RHEOLOGY AND PROCESSING OF NANOCLAY LOADED POLYETHYLENE RESINS

by

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ABSTRACT

Several compounds were prepared by melt mixing various formulations of a linear low density polyethylene, a graft modified polyethylene and an organically modified clay, in a twin screw extruder. X-ray diffraction, transmission electron microscopy and rheology were used to characterize the extent of intercalation of the silicate galleries. Incorporation of minimum weight fraction of 2% clay and 50% maleated polyethylene was found to introduce radical changes in the rheological behaviour of the nanocomposites. Broadening peaks in X-ray diffraction indicated increasing dispersion of silicate nanolayers inside polymer as a function of graft modification. With higher incorporation of maleated polyethylene, solid-like response begins to appear at low frequencies indicating possible networking. Flow activation energy was found to decrease with incorporation of clay. Dual flow behaviour of the nanocomposites beyond the Newtonian plateau in the form of a filler-like flow at low shear rates and polymer-like shear thinning flow at high shear rates was observed. Changes in flow energy of activation with respect to clay and fusabond concentration are analysed. Relaxation spectra determined using a parsimonious model were found to extend to higher relaxation time scales with exfoliation. The Cox-Merz rule was found to fail over the whole range of shear rates for exfoliated compounds, indicating increased interactions in the matrix resulting in highly anisotropic distribution of individual silicate layers. Fusabond induces higher elasticity into the composite and increases the tensile stress growth function during melt elongation. Fusabond exhibits highly ductile failure as opposed to the brittle failure of polyethylene. Hence, fusabond is observed to contribute towards the ductility of the nanocomposite. A combination of fusabond and clay was found to be complementary in initiating strain hardening. The mechanical properties of the nanocomposites did not show an impressive change at low clay concentrations. A unique dip at 0.1 wt% clay loadings to complement its role in processing was followed by a steady increase with increasing clay concentration. While fusabond and higher levels of clay accounted for the increased toughness of nanocomposites, 0.1 wt% of clay decreased the toughness. There exists a threshold level of clay concentration above which the intercalation and exfoliation phenomena play a significant role in enhancing the mechanical properties.
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CHAPTER 1

INTRODUCTION TO POLYMER-NANOTECHNOLOGY

The extraordinarily large surface area of nanoparticles presents diverse opportunities to introduce different reactive functionalities on their surface. Further, nanoparticles present an unique opportunity to devise and control strategies to modify their internal structure, morphology, shape and compositions and thus an ability to alter and achieve the desired properties in innovative applications and develop products to suit levels of performance that were otherwise underachieved by conventional fillers. The nanoparticles could be hollow, lobed, filament, magnetic or conductive. They may be functionalized to accommodate buffering properties or in-situ changes in shape and size with variable ambient pH or interact with biological entities. From more than a single perspective, nano-bio technology is calling!

The past decade has witnessed several attempts to extend the largely inorganic material nanotechnology into the vast realm of organics. A part of the primary efforts is to combine nanoparticles with organic polymers by making use of their ability to be functionalized. Such efforts to organically compatibilize nanoparticles have been largely successful thus opening the door for polymer nanotechnology. The present thesis work is intended to research the possibilities of effectively introducing stacks of nanolayers into polyethylene that belongs to polyolefin group, unarguably world's the most popular class of plastic material. The study aims at pragmatic user end applications and hence nanosilicates are chosen for polyethylene considering economic viability of process conditions in mass production.

This section introduces the reader to the evolution of nanocomposites, previous work, types of materials used and the experimental approach to the study.

1.1 Polymer as a matrix

Polymers are ubiquitous materials in various forms such as plastics, rubbers, fibres etc. Certain properties of polymers limit their applications. Such limitations are overcome by the addition of fillers that introduce strength and performance at various
temperatures, environments and other testing conditions. A matrix of polymer and reinforcement was developed as an alternative for perishable metals in response to rising demand for strong materials from aviation sectors for military applications during World War II. Initial innovations led to Fibre Reinforced Plastics (FRP) that were mostly made up of non-recyclable thermosets. Conventional inorganic fillers and fibres (e.g. glass, carbon, aramid etc.) and particulate solids (e.g. talc, carbon black, calcium carbonate, mica etc.) need to be accommodated at 30-40 wt% to achieve the desired high mechanical properties and such proportion of external material also introduces negative features into the polymer. Optical clarity, surface gloss made way for haziness and moisture streaks resulting in processing difficulties and appalling aesthetics. The high filler content resulted in high density and increased part weight. Processing screws needed to be specially redesigned to achieve a fair level of uniformity and consistent stress distribution in highly filled polymer and this lead to complications during processing e.g. degradation or pressure build up in the extruder. The product obtained could consist of stress concentration points that were prone to sudden failures.

1.2 Introduction of nanofillers and evolution of nanocomposites

A solution to all these shortcomings would be to reduce the size of the reinforcing component and incorporate it into the polymer matrix on nano scale. Incorporation of only 2-5 wt% of nano-dimensional fillers was found to achieve the desired enhancement in properties and eliminate the disadvantages associated with incorporating conventional fillers (Giannelis, 1996). Nanofillers are inorganic particles confined to nano-dimensions. Nanofillers can be classified as (Galgali, 2003)

- Symmetric nanoparticles e.g. cadmium sulphate
- Asymmetric 2-dimensional nanofillers e.g. layered nanoclays
- Asymmetric 1-dimensional nanofillers e.g. carbon tubes

The present work involves nanoclays. Nanoclays are two-dimensional nanometer thick platelets that are stacked up in layers about one nanometer apart. Because of their asymmetric nature and two-dimensional structure, nanoclays provide two-dimensional reinforcement. Due to their layered organizations in nanoscale dimensions, the surface area of nanoclay exceeds that of conventional fillers by orders of magnitude and hence
only a small amount of filler content suffices to achieve the desired target that requires much more quantity of conventional fillers. As a result, the density of the compound is not altered significantly. The system formed by dispersion of two-dimensionally arranged nanoclay sheets into the polymer matrix is generally referred to as Polymer Layered Silicate (PLS) nanocomposites.

### 1.3 Polymer Layered Silicate (PLS) nanocomposites

The layered silicates have an ability to disperse into individual layers and to fine-tune their surface chemistry through ion exchange reactions with organic and inorganic cations (Ray and Okamoto, 2003). These strong interactions between the polymer and the layered silicate in PLS nanocomposites lead to the organic and inorganic phases being dispersed at the nanometer level.

PLS nanocomposites are of enormous interest to researchers thanks to enormous improvements over conventional micro and macro-composites or virgin polymer in terms of high moduli (Giannelis, 1996; Giannelis et al., 1999; Biswas and Sinha, 2001; Ray and Okamoto, 2003), increased strength and heat resistance (Giannelis, 1998), decreased gas permeability (Messersmith and Giannelis, 1995; Bharadwaj, 2001) and flammability (Gilman, 1997; Gilman et al., 2000) and increased biodegradability of biodegradable polymers (Sinha et al., 2002). They are also a matter of interest in theoretical work simulating preparation of these materials (Vaia et al., 1995; 1997(28); 1997(30)); Ginsburg et al., 2000), and are considered to be model systems to study structure and dynamics of polymers in confined environments such as galleries (Krishnamoorti et al., 1996; Hackett et al., 1998; Manias and Kuppa, 2001; 2002; Anastasiadis et al., 2000). Although it has been long known that polymers can be intercalated with modified clay minerals and synthetic clays (Theng, 1974; 1979), polymer/clay nanocomposites gained momentum recently due to two major findings: the report of a nylon-6/montmorillonite material from Toyota research (Kojima et al., 1993), where very moderate inorganic loadings resulted in concurrent and remarkable enhancements of thermal and mechanical properties and the feasibility to melt-mix polymers with clays without the use of organic solvents (Vaia et al., 1993).
Layered silicates can be of two types - tetrahedrally substituted and octahedrally substituted. In tetrahedrally substituted layered silicates, the negative charge is located on the surface of the silicate layers that make the polymer matrix more interactive than the octahedrally substituted layered silicate. Montmorillonite, hectorite and saponite are the most widely used layered silicates.

