. Melt flow rate is inversely proportional to viscosity of the melt at the conditions of the test, though it should be borne in mind that the viscosity for any such material depends on the applied force. Ratios between two melt flow rate values for one material at different gravimetric weights are often used as a measure for the broadness of the molecular weight distribution.

Melt flow rate is very commonly used for polyolefins, polyethylene being measured at 190°C and polypropylene at 230°C. The plastics converter should choose a material with a melt index so high that he can easily form the polymer in the molten state into the article intended, but on the other hand so low that the mechanical strength of the final article will be sufficient for its use

2.8 Quiescent crystallization

2.8.1 Overview:

Crystallization is a phenomenon that takes place when a polymer, having the ability to be ordered (chemical and structural regularity), is cooled below the equilibrium melting point. The process that the polymer undergoes is a first order transition from a coiled, disordered condition to an ordered, semi crystalline form and is caused by a change in the thermodynamic state of the system. Differently from low molar mass compounds, polymers never turn into perfect crystals but always end up in a metastable state which is only crystalline in part, as the crystals usual remain in the sub-microscopic size regime.

A semi-crystalline polymer is composed of lamellar crystallites separated by amorphous layers with the polymer chain axis approximately normal to the face of lamellae (Mandelkern, 1964; Wunderlich, 1976). The lamellar structure is the universal feature of flexible crystalline polymers. Its finding allowed clarifying the unique way of organization of random coil chain molecules into crystalline form that distinguishes polymers from small molecules. As in a usual polymer the length of chain is far greater (10-100 times) than the thickness of the lamella, it follows that the chains must repeatedly fold back upon themselves so as to be accommodated by the lamella. The consequence is that one chain can participate in more than one crystalline unit. In addition, the slow molecular dynamics that characterize the long chains of polymers and the entanglements presence impose a kinetic barrier to the transition. This results in unrealizable slow crystallization at the melting temperature and in the necessity of a undercooling ($\Delta T = T°m-Tc$, where Tc is the effective crystallization temperature) to obtain practicable rates of crystallization. Of course the lowest limit of the crystallization temperature is the glass transition, due to the vitrification of the system.
Changes in the crystallization conditions yield to changes in structure parameters, like volume fraction or thickness of the crystallites. For instance, increasing the crystallization temperature, usually thicker crystallites are observed.

2.8.2 Brief description of the Hoffman–Lauritzen theory

The mechanism of polymer crystallization can be divided into two basic steps: nucleation and growth. The theory developed more than 40 years ago by Hoffman and Lauritzen (Hoffman and Lauritzen, 1961; Hoffman and Lauritzen, 1973; Hoffman *et al.*, 1975; Hoffman *et al.,* 1976), provides a general formalism to treat the crystalline nucleation. During this process, the relaxation of a metastable undercooled melt toward

the equilibrium state (which is rarely reached) is required to overcome a free-energy barrier, whose height depends on the degree of undercooling. In order to create a new phase in the metastable melt, interfaces must be introduced. If the resulting cluster, originated by the reactions of association and dissociation of chain segments, has a size smaller than a critical one, it is unstable, i.e. its probability of decrease is higher than its probability of growth. On the contrary, if a critical size is overstepped, the growth probability of the nucleus is greater than its probability of decrease. This kind of nuclei, called active, can continuously grow toward a stable crystalline phase. In general, if nucleation is initiated from a single phase, it is called homogeneous nucleation. Homogeneous nucleation generates primary nuclei without the help of any substrate or external nucleating particles. If the process is initiated from multiple phases, heterogeneous nucleation occurs. In this case the nuclei are formed on the surface of foreign bodies or crystals of the same material already present in the undercooled liquid. In practice homogeneous nucleation is an unusual and unlikely event. In most cases heterogeneous nucleation takes place. According to the theory, the growth of polymer lamellar evolves through a front provided by an existing crystal with a defined crystallographic Surface. Chain molecules deposit onto a growth plane and start crystallizing onto the lattice one stem at time to form lamellae. The kinetic model predicts three growth regimes, depending on the undercooling, as it is shown in Fig. 8.

At low ΔT, regime I takes places: the growth from a single nucleus covers the entire length of the growth plane, L. Once a nucleus is created through a surface nucleation at rate i, the rest front is quickly covered by lateral growth at rate g, creating a layer of thickness b0 (Fig. II.1a). The analytical expression for the growth rate, perpendicular to growth plane, in regime I, GI, is given by (Hoffman and Lauritzen, 1961; Hoffman and Crystallization of polymers: a review of literature findings Lauritzen, 1973; Hoffman *et al.*, 1975; Hoffman *et al.*, 1976; Hoffman *et al.*,1982):

G ib L I 0 = (II.1)

The surface nucleation *i* is derived on the basis of small crystal model and has this analytical expression (Turnbull and Fisher, 1949):

$$i = \left(\frac{NkT}{h} \right) \exp\left[-\frac{\left(\Delta G + \Delta G_\eta \right)}{kT} \right] \qquad \text{(II.2)}$$

Where h and k are the Planck and Boltzmann constants, respectively and N is the number of uncrystallized elements that act as single units in the nucleation process. The