Pristine layered silicates normally consist of hydrated Na\(^+\) or K\(^+\) ions and so, are miscible only with hydrophobic polymers, poly(ethylene oxide) - PEO (Aranda and Ruiz-Hitzky, 1992) or poly(vinyl alcohol) - PVA (Greenland, 1963)). To make them miscible with other polymers and thus impose intercalation, one can conduct ion-exchange reactions with cationic surfactants including primary, secondary or tertiary and quaternary alkylammonium or alkylphosphonium cations that transform the surface organophilic, lower the surface energy of the inorganic host and improve the wetting characteristics of the polymer matrix and result in a larger interlayer spacing. Such silicates are called Organically Modified Layered Silicates (OMLS).

Recent advances in polymer/clay and polymer/layered-silicate nanocomposite materials (Giannelis et al., 1999; Alexandre et al., 2000) have inspired efforts to disperse clay based fillers in almost any polymer available, usually with an expectation that complete exfoliation of the inorganic fillers in the polymer would yield the best performing systems. This is normally achieved by smart in-situ polymerization methods. However, due to wider availability and easier processability, melt intercalation in a twin screw extruder is utilised by many researchers to achieve reasonable exfoliation by using modified silicate and the polymer. Various polymers were used to prepare nanocomposites using layered silicates. These include vinyl polymers (e.g. PMMA, acrylates, PS, PTFE, PVA, PEG, polyamides), condensation polymers (e.g. poly(ε-caprolactone), PET, PBT, PC, poly(dimethyl siloxane), polybutadiene copolymers, IPR, EPR, phenolic resins, PU, fluoropolymer), polyolefins (PP, PE oligomers, EVA, EPDM) and some speciality polymers. Extensive study has been done using polyamide-12 (Aubry et al., 2005), polyamide-6 (Ayyer and Leonov, 2004; Fornes et al., 2004; Park et al., 2005) and polypropylene (Galgali et al., 2001; Manias et al., 2001; Lele et al., 2002; Wang et al., 2003).
Best enhancement in properties is achieved when the polymer succeeds in squeezing into the silicate galleries and scatters the individual nanolayers of silicates, thus creating an isotropic distribution, which is known as "exfoliation". Such exfoliated nanocomposites can be used in revolutionary applications viz defence, aviation, food and biological applications. Moreover, exfoliated polymer-nanoclay composites are known to exhibit superior mechanical, optical, thermal and barrier properties (Giannelis, 1996). If the polymer molecules are squeezed into the silicate galleries, thus increasing the intergallery distance considerably but not scattering the layer structure, such a phenomena/situation is called "intercalation".

It is imperative to thoroughly intercalate or exfoliate silicate galleries inside the polymer matrix to achieve the desired enhanced properties. It could be facilitated by ion exchange reactions with cationic surfactants by which the hydrophilic silicate is modified to become organophilic and the cohesive forces among the clay platelets are decreased; and by introducing an organophobic block at the tail of the polymer chain (Ray and Okamoto, 2003). Intercalation is favoured in tetrahedrally substituted silicates such as montmorillonites rather than octahedrally substituted silicates since the negative charge in the former is located on the surface of the silicate layers (Ray and Okamoto, 2003). Additionally, dispersion of silicate structures inside the polymer requires favourable enthalpic contribution to compensate for the entropic penalties originating from lack of conformational freedom (Giannelis et al., 1999). Sufficient excess enthalpy could be generated in polar polymers facilitating nanocomposite formation, but this is not a possibility in the case of highly non polar polymers such as polyethylene. In such cases, graft modified polymers containing pendant succinic maleic anhydride groups facilitate exfoliation of silicates (Galgali et al., 2001; Gopakumar et al., 2002).

There are several methods to blend polymer and clay. Some of these techniques such as in situ polymerization and solution polymerization are efficient in dispersing silicate layers (Ray and Okamoto, 2003). They are too expensive to be commercialized and also involve many organic solvents. It is widely accepted that twin screw melt compounding is an environmental friendly and economic alternative. Limited literature is available on polyethylene nanocomposites (Gopakumar et al., 2002; Kato et al. 2003). Our interests in this work lie in investigating the rheological significance of incorporating
graft modified polyethylene in the formation of polyethylene nanoclay composites in a systematic manner. This study also aims at studying the levels of graft modification required to make a significant difference to exfoliate minimum levels of clay by studying their rheological aspects. Another aspect of the study is to observe the influence of organically modified nanoclay as a processing additive in eliminating the instabilities during melt flow.

Focus of our work is on the rheological characterization of polyethylene-nanoclay composites. Polyethylene is among the most widely used polymers and clay is a readily available benign economic mineral. Rheology - the science of flow and deformation of matter is known to be a sensitive tool in identifying and/or detecting microstructural changes such as crystallinity, long chain branching, molecular weight distribution and relaxation of polymer chains in the confinement of silicate galleries (Giannelis et al., 1999). Rheological experiments determine the viscoelastic moduli (viscous and elastic) that can be used as probes in monitoring microstructural changes with dispersion kinetics. X-ray diffraction (XRD) is an indirect tool to distinguish the phase separated and intercalated states by estimating the inter-gallery distance. Transmission electron microscopy (TEM) is another powerful characterization technique to visualize the extent of intercalation or exfoliation with respect to the fraction of graft modification and clay. In this study, we make use of the above techniques to study the effects of graft modification and dispersion of organically modified clay on the rheological properties of polyethylene, more specifically to understand the interactions between the clay particles and graft modified polymeric molecules that lead to intercalation and to exfoliation; the quantities by proportion of these materials needed to be added to achieve significant effects on the rheological properties of polyethylene. Furthermore, the effects of the addition of nanoclays on the processibility of polymers are examined by using capillary flow. It is of particular interest to see whether or not flow instabilities such as melt fracture can be eliminated in the presence of small amounts of nanofillers (Hatzikiriakos et al., 2005). Extensional rheological study and the tests for mechanical properties complement the study of flow.
CHAPTER 2

REVIEW OF POLYMER-NANOCLAY TECHNOLOGY

This chapter describes the structure of nanoclays, preparation of nanocomposites, morphologies of nanocomposites, advantages of nanocomposites, thermodynamics of nanocomposites, rheology of nanocomposites, polymer processing instabilities and processing aids used to overcome these instabilities. The available literature and progress in these research topics are discussed.

2.1 Silicates

Silicates are naturally occurring minerals that constitute large part of sediments, rocks and soils. Approximately 30% of all minerals are silicates and some geologists estimate that 90% of the Earth's crust is made up of silicates. The basic chemical unit of silicates is the (SiO₄) tetrahedron shaped anionic group with a negative four charge (-4). The central silicon ion has a charge of positive four while each oxygen has a charge of negative two (-2) and thus each silicon-oxygen bond is equal to one half (1/2) the total bond energy of oxygen. This condition leaves the oxygen molecules with the option of bonding to another silicon ion and therefore linking one (SiO₄) tetrahedron to another and another and so on.