equation contains two opposing factors, the free energy of the nucleation barrier (ΔG) and the free energy of activation (ΔGη). The first contribution takes into account the probability that a nucleus of a given size exists at constant pressure and temperature, whereas ΔGη is the free energy for short-range diffusion across the crystal/amorphous phase boundary.
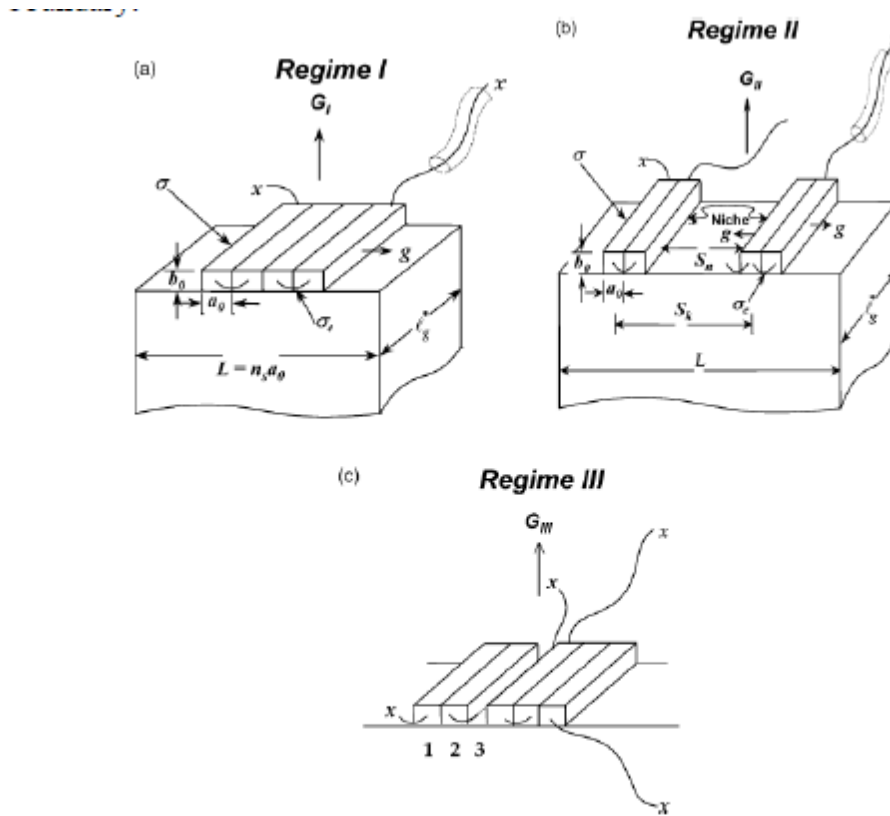
Figure II.1 *Schematic drawings of the three polymer growth regimes: (a) regime I; (b) regime II; and (c) regime III. The 'x' represents chain ends (Cheng and Lotz, 2005).*

With increasing ΔT, regime II takes place: on the substrate of width L, more than one nucleus is formed. The critical factor is the niche separation between two neighboring nuclei, which is continuously reduced increasing the undercooling. The multiple nucleation's at rate i, combined with the substrate completion at rate g, create a new layer. The analytical expression of the growth rate in regime II is given by:

$$G_{II} = \left(ib_0 g\right)^{1/2} \qquad\qquad (II.3)$$

32

where the symbols used have the meaning above discussed. Upon further decreasing of Tc, one enters in regime III (Fig. II.1c). The niche separation distance reaches the same order of magnitude as the stem width a0. Therefore, the lateral covering rate g is not a dominant factor, because the layer addition is governed mainly by the injection of stems at rate i.

Therefore the analytical expression for the growth rate returns back to:

$$G_I = ib_0L'$$
$$(II.4)$$

where L' is the width between two neighboring niches and is equal to nIIIa0, with nIII ~ 1–3.

2.8.3 Recent theories of polymer crystallization

For many years, the theories on polymer crystallization have considered that polymer crystal growth is essentially a stepwise process: the deposition of chain stems which span the lamellar thickness is made sequentially, i.e. more or less one at a time. In sharp contrast to the above views, various experimental evidences reported recently (and synchrotron X-ray data most prominently among these) have indicated that the actual formation of the polymer crystal is preceded by some type of "preordering" in the polymer melt. A vigorous debate on the route which through a polymer crystallizes is recently raised and a wide number of works in literature has tried to explain the mechanism of primary crystallization and subsequent growth, many times changing completely the conventional approach to the phenomenon. Among the others, the study of Imai and co-workers (Imai *et al.*, 1992a; Imai *et al.*, 1992b; Imai *et al.*, 1994; Matsuba *et al.*, 2000) is particularly interesting. In the classical picture of polymer crystallization it is expected that no wide angle X-ray diffraction peaks (WAXD) appear before the well-known induction time, which is the time required to obtain a significant probability of forming critical nuclei in the melt. The small angle X-ray scattering (SAXS) follows the WAXD, so in the same way any SAXS peaks during the induction period are expected. Imai and co-workers, instead, have Crystallization of polymers: a review of literature findings showed that, when the polyethylene terephthalate (PET) is crystallized from the glassy state just above the glass transition temperature, a peak in intensity, $I(q,t)$, of SAXS versus scattering wave vector q appears at early time before any signal in WAXD. This experimental observation suggested that a spinodal decomposition (SD) phase separation occurs before the primary crystal nucleation in the very early

stages of crystallization, because the peak intensity grow may be accurately fitted by the Cahn-Hilliard theory (Cahn and Hilliard, 1958).

The SD is a phase separation process usually occurring in solutions or blend, i.e. in systems of more than two components. However, the theory proposed by (Doi and Edwards, 1986) to explain the isotropic-nematic transition in liquid crystal polymers obeys a SD-type separation. On the basis of the Doi's theory and the light scattering results, Imai and co-workers (Imai *et al.*, 1993a; Imai *et al.,* 1993b) suggested that the unusual phenomenon of spinodal decomposition before the nucleation process is caused by the orientation process of rod-like polymer segments. The proposed model includes several stages. The conformation (atomistic arrangement of monomers along the backbone) of the chains changes at first, leading to the formation of rigid segments with specific length. If the length exceeds a critical value, the rigid segments are forced to orient parallel to each other in order to reduce the excluded volume. This ordering causes an isotropic to nematic SD-type phase transition (early stage of SD), similar to liquid crystal polymers. At the later stages, the oriented domains or clusters arrange and grow in crystallographic fashion yielding to crystal nuclei formation. Between the early and later stages of SD a complex transformation of the nematic to smetic phase (second microphase separation) occurs. Inspired by the Imai and co-workers findings, Olmsted et al. (Olmsted *et al.*, 1998) have built a polymer melt phase diagram as a function of density and temperature (Fig. II.2). Nevertheless, if the temperature is taken down to a transition temperature, called binodal (Tb), and then to the metastable region (bimodal), a separation into an unoriented (isotropic) phase and an oriented (nematic) phase by a mechanism of nucleation and growth takes place. Finally, if the crystallization temperature is in the unstable region (spinodal), a SD-type transition into an ordered dense liquid and a disordered less dense liquid is observed. The same concepts of the Olmsted diagram are shown in the general model for the crystallization mechanism developed recently by Kaji et al. (Kaji *et al.*, 2005), which is schematically proposed in the **Fig. 2.7**

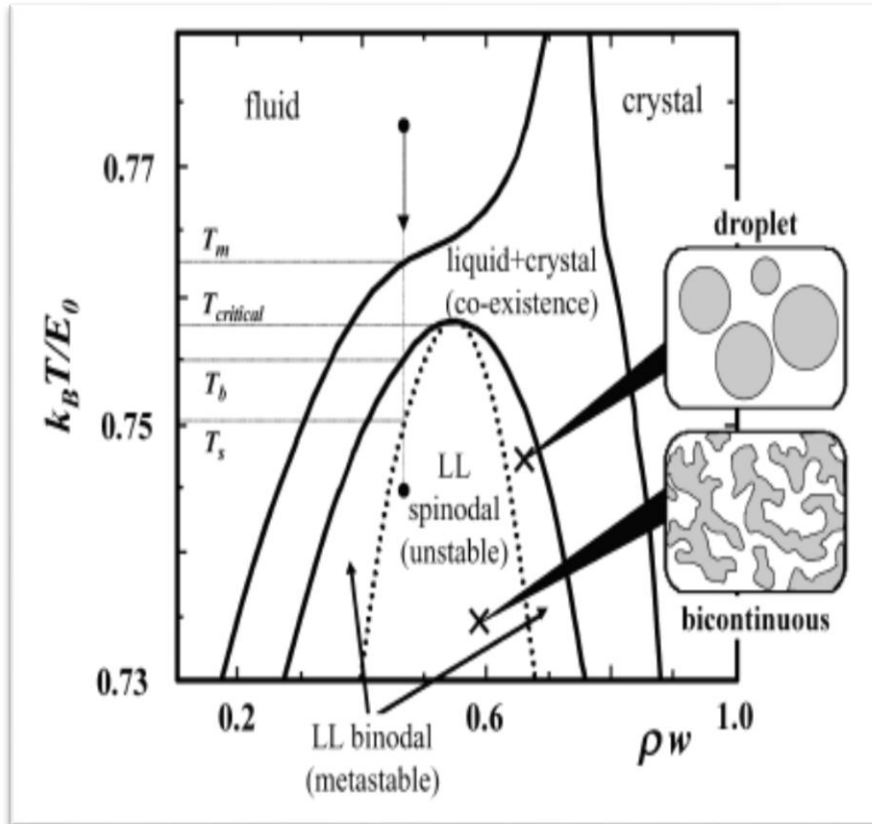Figure 2.7 *Generic phase diagram for a polymer melt proposed by Olmsted et al. Tm, Tb and Ts are respectively the melting, binodal and spinodal temperatures encountered along the quench path (constant density). The abscissa indicates the normalized density ρw, i.e. the average mass density of the melt multiplied by the specific volume of the monomer core* (Olmsted *et al.*, 1998; Kaji *et al.*, 2005).
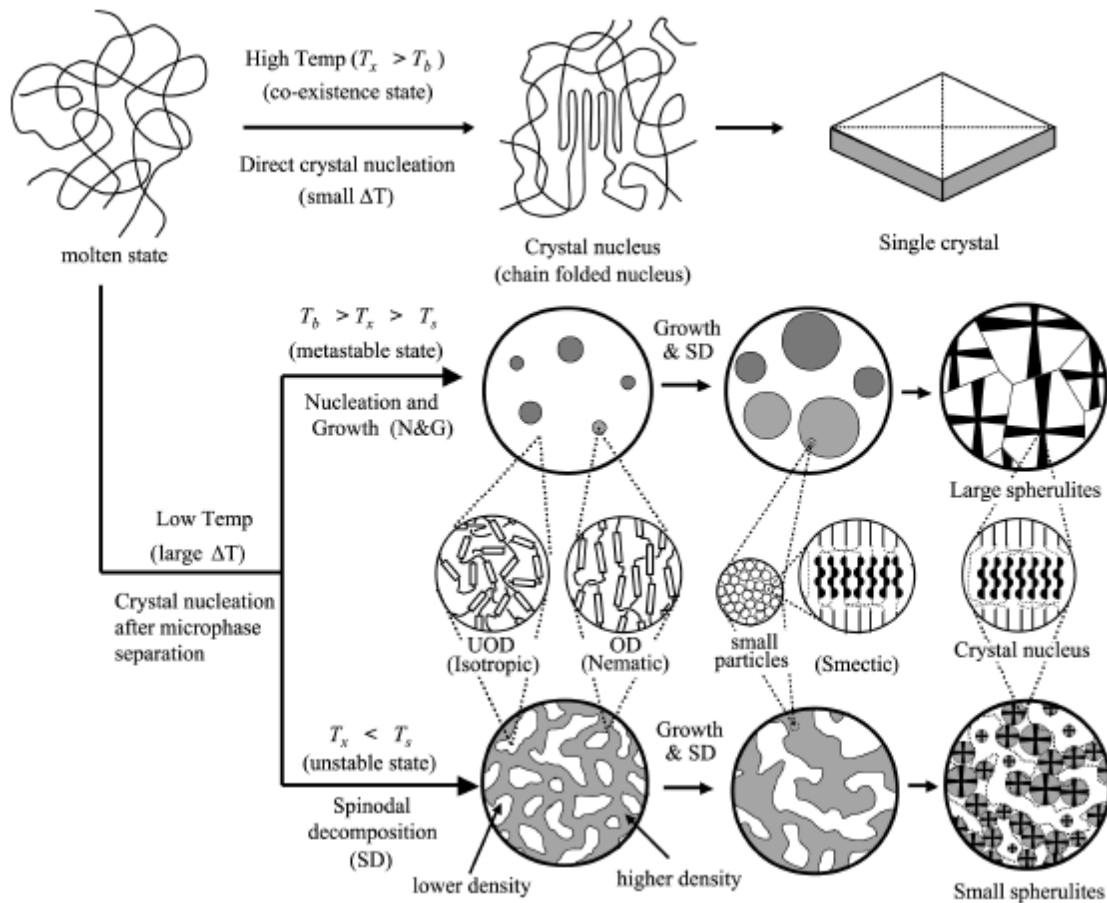
Fig. 2.8 : *Schematic general model for the crystallization mechanism :* (Kaji Wang, Hsiao and co-workers (Wang et al., 2000; Wang et al, 2001)