Silicates are classified on the basis of their structure and the most commonly used clay in nanocomposite applications is a subclass called phyllosilicates which is characterized by sheet structures. These are aluminosilicates found as large mineralogical deposits. They are also commonly known as layered silicates since their structural framework consists of Al octahedral and Si tetrahedral layers, joined together in varying proportions and stacked on top of each other. In this subclass, rings of tetrahedrons are linked by shared oxygens to other rings in a two dimensional plane that produces a sheet-like structure. Typically, the sheets are then connected to each other by layers of cations. These cation layers are weakly bonded and often have water molecules and other neutral atoms or molecules trapped between the sheets. This explains why this subclass produces very soft minerals such as talc, which is used in talcum powder. Some
members of this subclass have the sheets rolled into tubes that produce fibers as in asbestos serpentine. The silicon to oxygen ratio is generally 1:2.5 (or 2:5) because only one oxygen is exclusively bonded to the silicon and the other three are half shared (1.5) to other silicons. The symmetry of the members of this group is controlled chiefly by the symmetry of the rings but is usually altered to a lower symmetry by other ions and other layers; but the overlying symmetry of the silicate sheets will usually still be expressed in a higher pseudo-symmetry. The typical crystal habit of this subclass is flat, platy, book-like and most all members display good basal cleavage. Although members tend to be soft, they are remarkably resilient. Members of this group are often the last to chemically breakdown in erosional and weathering processes and thus constitute a significant amount of soils and fine grained sedimentary rocks. This group is also generally tolerant of high pressures and temperatures and they make-up a large part of metamorphic rocks.

Aluminosilicate condensates in 2:1 ratio of tetrahedral Si sheets with an octahedral Al sheet are called 2:1 phyllosilicates. Coupling of only one Si sheet to one Al sheet gives rise to 1:1 phyllosilicates called kaolinite. In many phyllosilicates either Al$^{3+}$ or Si$^{4+}$ ions are isomorphically substituted partially by lower valency metal cations of similar sizes like Mg$^{2+}$ and Fe$^{2+}$. The type of the cation occupying the tetrahedral and octahedral sites is dependent on the ionic size and coordination rather than the valency. Phyllosilicates are categorized broadly depending on the type and location of these substituted lower valency cations as 1) Trioctahedral, in which all Al$^{3+}$ in the octahedral sites are substituted by lower valency cations, e.g., three Mg$^{2+}$ cations replace two Al$^{3+}$, and 2) Dioctahedral, in which two-thirds of the Al ions are substituted by the lower valence cations.

The isomorphic substitution gives rise to a deficiency of positive charge. This deficiency is balanced by the sorption of external cations such as alkaline earth ions (e.g. Ca$^{2+}$) or alkali metal ions (e.g., Na$^+$). The unit cell of smectite clay comprises of eight silica tetrahedrons and six alumina octahedrons. The charge per unit cell ranges from 0 to 2 depending on the extent of the type and the extent of the substitution. Apart from the external cations balancing the charge deficiencies, water is also present in the interlamellar space. It may associate with the cations, forming hydration shells around them.
The deficiency of positive charge on the layers of smectites is intermediate between the end member mica and the starting pyrophyllite groups of phyllosilicates. The externally sorbed mobile hydrated cations, which balance the positive charge deficiency, can be replaced with other cations by simple ion exchange methods. The ability to exchange cations, usually referred to as the Cation Exchange Capacity (CEC), distinguishes smectites from other phyllosilicates, which do not have any ion exchange ability. These cations can be exchanged with suitable organic cations to make silicate surface more organophilic.

The clay minerals are a part of a general but important group within the phyllosilicates that contain large percentages of water trapped between the silicate sheets. Most clays are chemically and structurally analogous to other phyllosilicates but contain varying amounts of water and allow more substitution of their cations.

Clay minerals are divided into four major groups. These are the important clay mineral groups:

- The Kaolinite Group
- The Montmorillonite/Smectite Group
- The Illite (or the clay-mica) Group
- The Chlorite Group

Most widely used smectite clay in polymer nanocomposites is montmorillonite due to its easy availability and lower cost. The mineral montmorillonite's chemistry is \((\text{Na, Ca})(\text{Al, Mg})_6(\text{Si}_4\text{O}_{10})_3(\text{OH})_6 - n\text{H}_2\text{O}, \) Hydrated Sodium Calcium Aluminum Magnesium Silicate Hydroxide (Papke, 1970). Montmorillonite is a dioctahedral 2:1 phyllosilicate and has silica tetrahedrons having oxygen and hydroxyl ions tetrahedrally arranged around central \(Si\) atoms. The base of the tetrahedron is made up of oxygen atoms while the hydroxyl group makes up the tip of the tetrahedron and is fused with the aluminium octahedron. The aluminum octahedral sheet has \(\text{Al}^{3+}\) ion octahedrally coordinated to the hydroxyl groups. Two third of the \(\text{Al}^{3+}\) ions are substituted by lower valency cations such as \(\text{Mg}^{2+}\) and \(\text{Fe}^{2+}\) in octahedral sites as shown in Figure 2.1.
Montmorillonite is further classified into different chemical varieties depending on the isomorphic substitution as: 1) Bentonite, where $Al^{3+}$ is substituted for $Si^{4+}$, and 2) Nontronite, in which $Fe^{2+}$ substitutes $Al^{3+}$. Montmorillonites have a highly asymmetric structure, in which each two dimensional aluminosilicate platelet or clay layer is about 0.95-1.3 nm thick and about 500-1000 nm in lateral dimensions. For nanoclays, an aspect ratio may be defined as $D/t$, where $D$ is the average platelet diameter and $t$ is the thickness of either individual platelet or a stack of platelets (called tactoids). For montmorillonite, the aspect ratios are as high as 1000 for individual platelets and 300-500 for tactoids. The clay is white-pale yellow in colour. An interlamellar space or gallery of about ~1 nm separates these platelets. Consequently montmorillonite has a large surface area of about 700-800 m$^2$/g. It has a high CEC of 70-150 meq/100g for a comparatively lower isomorphic substitution of ~0.25-0.6. The successive layers in montmorillonite are more randomly stacked compared to pyrophyllites. These structural features endow montmorillonite with peculiar swelling properties and allow a wide range of moieties to be intercalated. A SEM image of montmorillonite is shown in Figure 2.2.
Apart from montmorillonite, other types of layered silicates both naturally occurring (e.g. vermiculite) and synthetic clays (e.g. hectorite) have been used for making polyolefin nanoclay composites. Tjong et al (2002) have used vermiculites for preparing polypropylene nanocomposites. Vermiculite is a dioctahedral smectite clay. The $\text{Al}^{3+}$ and $\text{Si}^{4+}$ ions are partially substituted by $\text{Fe}^{2+}$ and $\text{Mg}^{2+}$ respectively. The extent of this isomorphic substitution is greater compared to montmorillonite and much of this substitution occurs in the $\text{Si}$ tetrahedral sheet.

Tudor et al (1996) have prepared PP nanocomposites, using Laponite by in-situ polymerization method. They envisaged these clays to support the polymerization catalyst. The basic unit structure consists of a magnesium oxide octahedral layer sandwiched between two tetrahedral silica layers. The CEC of about 60-70 meq/100g arises from isomorphic substitution of $\text{Li}^+$ for $\text{Mg}^{2+}$.

### 2.2 Preparation of polymer-nanoclay composites

In this section, the various ways used to prepare/synthesize polymer-nanoclay composites are reviewed. In general, there are four different methods discussed in detail below (Galgali, 2003).

#### 2.2.1 Sol-gel process

The sol-gel process involves hydrolysis and polycondensation of metal alkoxides $\{\text{M(OR)}_n\}$ in aqueous acid or base, to form an inorganic gel network in an organic polymer matrix.
Most of the efforts in this method have been concentrated on metal organic alkoxides, especially tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS), since they can form an oxide network in an organic matrix. The mild conditions allow for the incorporation of an organic matrix in the inorganic network. Polymethylmethacrylate (PMMA) nanocomposites are reported to be synthesized by the sol-gel method.