The above researchers have questioned about the basis of spinodal decomposition hypothesis, which lies on the observation of SAXS peaks before WAXD. The authors have emphasized that the problem in probing the early stage of crystallization is the weak signal from the small volume fractions of crystals. In particular, the study performed on fractioned isotactic polypropylene (iPP) has shown that SAXS is able to detect much lower level of crystallinity (~0.1%) than WAXD (~1%). This, of course, led to some questions about the validity of spinodal decomposition mechanism. However, in the opinion of Kaji et al. (Kaji et al., 2005) the results obtained on iPP depend upon the crystallization temperature, which is in the metastable region (binodal), such that no spinodal decomposition can occur. Synchrotron X-ray results of other authors (Ryan *et al.*, 1999; Heeley *et al.*, 2003), obtained for an i-PP system by means of a new position sensitive detector, showed an emergence of SAXS before WAXD supporting the thesis of spinodal mechanism.

Another hypothesis regarding the crystallization mechanism was defended by Strobl (Strobl, 2000), provoking a debate that involved Lotz, Cheng and Muthukumaru (Lotz, 2000; Cheng *et al.*, 2000; Muthukumar, 2000). The polymer crystallization is viewed by Strobl as a process which involves a few specific steps instead of a continuous spectrum of events. In particular the author proposed the following route: the first stage is a creation of a mesomorphic layer with a relative degree of order; this preoriented liquid crystalline zone spontaneously thickens in the second step up

to a critical value, followed by a transition which produces a planar array of block crystallites or "granular crystal layer"; in the final step a transformation of this granular crystal layer into homogeneous lamellar crystallites occurs (Fig. II.4).
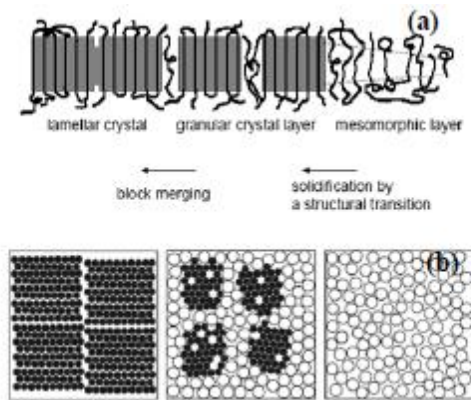
Figure II.4 (a) *Sketch of the route proposed for the formation of polymer crystallites. Stages passed through as reflected in the structural states found along a layer.* (b) *Sketch of the changes in the internal layer structure: liquid-like packing in the mesomorphic state (right), pattern of crystal blocks after the transition in the granular state (center), lamellar crystals with mosaic block structure (left)* (Strobl, 2000).

CHAPTER 3: EXPERIMENTS

3.1 Chemicals Used

The chemicals used in the present work along with their suppliers have been reported in table.

TABLE 3.1 Chemicals Used

Chemical	Supplier
High Density Polyethylene(HDPE)	Reliance Industries Ltd, India
Ultra High Molecular Weight Polyetylene(UHMWPE)	Reliance Industries Ltd, India
Polypropylene High MFI (PP HMFI)	Reliance Industries Ltd, India
Polyetylene Glycol (PEG)	Merck, Germany
Decaline	Lambort , India
Irgnox-1010	Aldrich Chemicals
Calcium Sterate	Aldrich Chemicals
Closite	Aldrich Chemicals

3.2 Instruments Used:

Following instruments were used during my project work & seized the opportunity to learn its use ability &MFI measurement, making of compressed moulded sheets etc, BussCo kneader for extrusion experiments etc during my work.

3.2.1 Melt Flow Index Tester

CEAST Computer operated Melt Flow Index Tester.

3.2.2 Extruder: BussCo Kneader Unit

BussCo Kneader Unit

3.2.3 Compression Moulding

3.2.4 : EXTRUSION OF HIGH DENSITY POLYETHYLENE (HDPE) ON LAB. BUUSCO-KNEADER:

Preparatory step of extrusion:

1. Reactive Processing:

 Batch preparation: Batch of 150 g HDPE comprising required quantity of UHMWPE (4M MW-RIL) along with required amount antioxidant (Irganox1010:1500-2000ppm), lubricant (Polyethylene glycol: PEG) & other additives were mixed together for making the formulation. However, hand mixing operation was repeated several times to ensure proper mixing. Once, material was ready, we go for extrusion.

2. Reactive Extrusion:

The extrusion of above prepared batch was carried out in a single screw   bench scale extruder of screw diameter 25 mm and L/D ratio 25:1.The temp. in the four zones of the barrel was maintained as required typically for the extrusion of HDPE containing entangled UHMWPE as an additive with an objective to improve melt strength as well as mechanical properties in presence of lubricant with or without high MFI –PP with lower conc.(2.5-5 wt%).More importantly, decaline is used here (5-15 %) as plasticizer to facilitate dispersion & melt compatibility between primary linear polyolefin matrix & UHMWPE under a typical temp. profile & rpm given below.

Z-1 : 170 ^{0}C ; Z-2 : 230 ; Z-3 : 250 ; & Z-4 (die zone) : 260; rpm : 90

Cutter rpm: 120

The optimum screw speed was found to be 90 rpm & same was maintained for all experiments. In all experiments normal dose of stabilizers (i.e. Irganox 1010: 1500-2000) were used along with Calcium stearate (CaSt)**:** 600ppm. Finally, the extrudates were used for characterization.

CHAPTER-4 : RESULTS & DISCUSSION

**4.1 Known technical insight for high melt strength Polyolefin:**

Due to the higher melting point, lower density, higher chemical resistance, and better mechanical properties of polypropylene (PP) in comparison to polyethylene (PE), it is widely employed for many industrial applications. However, the linear structure of L-PP limits its applications for processes where good extensional properties and melt strength are required such as thermoforming, film blowing, foaming and fiber spinning.
On the other hand, it is well known that branched polymers have enhanced extensional properties and their blending with linear counterparts can improve their elongational behavior. With the recent development of branched PP, it is expected that the elongational properties of L-PP can be effectively enhanced when blended with a LCB-PP are commonly introduced to linear PP via electron beam irradiation and post reactor chemical modification (Auhl et al., 2004; Tian et al., 2006a). Their effects on the processability have been reported in the literature (Gotsis et al., 2004; Stange and Münstedt, 2006). Gotsis et al. (2004) showed that branching up to an optimum level improved the process ability in foaming and thermoforming processes, while further branching did not have a dramatic effect.In several cases (Ajji et al., 2003; Stange et al., 2005; McCallum et al., 2007; Fang et al., 2008), the rheological behavior of blends of linear and branched polypropylene and polyethylene has been investigated. It has been reported that branched polymers exhibit higher shear thinning, elasticity, and strain hardening compared to linear ones.
Further, McCallum and coworkers (2007) realized that the blending of branched and linear PP not only promoted the melt strength, but the mechanical properties increased as well. Recently, Fang et al. (2008) concluded that an increase in the length of short branches and, possibly, the presence of a few long branches in metallocene LLDPEs and comparable MW-LDPE could improve the
Miscibility of LLDPE/LDPE blends.

Generally, PP cross linking reaction is based on a free radical formation & subsequent recombination of macro radicals. The ratio of macro radicals decaying from PP by recombination & fragmentation depends on, mostly, reaction temp., initiator concns & cross linking co agents. Various methods to crosslink PP melt have been studied by Chodak (1,17b) . Chodak suggest that the principal mechanisms involved in PP macro radical reaction are as follows:

- .A temp. rise increases the fragmentation probability because the activation energy of fragmentation is higher than that of recombination.
- High macro radical concentrations also leads to a higher rate of bimolecular recombination, compared to competing monomolecular scission.

Further, Borsig et.al investigated the role of a polyfunctional monomer such as Pentaerythritol tetraallyl ether, with peroxide, in raising the cross-linking efficiency of PP in the solid state at 170˚C. Polyfunctional monomer grafted to PP is an active site for trapping another macro radical and for formation of a cross-linked structure by connecting the chains. The reaction scheme is as follows.
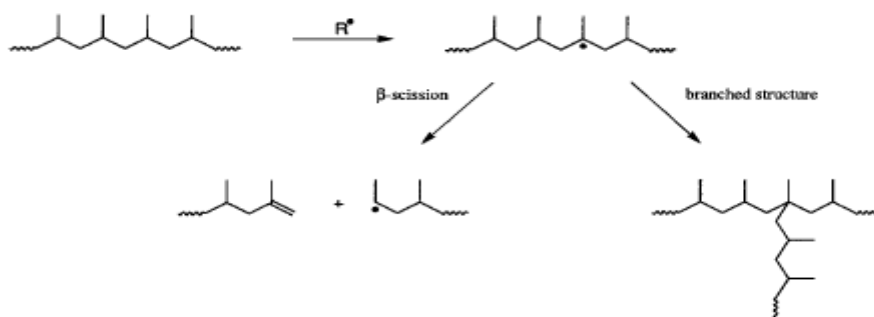
Practically, it would be possible to obtain a high degree of crosslinking by using a higher initiator concn but the high degree of fragmentation will lead to excessive degradation. Another procedure to increase the crosslinking efficiency is addition of cross linking agents. Different structure was depicted in Fig 4.1.
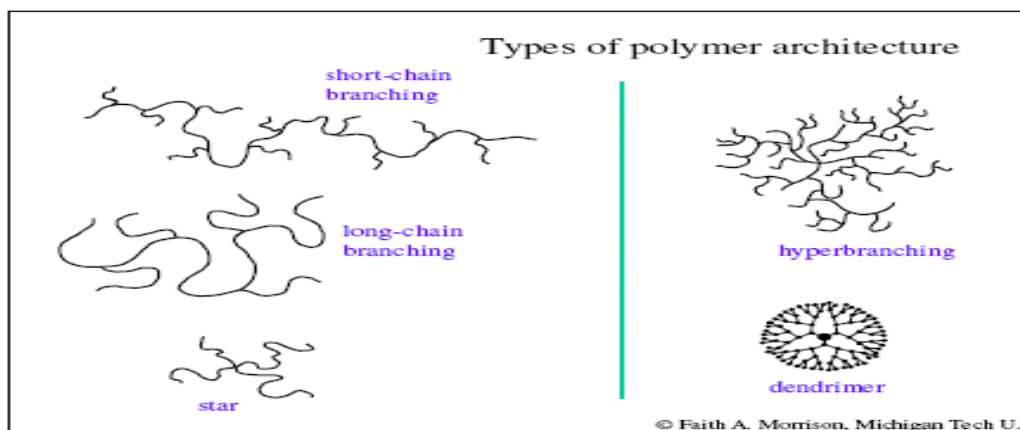
Fig. 4.1: Type of polymer architecture

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The widely accepted mechanism of long chain branch (LCB) formation, i.e. random macromer incorporation, conflicts with many of the experimental trends observed in polyethylene production. This includes the response of LCB to common reactor variables, the surprisingly high LCB incorporation efficiency, and in particular the effect of metallocene structure on LCB levels. Many metallocenes are known to produce comparatively high amounts of LCB, while others produce little or none. In contrast to expectations from the widely accepted mechanism, this frequently has little to do with the site's ability to incorporate comonomer. Instead, LCB and SCB (short chain branch) incorporation are found
to be relatively independent of each other.