However, composites synthesized by this method are found to be very difficult to process, because often initially soluble polymers phase-separate once the gelation begins. Also, the choice of suitable solvent-polymer pairs further limits the applicability of this method.

2.2.2 *In-situ* polymerization

In this method, the nano-dimensional clay is dispersed in the monomer, which is then polymerized. The monomer may be intercalated with the help of a suitable solvent and then polymerized. Polycaprolactone and nylon nanocomposites are commonly synthesized by the intercalation of monomer.

*In-situ* polymerization of monomer very often produces nearly exfoliated nanocomposites. However, commercialization of this method would require separate production lines or major changes in the existing production facilities to suit the heterogeneous polymerization of monomer in the presence of clay. Such factors severely limit the commercialization of this method.

2.2.3 Solution intercalation

In this method, the polymer is dissolved in an appropriate solvent, in which the nano-clay is dispersed. Intercalation of polymer chains into the clay galleries occurs from solution. The operating temperatures are typically low. Nanocomposites of polymers like polyethylene oxide and polylactide have been synthesized by this method.

This method can be useful for few polymers, for which suitable solvents are available. This route is also preferred for polymers that require high processing temperature at which the organoclay may degrade. Apart from the limited choice of
suitable solvents, factors like the cost of the solvents and the recovery of the solvent, would further restrict the commercial viability of this method.

2.2.4 Melt intercalation

In this method, the polymer is mixed with clay above the glass transition or melting temperature of the polymer under shear. At higher temperatures polymer chains are sufficiently mobile to diffuse into the galleries of the clay. Vaia et al. (1995, 1996) have shown that intercalation can be improved with conventional processing techniques. Twin-screw extrusion has been found to be effective for the dispersion of silicate layers. Cho et al. (2000) found that an organoclay, if compatible with the polymer, may even exfoliate during extrusion due to shear. The dispersion of clay depends on the parameters like residence time, level of shear etc.

Melt intercalation is an environmentally friendly technique, as it does not require any solvent. It is also commercially attractive due to its compatibility with existing processing techniques. However, the resulting morphology of the nanocomposite is often an intercalated microstructure rather than the preferred exfoliated state.

Apart from the four main techniques listed above, a few other techniques for the preparation of polymer nanocomposites include sonification and micellar intercalation.

2.3 Morphologies of polymer nanocomposites

The structure and properties of the polymer nanoclay structures can be conveniently mediated by controlling subtle guest-host interactions. Nanoclays exhibit different types of dispersion in the polymer matrix (Giannelis, 1996; Giannelis et al, 1999). Conventional type is phase separated polymer/silicate composites, in which the polymer and the inorganic host remain immiscible and the pristine gallery height remains unaltered. Another structure is an intercalated one in which a single, extended polymer chain is intercalated between the host layers resulting in a well ordered multi-layer with alternating polymer/inorganic layers and a repeat distance of a few nanometers. In this case, polymer chains penetrate inside the galleries and effectively expand the silicate layers. The crystallographic regularity doesn't have to do with clay to polymer ratio and the material behaves more or less like a ceramic. A sub category in this case could be
called flocculated nanocomposites where silicate layers are sometimes flocculated due to hydroxylated edge-edge interaction of the silicate layers. Another type is characterized by *exfoliation* or delamination, in which the silicate layers (1 nm thick) are exfoliated and isotropically dispersed in a continuous polymer matrix. In this state, the clay loading governs the average gallery height. Low loadings result in disordered exfoliated nanocomposites in which the single clay platelets are randomly suspended in the polymer matrix and are typically separated by an average distance of >10 nm. Above a critical loading, the platelets arrange themselves to form ordered exfoliated nanocomposites (Vaia *et al*, 2000). In normal cases, exfoliation is achieved with less clay loading than intercalation. In practical cases, nanocomposites are combinations of all of these idealized morphologies.

![Diagram](image)

Figure 2.3: Schematic of various morphologies of composites (a) immiscible composite (b) intercalated nanocomposite (c) ordered exfoliated and (d) disordered exfoliated nanocomposite (adopted from Galgali, 2003)

2.4 Advantages of PLS nanocomposites

Any physical mixture of a polymer and an inorganic material does not form a nanocomposite. Conventional polymer composites that are prepared by reinforcing a
polymer matrix with inorganic materials like reinforcing fibres and minerals have poor interaction between the organic and the inorganic components, which leads to separation into discrete phases. Therefore the inorganic fillers are required to be added in higher concentrations to achieve enhancements in the thermomechanical properties of the polymer. Table 1 shows a comparison of the physical properties of nanocomposites and conventional composites of polyamide.

<table>
<thead>
<tr>
<th></th>
<th>Nylon-6 unfilled</th>
<th>Nylon-6 5% Organo-Clay</th>
<th>Nylon-6 30% Mineral</th>
<th>Nylon-6 30% Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>7,250</td>
<td>11,800</td>
<td>8,000</td>
<td>23,000</td>
</tr>
<tr>
<td>Flex. Modulus</td>
<td>120,000</td>
<td>500,000</td>
<td>650,000</td>
<td>1,100,000</td>
</tr>
<tr>
<td>Notched Izod</td>
<td>1.2</td>
<td>1.2</td>
<td>1.6</td>
<td>1.8</td>
</tr>
<tr>
<td>HDT (@ 264 PSI), °F</td>
<td>150</td>
<td>230</td>
<td>248</td>
<td>380</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.13</td>
<td>1.14</td>
<td>1.36</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Table 2.1: Comparison of physical properties of Nylon nanocomposites and conventional composites (Source: RTP company, MN)

It is observed that in contrast to conventional composites, significant property enhancement is still achieved at much lower filler loading for nanoclay. Importantly, this is achieved with negligible increase in the weight of the part.

The reasons for the greater effectiveness of the nanoclays are two-fold. Firstly, the nanoclays can be dispersed to the level of individual platelets. This nano scale dispersion of silicates provides very high surface area for polymer-clay interaction. Secondly, the lamellar surfaces of the nanoclays can be modified through an ion exchange reaction to make them compatible with the polymer matrix. Layered silicates in the pristine state are highly hydrophilic. However, the interlayer cations like Na\(^+\), Ca\(^{2+}\) can be exchanged with various organic cations like alkylammonium cations and cationic surfactants. The cationic head of the modifier molecule preferentially resides on the clay surface and the aliphatic tail radiates away from the surface. The organic cations lower the surface energy of the silicate surface and make it compatible with the polymer
matrix. Furthermore, the organic modifier may contain various functional groups, which can interact with the polymer matrix. It may also expand the interlayer galleries to an extent that facilitates the intercalation of polymer chains. The equilibrium gallery distance depends on the CEC (cation exchange capacity) of silicate and the chain length of the modifier. Thus organosilicates are more compatible with polymer matrix. These two advantages namely, the high surface area and the ability to render it hydrophobic are interrelated in a sense, as for a given matrix, the surface area is determined by the dispersion of the clay, which in turn depends on the interaction between clay and polymer.

In addition to the above-mentioned advantages, nanoclays offer other interesting features. For instance, polymer nanoclay composites can potentially form optically clear films under certain conditions. This is possible in the case of exfoliated composites wherein the clay platelets are oriented with their surface normal or parallel to the direction of the incident beam of light. Under these circumstances the nanocomposites will not scatter light, because the thickness of the platelets is less than the wavelength of the visible radiation. Another interesting feature of nanoclays is that the intergallery distance (2-3 nm) of the organo clays approximately matches the typical persistence length of flexible polymers, thus making the diffusion of polymer chains easier.

Incorporation of nanoclays is believed to increase the barrier properties by creating additional tortuous path that impedes the diffusion of gas or solvent molecules while passing through the matrix resin. Some of these unique properties of nanocomposites are discussed in detail with examples below:

2.4.1 Mechanical properties

Gopakumar et al (2002), Galgali et al (2003) and Manias et al (2003) have discussed the mechanical properties of polyolefin nanocomposites with a critical perspective. With improved polymer/inorganic adhesion, the stresses are effectively transferred from the polymer matrix to the inorganic filler and thus a higher increase in the Young's modulus is achieved. The tensile results obtained from thermodynamically stable hybrids are not affected by processing conditions (since the nanocomposite structure remains the same) whereas, in the absence of favourable organic-inorganic
thermodynamics, the structure and the tensile properties vary strongly with the processing
conditions. Similar improvements in mechanical properties can also be achieved by other
layered particulate fillers, however, much higher filler loadings will be required.

2.4.2 Thermal properties

In the case of a well exfoliated compatibilized nanocomposite, there is a marked
increase in the heat deflection temperature (HDT) (Manias et al, 2001). There is a strong
dependence of the HDT on the processing conditions during the composite formation,
similarly to the tensile properties. The enhancement in HDT is difficult to achieve by
chemical modification or reinforcement by other fillers. The improvement of the HDT in
PP-montmorillonite is found to originate from the better mechanical stability of the
nanocomposite, compared to the neat-PP, rather than any increase in the polymer melting
point. In all the PP/montmorillonite hybrids studied by Manias et al (2001), the melting
temperature was not found to change markedly from that of the respective neat polymer.
This is qualitatively different from the behaviour of other polymers (e.g. nylon-6), where
the montmorillonite layers stabilize a different crystalline phase than that found in the
neat polymer, with higher melting point and also higher HDT.

2.4.3 Barrier properties

Generally, polymer/silicate nanocomposites are characterized by very strong
reductions in gas and liquid permeabilities and at the same time, the solvent uptake
decreases accordingly. Polymers ranging from epoxies and good sealants to semi-
permeable poly(urethane-ureas), to very hydrophilic PVA, are all improved up to an
order of magnitude, for 5-7 wt% clay loadings. This improvement can be attributed to
tortuosity of the path of travel, as well as the higher modulus promoted by the inorganic
fillers.

2.4.4 Flame retardancy

Montmorillonite-based fillers also promote the flame retardancy of polymers,
across a wide range of different chemistries. Cone calorimetry studies by Gilman et al.
(2000), showed dramatic enhancements to polymers like PP, PS, nylon-6 and epoxies.
This flame retardant character is traced to the response of a carbonaceous-char layer, which develops on the outer surface during combustion. This surface-char has a high concentration of monmorillonite layers and becomes an excellent insulator and a mass transport barrier (slowing down the oxygen supply as well as the escape of the combustion products generated during decomposition).

2.4.5 Optical clarity

Albeit their micron lateral size, clays are just 1 nm thick. Thus, when single layers are dispersed in a polymer matrix, the resulting nanocomposite is optically clear in the visible region. Whereas there is a loss of intensity in the UV region mostly due to scattering by the montmorillonite particles, there is no marked decrease in the clarity due to nano-dispersed fillers. This is a general behaviour as seen by UV/visual transmittance for thick films (3-5 mm) of polymer/mmt nanocomposites, based on PVA, PP and several epoxies.

2.4.6 Processing and synergy with other fillers

Where there exists favourable thermodynamics for polymer/clay miscibility, the organo-clay can be incorporated in the final stages of polymer processing (e.g. extrusion, injection/compression molding) and obtain nanocomposite hybrids. Thus, polymer/montmorillonite nanocomposites are amiable to most of the common processing techniques in today's industrial practices, which lowers the barriers towards commercialization for these nanocomposite hybrids. Additionally, organically modified montmorillonite fillers can be used in conjunction with other reinforcements, such as fibres, thus combining the advantages of nanofillers with those from the fibre reinforcement in one composite material.

All the above improvements in properties are subject to compatibility of the inorganic filler with the organic matrix and also the degree of dispersion. Hence, recent advances in polymer/clay and polymer/layered-silicate nanocomposite materials have inspired efforts to disperse clay-based fillers in almost any polymer available, usually expecting that complete exfoliation of the inorganic fillers in the polymer would yield the best performing systems.
2.5 Thermodynamics of nanocomposite formation

Giannelis et al., (1999) have discussed thermodynamics of nanocomposite formation in detail, part of which is reproduced here to emphasize the functionalization of the polymer matrix. The formation of equilibrium structure of polymer layered silicate nanocomposites, in particular, with organically modified layered silicates, has been shown to be a strong function of the nature of the polymer (polar or apolar), the charge carrying capacity of the layered silicate, as well as the chain length and structure of the cationic surfactant. However, both the polymer/silicate compatibility and hybrid equilibrium structure for these nanocomposites are observed to be independent of polymer molecular weight. The experimental results have been summarized by Vaia et al (1997) and a lattice based mean field theory has been developed to explain these results.

![Figure 2.4](image)

**Figure 2.4:** The change of entropy per area versus the change in gallery height, for the polymer and the surfactant (octadecylammonium) functionalized surface based on a thermodynamic model. (adopted from Giannelis et al, 1999)

In general, interplay of entropic and enthalpic factors determines the outcome of polymer intercalation. Confinement of the polymer inside the interlayers results in a decrease in the overall entropy of the polymer chains. However, the entropic penalty of
polymer confinement may be compensated by the increased conformation freedom of the tethered surfactant chains in a less confined environment, as the layers separate. Since for small increases in gallery height the total entropy change is small, modest changes in the system's total enthalpy will determine if intercalation is thermodynamically possible. Complete layer separation, though, depends on the establishment of very favourable polymer-surface interactions to overcome the penalty of polymer confinement (Figure 2.4). The enthalpy of mixing can broadly be classified into two components – apolar, which is generally unfavourable and polar which originates from the Lewis acid/Lewis base character of the layered silicates and which could be rendered favourable. A favourable enthalpy change is accentuated by maximizing the magnitude and number of favourable polymer-surface interactions while minimizing the magnitude and number of unfavourable apolar interactions between the polymer and the functionalising aliphatic chains.

Although simple in comparison to contemporary thermodynamic descriptions of polymer phenomena, the greatest advantage of the model by Giannelis et al (1999) is the ability to analytically determine the effect of various aspects of the polymer and organic layered silicate (OLS) on hybrid formation. The variation of the free energy of mixing on the gallery spacing and its dependence on enthalpic and entropic factors, based on this model, suggest three possible equilibrium states – immiscible, intercalated and exfoliated. The model has been successful in addressing some of the fundamental and qualitative thermodynamic issues associated with hybrid formation. However, assumptions such as the separation of configurational terms and intermolecular interactions and the further separation of the entropic behaviour of the constituents, somewhat limit the usefulness of the model. Additionally, this model is not applicable to situations where the OLS's interlayer is not completely occupied by tethered-chain segments, which is the case for many silicates with low charge densities or modified by short aliphatic chains.