These problems are addressed and a modification of the LCB mechanism is proposed, that is intra- versus intermolecular macromere incorporation. The ability of a metallocene site to incorporate LCB may be mainly determined, not by its ability to incorporate comonomer, but rather by its ability to coordinate and hold on to terminated macromer. Consistent with intramolecular LCB formation, no evidence was found in slurry polymerization experiments of cross-insertion between sites, i.e., the incorporation by one site of macromer produced from another site. This has implications for the predicted architecture of polyethylene
(eg: Y's, trees, Combs etc.)

4.2 Genesis & objective of current study:

Post modification approaches known so far restricts commercialization due to inherent process complication/limitation as well as cost factor.
More importantly, to the best of our knowledge, extensive studies were not carried out particularly to improve melt strength & mechanical properties using UHMWPE as an additive because of poor melt compatibility & dispersion with polyolefin matrix (**PP / HDPE**) during extrusion. This limitation is due to the high degree entanglement of UHMWPE. Therefore, a scheme was judiciously conceptualize for better compatibility/dispersion of UHMWPE using a suitable lubricant with option of singularly decaline/ High-MFI-PP or in combination .Also, the effect Closite in such formulation was evaluated to multiply the merits of formulation for meeting the objectives of the project goal.

Modification of polyolefin matrix with described approach is quite commercially challenging .Therefore sincere attempt was made to verify the concept & then to screen

/ scrutinize key components for optimum formulation where UHMWPE capable to act as additive for achieving desired melt rheological characteristics of HDPE after modification.

4.2 RESULTS & DISCUSSIONS:

Concept Verification for polyolefin matrix (PP / HDPE):

In current study attempt was made to modify polyolefin matrix here HDPE using UHMWPE as an additive in presence of a suitable lubricant & low doses of High MFI-PP with or without lower doses of decaline under optimum melt processing condition on a Busco-kneader to verify concept. Antioxidants are used to prevent thermal degradation along with normal doses of calcium stearate in the formulation. Experiments were planned & executed .Results were summarized in Table-4.1

Table 4.1 : Modification of HDPE with UHMWPE   (Trend-1)

Experiments	HDPE (g)	PP HMFI (g)	PEG (g)	Decaline (g)	UHMWPE (g)	Cloisite (g)	MFI(g/10mins) 230°C
PPS-0	150	-	-	-	-	-	19.453
PPS-1	150	5	1.0	-	25	-	7.868
PPS-2	150	10	1.50	25	50	0.25	1.536

Results shown in Table-1 clearly exhibited a decreasing trend of MFI but the MFI reduction is more pronounced in presence of high doses UHMWPE when Closite & decaline were present in the formulation. Interestingly in absence of Closite & decaline the decrease in MFI of modified sample was not very significant .Of course, amount of UHMWPE in this formulation was just half of PPS-2. Therefore, an expt need to be repeated using PPS-2 condition with 25 g UHMWPE particularly to verify the observation weather it's a fact or artifact. But right now, looking into the observation for PPS-2, probably MFI had reduced significantly as shown in Table-4.1 (trend-1) due to reduced chain entanglement of normal UHMWPE in presence of decaline which is the reflection in significant change in MWD & melt rheological properties of HDPE (PPS-2) after modification as compared to ref. sample PPS-0 as shown in Fig.4.1 . Perhaps Closite indirectly facilitates the disentangling and nucleation process collectively & cleverly to

show rise in crystallization temp & thereby to improve mechanical properties of compressed molded samples as shown in Fig.4.3 & Tab-4.1b
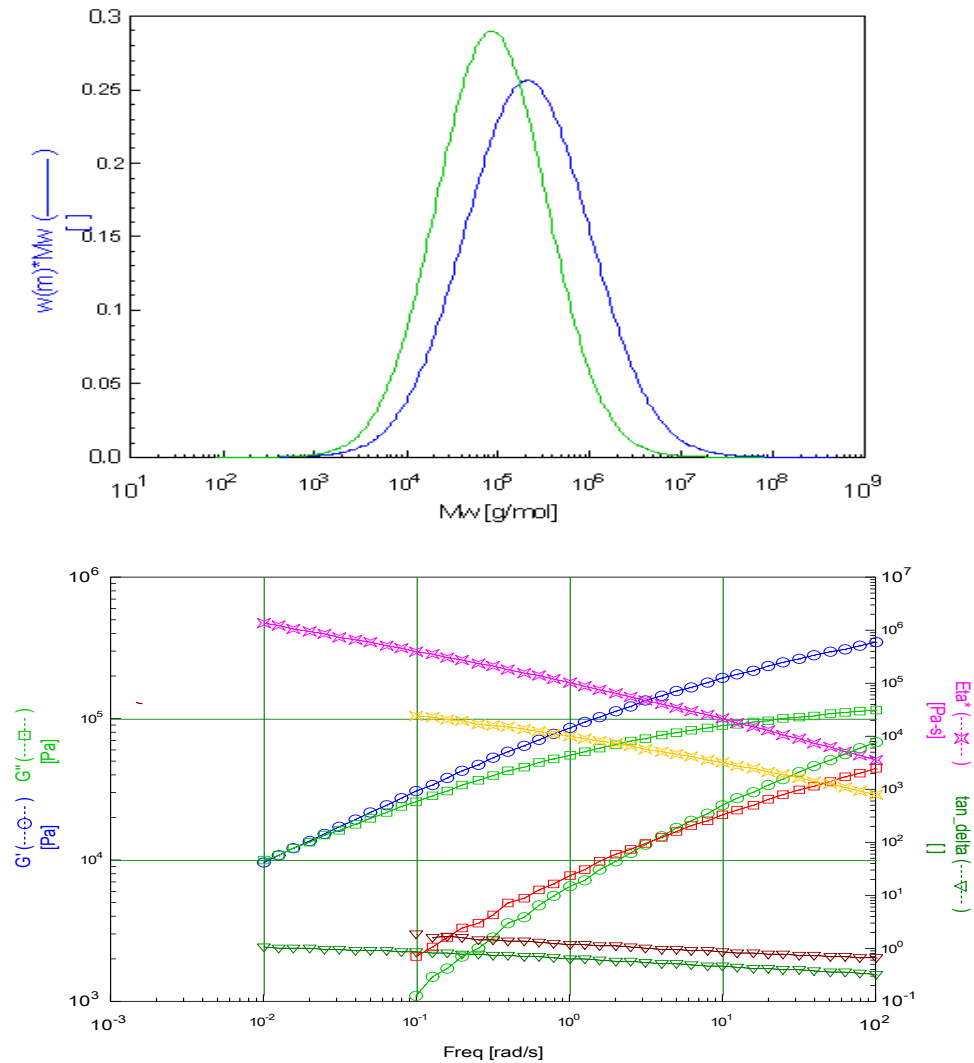