Some of the limitations and gross approximations of the current mean-field, lattice-based model, such as the decoupling of the tethered chain and polymer conformations in the interlayer, may be addressed by developing more sophisticated models of hybrid formation based on theories of Scheutjens and Fleer (1980) and Szleifer and Carignano (1993). Additionally, Monte Carlo simulations of hybrid formation or
intercalation of small-molecules in layered materials could lead to additional insights into the mechanisms and important factors associated with intercalation. One very well studied problem is the hydration (water intercalation) in 2:1 silicates which was approached both by Monte Carlo and molecular dynamic simulations. From the simulation of the thermodynamic properties of the systems – such as disjoining pressure and free energy – can be obtained, and thus the stable d-spacings, can be located. The extension of such simulation schemes to the study of polymer/organo-silicate systems is currently underway and will obviously provide a more detailed picture of the thermodynamics of these systems.

As said, the entropic penalty of polymer chain confinement is compensated by the increased conformational freedom of the surfactant, when the layers are separated. When the total entropy change is small, small changes in the internal energy of the system will determine whether the intercalation is thermodynamically possible.

However, exfoliation requires complete layer separation [i.e., interlayer distance (h)> radius of gyration of polymer chain (R_o)]. This requires very favourable polymer-OLS interactions to overcome the polymer-polymer and clay-clay interaction. Thus, the dispersion of OLS in polymer matrix requires sufficiently favourable enthalpic contribution to overcome any entropic penalties. Favourable enthalpy of mixing is achieved when the polymer-OLS interactions are more compared to surfactant-OLS interactions. For polar polymers like nylons, alkylammonium surfactant (most commonly used organic modifier) is sufficient to offer the excess enthalpy, required for the formation of PLS nanocomposite. However, this is not true for the non-polar polymers like PP. There are two ways to promote nanocomposite formation in these cases:

1. Improve the interactions between the polymer and the OLS. The most convenient way to achieve this is to functionalize the polymer matrix by polar or polarizable groups like the anhydride group.

2. Decrease the interaction between the surfactant and OLS, which effectively makes the polymer-OLS interaction dominant. Manias et al. (2001) have claimed to reduce the alkylammonium surfactant-montmorillonite interaction by fluorinating the surfactant.
2.6 Rheology of filled polymers and nanocomposites

The low shear viscosity of a dilute suspension is given by Einstein equation (Larson, 1999)

\[ \eta_0 = \eta_{_o} (1 + K_E \phi) \]  \hspace{1cm} (2.1)

where, \( \eta_{_o} \) is the viscosity of the matrix fluid, \( \eta_0 \) is the viscosity of the suspension, \( \phi \) is the volume fraction of the suspended rigid particles and \( K_E \) is the Einstein coefficient which is 2.5 for spherical particles. This equation holds good for very low filler loading (\( \phi \leq 0.03 \)). When the filler loading increases, the filler particles get close enough and the drag on one of them is influenced by a second nearby particle. The particles are then said to experience hydrodynamic interactions. The viscosity of a suspension of spherical particles at higher filler loading (\( \phi \leq 0.1 \)) is given by (Larson, 1999)

\[ \frac{\eta_0}{\eta_{_o}} = 1 + 2.5\phi + 6.2\phi^2 \]  \hspace{1cm} (2.2)

At still higher filler concentration, the viscosity of the suspension increases dramatically with the filler loading and may be modelled by an exponential function as shown in Figure 2.5 (Larson, 1999).

\[ \eta_0 = \eta_{_o} \exp(\phi) \]  \hspace{1cm} (2.3)

![Figure 2.5: Zero shear viscosity variation with filler concentration](image-url)
These relations are valid for affine deformation. At higher shear rates, the suspensions may exhibit shear-thinning behaviour. Then a dimensionless shear rate or Peclet number \( (P_e) \) may be defined as (Larson, 1999)

\[
P_e = \frac{\eta \dot{\gamma} a^3}{k_B T} \propto \dot{\gamma} t_o
\]  

(2.4)

where, the time \( (t_o) \) for a particle to diffuse a distance equal to its radius \( (a) \) is given as

\[
t_o = \frac{6 \pi \eta \sigma a^3}{k_B T}
\]  

(2.5)

where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature.

Asymmetric filler particles like clay particles used in this study can be oriented in the flow direction. Orientation relaxation of individual particles under quiescent conditions is expected to occur by Brownian motion, given as (Larson, 1999).

\[
\frac{\partial f}{\partial t} = \Theta \frac{\partial^2 f}{\partial \phi^2}
\]  

(2.6)

where, \( f(\phi,t) \) is the fraction of particles oriented at an angle \( (\phi) \) at time \( (t) \) and \( (\Theta) \) is the rotational diffusion coefficient.

Nanoclays have been used as popular fillers by various researchers in the past decade. Extensive references to previous studies regarding nanoclay composites using several different polymers have been provided in chapter 1 of this thesis.

2.7 Time Temperature Superposition

Rheological properties of molten polymers such as those obtained from parallel plate or capillary rheometer are usually highly dependent on temperature. This means that to obtain a complete picture of the behavior of the polymer, experiments must be carried out at several temperatures. It is often found that rheological data measured at several temperatures can be brought together on a single master curve by means of "time-temperature superposition" (Dealy and Wissbrun, 1990). This greatly simplifies the description of the effect of temperature. Furthermore, it makes possible the display on a single curve of material behavior covering a much broader range of time or frequency than can ever be measured at a single temperature. Materials whose behavior can be
displayed in this way are said to be "thermorheologically simple" (Dealy and Wissbrun, 1990).

It is found that data for different temperatures can often be superposed by introducing a shift factor, $\alpha_T$, determined empirically. Thus, if one makes a plot of a rheological property vs. a quantity with a time unit, $\alpha_T$ is obtained from the horizontal shift necessary to bring the data corresponding to a specific temperature $T$ onto the same curve as data corresponding to another temperature $T_0$. For example, to superpose flow curves (shear stress vs. shear rate) obtained from different temperatures, the curves have to be plotted on a shear stress vs. (shear rate$\times\alpha_T$) scale. It's to be noted that no shift factor is required for quantities containing no units of time. This implies that a plot of such a quantity versus another, both containing no units of time, will be temperature independent.

The shift factor is a function of temperature, and the WLF equation has been found to be a useful relation for $\alpha_T$ (Ferry, 1980):

$$\log(\alpha_T) = \frac{-C_1^0 (T - T_0)}{C_2^0 + (T - T_0)}$$

(2.7)

where $C_1^0$ and $C_2^0$ are constants determined at $T_0$ for each material. This equation holds at temperatures very close to glass transition temperature, $T_g$. At temperatures at least 100 K above $T_g$, an empirical relationship, the Arrhenius equation, has been found to be valid (Dealy and Wissbrun, 1990):

$$\log(\alpha_T) = -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right)$$

(2.8)

where $E_a$ is the flow activation energy, $R$ is the gas constant, and $T_{ref}$ is the reference temperature. Since the processing temperatures of both polymers used are much above their respective $T_g$, equation 2.8 is chosen to be used in this present work.

The present work requires only vertical shifting. However, time-temperature superposition can be applied both horizontally and vertically. This case is still under investigation by many researchers in order to come up with models that perfectly predict
the polymers behaviour. One such model is the modified Rouse model (Van Gurp and Palmen, 1998), which is capable of predicting both horizontal and vertical shift factors. The shift factors are defined as:

\[
\alpha_T = \frac{\tau_r(T)}{\tau_r(T_0)} \tag{2.9}
\]

\[
b_T = \frac{G_r(T)}{G_r(T_0)} \tag{2.10}
\]

where \(\alpha_T\) and \(b_T\) are called horizontal and vertical shift factor respectively, \(\tau_r\) is the relaxation time and \(G_r\) is the relaxation modulus.

When both horizontal and vertical shifting exist, the modified Rouse theory predicts that the product of the horizontal and vertical shift factors equals the shift factor determined from the zero shear viscosity:

\[
\alpha_T b_T = \frac{\eta_0(T)}{\eta_0(T_0)} \tag{2.11}
\]

which is consistent with the above discussion and references.