Fig4.2 : RDA Plots on frequency sweep: MWD; Melt viscosity, Tan delta & G'/G'' at 190 0C of PPS-0 & PPS-2

**4.2: Mechanical properties of compressed molded sheets**

Samples	Modulus kgf/cm2	Strength at yield kgf/cm2	Strength at break kgf/cm2
PPS-0	3233	92	0.21
PPS-2	4200	124	196

Compressed molded Sheets: Temperature: 175 0C & Pressure: 250-300 Kg, Fusion Time: 30 mint.

In all rheological plots , with uhmwpe , the complex viscosity curves became higgher than that of plain linear matrix homo-HDPE but interestingly .this shows degree of modification / branching which was facilitated by uhmwpe in presence of lubricant/plasticizer & closite respectively.There was also no evident of newtonian-plateau at low frequency & the shear thinning starts at lower frequency as compared to   the plain HDPE.These are typical characteristics of   polymers with long chain branching.

further it has been shown that the loss angle (tandelta) is independent of the frequency in a limited frequency range since polymer with lcb have the gel –like rheological behaviour.Moreover, with the lcb level increasing ,the plateau of delta decreases which is very significant with hdpe modified sample as shown in Fig. 4.2.
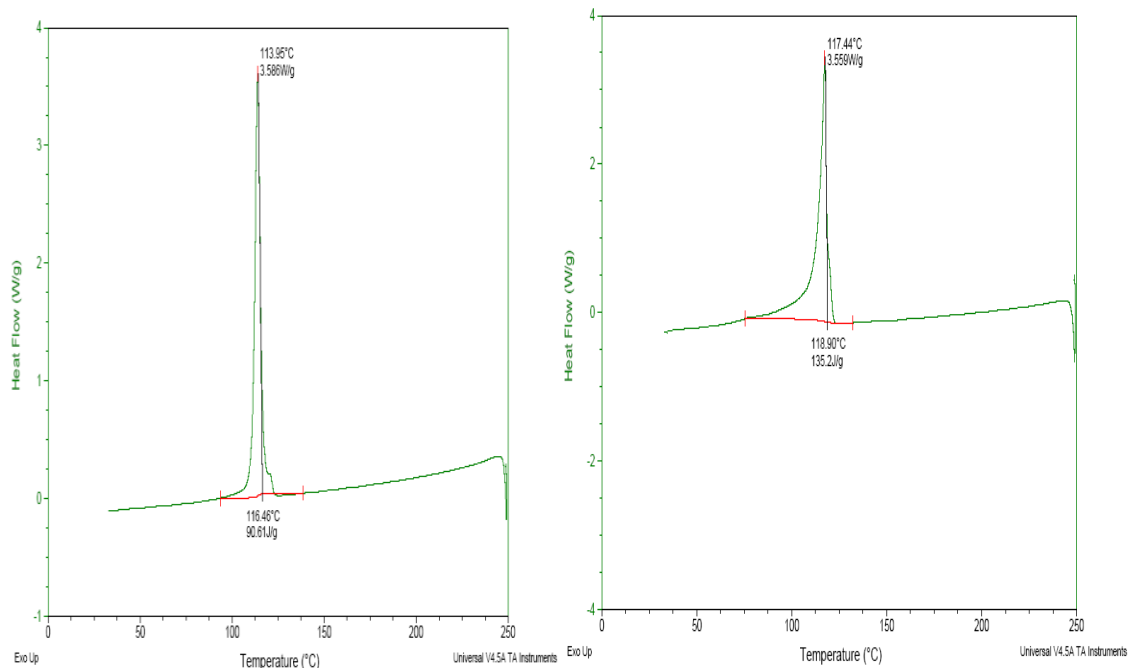
Unmodified HDPE (PPS-0; Tc 113 0C)   Modified HDPE (PPS-2; Tc: 1170C)

Screening of Components for optimum formulation:

In current study, an attempt was made to scrutinize effective component one after another. It was found that with & without decaline MFI had reduced to many folds as compared to reference & interestingly was almost same while other variables were fixed (PPS-3 & PPS-4) as shown in Table 4.2

Table 4.3: Modification of HDPE with & without Decaline (Trend-2)

Experiments	HDPE (g)	PP HMFI (g)	PEG (g)	Decaline (g)	UHMWPE (g)	Cloisite (g)	MFI(g/10mins) 230°C
PPS-0	150	-	-	-	-	-	19.453
PPS-3	150	5	1.0	-	50	0.25	0.492
PPS-4	150	5	1.0	20	50	0.25	0.477
PPS-5	150	5	1.0	20	50	1.0	0.518

Further, It was found that presence of UHMWPE influenced to reduce MFI significantly in presence & ABSENCE of HMFI-PP but without this lower MFI was achievable (PPS-8) by choosing a combination of PEG & Closite with optimum composition as shown in Table-3.The trend-3 characteristic is worth verifying.

Table-4.4: HDPE Modification With & without HMFI-PP (Trend-3)

Experiments	HDPE (g)	PP HMFI (g)	PEG (g)	Decaline (g)	UHMWPE (g)	Cloisite (g)	MFI(g/10mins) 230°C
PPS-0	150	-	-	-	-	-	19.453
PPS-6	150	5	1	-	25	0.25	1.20
PPS-7	150	-	1	-	25	0.25	1.25
PPS-2	150	10	1.50	25	50	0.25	1.536
PPS-8	150	-	3	25	50	0.25	0.530

Another trend-4 was planned / initiated to understand the effect of Closite in a batch formulation. It was found that without Closite & decaline, UHMWPE does not show aggressive effect on improving melt characteristics of HDPE rather MFI showed increasing trend as shown in Table-4 (PPS-9). Even alone Closite in absence of decaline was found effective in reducing MFI profoundly with UHMWPE as clear in Table-4.4 (Sample-PPS-6).