2.8 Melt Fracture

Melt fracture is a term, used collectively for appearance of instability, which occurs beyond a critical shear rate in a capillary, slit or annular dies during extrusion of polymers. The term melt fracture was introduced by Tordella (1956) because of the audible tearing noises which accompanied the distortion of the extrudate. Melt fracture is a major problem in the extrusion of polyolefins and many other commercial polymeric materials. In addition to shear rate or processing speed, it depends on various operational and geometric factors which mainly include the polymer structure and its molecular characteristics, die geometry and the process temperature.

There are various types of flow instabilities observed in the flow of polymeric liquids through capillary, slit and annular dies. These are also reflected in the apparent flow curve, determined by means of a capillary rheometer. This is essentially a log-log plot of the wall shear stress, \(\sigma_w\), vs. apparent shear rate, \(\dot{\gamma}_A\). A typical apparent flow curve for a linear polymer such as HDPE and LLDPE is shown in Figure 2.6.
Fig. 2.6: A typical apparent flow curve of a linear polymer

One can easily identify the five different flow regions. Initially there is a stable region where the extrudate appears smooth and glossy (region 1). In this region, the behavior of the melt resembles that of a non-Newtonian fluid and the viscosity can be represented by a power-law expression. In this region, the no-slip boundary condition can be assumed to be valid. Beyond some critical wall shear stress, $\sigma_{c1}$, which is typically of the order of 0.1-0.2 MPa, the first visual manifestation of an extrusion instability appears as a high-frequency, small-amplitude distortion of the extrudate known as sharkskin or surface melt fracture (region 2). As the name implies, sharkskin is a roughness that usually modulates the extrudate diameter by no more than 1% and consists of semiregular cracks or grooves that run mainly perpendicular to the flow (Benbow and Lamb, 1963; Piau, 1990). The onset of sharkskin appears to coincide with a change in the slope of the apparent flow curve.

At a second critical value $\sigma_{c2}$ and within a certain range of apparent shear rates, the flow ceases to be stable (region 3). It is the region of oscillating, cyclic or stick-slip melt fracture where the extrudate has the appearance of alternating smooth and distorted portions. In this region, the pressure drop oscillates between two extreme values. The periodic variations of the pressure and apparent shear rate define a hysteresis loop that connects the two branches of the apparent flow curve. Despite the scatter in the reported
values of the second critical shear stress, it is generally accepted that gross melt fracture is a basic characteristic of the particular polymer systems. The greater the molecular weight and the narrower its distribution, the greater the amplitude of the hysteresis loop.

At higher throughputs there is sometimes a transition to a second stable flow regime in which the extrudate again becomes smooth. This is a superextrusion region (region 4). Finally, at still higher shear rates, there is a transition to a wavy chaotic distortion (gross melt fracture), which gradually becomes more severe with increase in apparent shear rate $\dot{\gamma}_A$ (region 5). This typical behavior has been observed in the capillary extrusion of many linear polymers such as high density and linear low-density polyethylene (Kalika and Denn, 1987), polytetrafluoroethylene (Tordella, 1969), polybutadiene (Vinogradov et al, 1972) and others.

2.8.1 Mechanisms to explain melt fracture

As a result of the large number of research work and the use of sophisticated flow visualization techniques, there is a general agreement among the researchers about the causes of two types of melt fracture – Sharkskin Melt Fracture (SMF) and Gross Melt Fracture (GMF).

2.8.2 Die exit effects: sharkskin / surface melt fracture

There is universal agreement that sharkskin is initiated at the die exit. The first theory about surface melt fracture (sharkskin) was proposed by Howells and Benbow (1962) and later by Cogswell (1977). They hypothesized that the polymer fractures due to high stretching rates and high stresses as a result of the abrupt change (shear to free surface flow) in the boundary condition at the exit of the die. The melt leaving the die in the neighborhood of the wall experiences a large, rapid, tensile deformation as the velocity field adjusts from the no-slip boundary condition to the free-surface condition. Polymer chains are stretched during the tensile deformation, which causes the highly entangled polymer to respond like a rubber. The large stresses on the free surface cause the cracks to open up giving them the appearance of sharkskin. There are several other views available on the origin of sharkskin. However, this original proposition of fracture at the die exit as the cause of sharkskin has been substantiated by the microscopic flow...
visualization observations made by Migler et al (2001). Figure 2.7 presents a schematic view of the surface melt fracture taking place at the die exit.

![Diagram of melt fracture](image)

**Figure 2.7:** Schematic view of surface melt fracture occurring at the die exit

If we analyze the dynamics of polymer melt movement near the die exit, as shown in the above figure, we realize that inside the die, there is a typical boundary layer velocity distribution having zero or a small sliding velocity close to the wall and maximum at the centre. Outside the die, the velocity distribution is uniform throughout the cross-section as there is no resistance to flow. Therefore, as the melt is extruded, it experiences a sudden jump in velocity near the die exit leading to large extensional stresses on the polymer surface, which result in the surface distortion or sharkskin. In short, the absence of lubrication at the die exit is considered as the main cause of sharkskin.

2.8.3 Die Entry Effects: Gross Melt Fracture

Most authors agree in claiming that above a certain extrusion rate, the flow upstream of the die contraction becomes unstable. These instabilities occur in the form of sudden pulsations or cavitation which were confirmed by visualization (Piau et al, 1990; Kazatchkov et al, 2000; Migler et al, 2001) and birefringence measurements (Tordella, 1969). They have shown that such instabilities started along the upstream flow axis owing to the high elongation stresses that develop in this area. These instabilities trigger
the phenomenon of gross melt fracture, which is often seen in the form of a regular helix oscillating at the same frequency as that of the pulsations of the upstream elongational flow (Piau et al, 1990).

2.9 Polymer processing aid

As discussed before, melt fracture poses an undesirable constraint on the rate of production. It is necessary to eliminate melt fracture or postpone it to higher rates in order to increase the rate of production. Processing aids used for melt fracture elimination include additives and surface coatings, which mainly target at slip promotion at the die exit, thereby eliminating surface melt fracture. This in turn reduces the extrusion pressure. Typical polymer processing aids are fluoropolymers, stearates and certain waxes which have been used traditionally for surface melt fracture elimination. These are used in small quantities in the order of about 1000 ppm. They have a tendency to migrate towards wall and make a fine coating on the die wall during extrusion. The extruding polymer then slips along the smooth coating on the die, thus eliminating the surface melt fracture (Rudin et al, 1985; Migler et al, 2001).

Priester and Stewart (1992) suggested that the factors that may affect the performance of the processing aid include the level of additive, dispersion quality and the interaction with other ingredients (antioxidants and stabilizers) in the resin. They have also mentioned that a large number of small particles of the additive can result into a better dispersion quality than a small number of large particles. Stewart et al (1992) reported that a masterbatching step was required in order to provide a good quality of dispersion of additives into the resin.

In general, fluoropolymer based processing aids reduce the pressure required to extrude the resin at a particular flow rate and eliminate or postpone melt fracture to higher extrusion rates. These additives can eliminate only sharkskin and the so-called stick-slip (oscillating or cyclic) melt fracture. They do not appear to have an effect on the extrudate appearance in the gross melt fracture region (Rosenbaum et al, 1998).

Recently, it has been reported that certain Boron Nitride (BN) based compositions may act as effective processing aids in the extrusion of a number of fluoropolymers and polyolefins (Buckmaster et al., 1997; Rosenbaum et al., 1998; Yip et al., 1999; Lee and
It has been reported that BN can successfully be used as a processing aid to eliminate not only sharkskin melt fracture but also substantially postpone gross melt fracture to significantly higher shear rates well within the gross melt fracture region. It is noted that conventional fluoropolymers can only eliminate sharkskin; they do not appear to have an effect on the gross melt fracture phenomena.