Table-4.5 : HDPE Modification With & without Closite (Trend-4)

Experime nts	HDPE (g)	PP HMFI (g)	PEG (g)	Decaline (g)	UHMWPE (g)	Cloisite (g)	MFI(g/10mins) 230°C
PPS-0	150	-	-	-	-	-	19.453
PPS-6	150	5	1	0	25	0.25	1.20
PPS-9	150	5	1	0	25	-	23.68
PPS-2	150	10	1.50	25	50	0.25	1.536
PPS-10	150	10	1.5	25	50	-	0.955

However, Closite was found to be important filler as nucleator to regulate the melt characteristics of HDPE of course with an indispensible role of UHMWPE as an additive during post modification process.

This study indeed prompt us to screen & quickly optimize few formulations as summarized in Table-5.It was observed that in all cases MFI had reduced significantly whereas melt viscosity also proportionately increased as shown in Table-4.6 .Results also indicates that decaline can be an option but not indispensible in order to tailor macromolecular structure of linear polyolefin matrix & thereby to achieve target melt rheological characteristics ultimately to qualify as niche grade polyolefin. **Interestingly, melt viscosity of modified samples were found to be increased to many folds as compared to plain sample. This is worth verifying for its reproducibility.**

Table-4.6: Modification of HDPE using screened components

Experime nts	HDPE (g)	PP HMFI (g)	PEG (g)	Decaline (g)	UHMWPE (g)	Cloisite (g)	MFI(g/10 mins) 230°C	MV at 230 °C
PPS-0	150	-	-	-	-	-	19.453	1878
PPS-4	150	5	1.0	20	50	0.25	0.477	75907
PPS-11	150	5	1	0	50	0	0.577	114095
PPS-12	150	5	0	-	50	0.25	0.315	140060
PPS-13	150	5	3.5	-	50	0.25	0.253	141884

Finally, It was successfully demonstrated that UHMWPE could be a potential additive to enhance melt strength of polyolefin (PP or HDPE) & to improve mechanical properties of

compressed molded sheet. In the long run, this could be an commercial outlet for polyolefin family to be tagged as niche grade wide spectrum products as summarized in Table-4.1a & in page-46.The same table is shown below.

Table 4.7: Mechanical properties of compressed molded sheets

Samples	Modulus kgf/cm2	Strength at yield kgf/cm2	Strength at break kgf/cm2
PPS-0	3233	92	0. 21
PPS-2	4200	124	196

Compressed molded Sheets: Temperature: 175 0C & Pressure: 250-300 Kg, Fusion Time: 30 minute.

CHAPTER 5: SUMMARY & CONCLUSIONS:

The characteristic properties of macromolecules—great length, large anisotropy and high segmental flexibility—give rise to a complex structural organization and to unique properties.

UHMWPE is a linear structure with excellent overall performance thermoplastic Engineering plastics. UHMWPE molecular weight of about 3.5 million to 8 million, due to high molecular weight with the other plastic unparalleled excellent impact resistance, wears resistance, self-lubrication, and resistance to chemical corrosion properties. Moreover, UHMWPE low temperature performance, -40 ℃, remains in the high impact strength, even at -269 ℃ to use.

Excellent physical and mechanical properties of UHMWPE to make it widely used in machinery, transportation, textile, paper, mining, agriculture, chemical industry and areas such as sports equipment, of which large containers and pipelines on the most widely used. In addition, since UHMWPE excellent physical inertia, has been circulated as heart valves, orthopedic surgery parts, artificial joints used in clinical medicine.
Because the viscosity of molten UHMWPE up 108Pa * s, poor liquidity, its melt index is almost zero, it is difficult to use in general mechanical processing method for processing. In recent years, UHMWPE processing Technology has been rapid development, through the transformation of ordinary processing equipment has led to UHMWPE from the initial repression - sintering development of extrusion, blow molding and injection molding, and other special methods of molding.

Due to high degree entanglement & extremely high melt viscosity dispersion & melt compatibility of UHMWPE in polyolefin matrix is very difficult & therefore it is challenging to introduce a concept of meeting these properties for ease processability of UHMWPE with polyolefin for making niche grade products.

Conceptually, it was successfully demonstrated that UHMWPE could be a potential additive for making niche grade Polyolefin (here, HDPE) product using suitable lubricant alone or in combination with plasticizer decaline at lower doses in the formulation. Closite on the other hand could improve the merits of such formulation. However, following conclusions were drawn from this current study.

- Concept was verified & established
- UHMWPE can be a potential additive for making niche grade polyolefin (HDPE /PP) products which has been successfully demonstrated in current study.
- Conceptually open up outlets for oriented products via melt processing
- Observed significant reduction in MFI (>10 folds) after modification of HDPE & consequently melt viscosity enhanced significantly (>10 folds)
- Melt Rheological properties namely, melt viscosity, G' & G", Tan delta etc. after modification distinctly differentiates from plain HDPE.
- Broadening in MWD was quite distinct after modification of HDPE
- Exhibited improvement in dispersion & melt compatibility of UHMWPE in HDPE matrix
- Closite in presence of UHMWPE facilitates nucleation & thereby crystallization temp (Tc) increased to4-5 0C as compared to plain HDPE.
- Compressed molded sheet showed improvement in mechanical properties.

CHAPTER 6: FURTHER SCOPE OF STUDY:

There is further scope of investigation .Some of them are worth pursuing to establish outlet for commercialization.

- Choice of polyolefin matrix to act   UHMWPE as smart additive.
- Choice & scrutinization of lubricants
- Mechanistic study of polyolefin modification with UHMWPE
- Rheology insight of modified polyolefin
- Screening of fillers for polyolefin modification

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