Yip et al. (1999) reported that BN is an effective processing aid when it possess the following characteristics: (i) average particle size of up to about 10μm, (ii) no agglomerations, (iii) absence of boron oxides in its structure and (iv) good dispersion into the resin under process. Also, BN must be used at its optimal concentration depending on the type of polymer and the extrusion temperature. It is observed that the presence of BN does not alter the flow curve during extrusion, however, it has significant effect on extrudate appearance (Rosenbaum et al., 1998; Kazatchkov et al., 2000).

It had also been reported that the BN additive has little additional effect on the extrudate appearance in the capillary geometry (both capillary and orifice dies with different entrance angle) compared to the effect seen in the case of fluoroelastomer. The greatest influence of the additive occurred in crosshead dies and tips where the additive particles seemed to enhance melt slippage and relieve internal stresses (Rosenbaum et al., 1998; Yip et al., 2000). Lee and Kim (2000) reported that the critical apparent shear rate for onset of melt fracture and the shape of extrudate are highly dependent on processing temperature, $L/D$ and content of the BN. They found that the addition of 0.5 wt % of BN in LLDPE eliminate or delay sharkskin, stick-slip melt fracture and gross melt fracture to much higher rates, even though there is no difference in the linear viscoelastic and mechanical properties between virgin and LLDPE containing BN.

Combining a BN powder with fluoropolymer has an enhanced effect on melt fracture elimination. Fluoropolymers mainly act as slip promoters, eliminating sharkskin and reducing the extrusion pressure whereas BN primarily influences the melt flow in die entrance region, delaying the gross melt fracture. The fact that these two additives act by different mechanisms for suppressing the instabilities, explains why their combination results in a synergistic effect for melt fracture elimination (Rosenbaum, 2000; Achilleos et al., 2002).
Hatzikiriakos et al. (2005) studied the effect of nanoclays on the processibility of polyolefins. They used both polyethylenes and polypropylene with organically modified and unmodified clays. They have reported that organically modified clays eliminate sharkskin melt fracture and delay the onset of gross melt fracture while unmodified clays exhibit no clear effects on processibility. Such an effect was related to decrease in extensional stresses in the presence of organically modified clay. They also demonstrated that organoclay combined with fluoropolymer have similar effects in eliminating or postponing melt fracture. The same organically modified clays are used in the present work. By using them at relatively higher amounts (2 - 4 wt%), their influence on the rheology, processing and mechanical properties of the polymers will be studied. In addition, their influence as processing aids when used at low concentrations (0.1 wt%) will also be examined.
CHAPTER 3

THESIS OBJECTIVES AND STRUCTURE

3.1 Objectives

This section enlists the core objectives of the present thesis, as follow:
1. To improve the uniform dispersion in terms of intercalation and exfoliation of nanoclay in polyethylene resins by means of twin screw melt compounding.
2. To study the influence of graft modification in polyethylene over intercalation/exfoliation
3. To study the rheological significance of polyethylene nanoclay composites with respect to intercalation/exfoliation
4. To study the mechanical properties of polyethylene nanoclay composites with respect to intercalation/exfoliation
5. To study the effect of organically modified nanoclay and graft modified polyethylene over processing instabilities in polyethylene.

3.2 Thesis organization

This thesis is structured and organized in order to provide the reader with basic understanding of the nanocomposites and then an introduction to various methodologies used to study their structure, rheology and processing as well as their inter relationships.

Chapter 1 introduces the reader to the field in general and the prospects. It briefly covers the development of interest in this particular research topic and the areas covered by the previous researchers. A brief introduction of the problem under study is discussed.

Chapter 2 describes the core material i.e. nanoclays. Then, it proceeds to describe the various ways of preparing polymer layered silicates and the different types of morphologies formed. The advantages of nanocomposites are listed followed by a brief introduction to thermodynamics and rheology of nanocomposites. It also presents background information on polymer melt instabilities and processing aids.

Chapter 3 outlines the objectives of the present thesis and its organization.

Chapter 4 describes the materials used and the various experimental parameters.

Chapter 5 analyses the results obtained from characterization and testing of the nanocomposites. Finally, chapter 6 concludes and summarizes this work.
The materials used in this study and their properties are discussed. The method used to prepare the samples and specimens for testing are explained. A list of compounds prepared is given with their formulations. The experimental procedures and parameters used during various characterization and other testing methods are narrated along with technical specifications of the instruments used.

4.1 Materials

4.1.1 Polyethylene

An ethylene based octane-1 plastomer (Exact 0201) from ExxonMobil has been used as the base polymer. It is produced by solution polymerization process using a metallocene catalyst. The molecular weight distribution is relatively narrow with a polydispersity index of about 2. Its typical melt flow rate is 1.1 dg/min at 2.16 kg/190°C (ISO 1133) and the density at 23°C is 0.902 g/cc (ISO 1183).

4.1.2 Graft modified polyethylene

Fusabond E MB-226DE, a commercially available chemically modified polyethylene from Dupont is used as the compatibilized polyethylene. Fusabond is functionalized by maleic anhydride grafted to help bond together polymers used in toughened, filled and blended compounds. It increases the filler acceptability of the polymers by a good margin. However, it has to be dosed keeping in mind its influence on the mechanical properties of the base polymer. The maleic anhydride graft level in the fusabond used is said to be 0.89% and the typical density is 0.93 g/cc at 23°C (ASTM D1505). The melt flow rate at 190°C/2.16 kg is 1.82 dg/min (ASTM D1238 / ISO 1133) and the melting point is about 120°C (ASTM D3418 / ISO 3146). The rationale behind this choice was that the melt flow rate matches closely with that of the base polyethylene used and hence hardly influences the viscosity levels of the compounds produced.
Therefore, this eliminates the possibility of fusabond itself increasing the viscosity of the compound.

4.1.3 Organically modified nanoclay

Nanomer 1.44 P, from Nanocor Inc., is used in this study as the organically surface modified montmorillonite clay. Montmorillonite belongs to a dioctahedral 2:1 phyllosilicate class of silicates wherein tetrahedral sheets of silica having oxygen and hydroxyl ions tetrahedrally arranged around central Si atoms are fused with octahedral sheets of aluminium have Al\(^{3+}\) ions octahedrally coordinated to the hydroxyl groups. Two third of the Al\(^{3+}\) ions are substituted by lower valence cations such as Mg\(^{2+}\) and Fe\(^{2+}\) in octahedral sites. The aspect ratios of montmorillonites are as high as 1000 for individual platelets and 300-500 for tactoids with an inter-lamellar space or gallery of about 1 nm separating the platelets. Thus structural asymmetry of montmorillonites combined with a large surface area of about 700-800 m\(^2\)/g and a high cation exchange capacity (CEC) of about 70-150 meq/100g render this class of silicates open to intercalation (Galgali, 2003). In their pristine or unmodified states, they contain hydrated Na\(^+\) or K\(^+\) ions, they are naturally immiscible with hydrophobic polymers. Nanomer 1.44 P used here is organically modified to accommodate an organophillic polymer.

4.2 Sample Preparation

Aimed at both individual and synergistic study of effect of fusabond and clay on intercalation and exfoliation and its significance on the rheology of polyethylene, different formulations were prepared by using varying proportions of fusabond and clay. The compounds prepared are listed in Table 4.1. The pellets and powder were introduced into the extruder through separate feeders into a co-rotating twin screw extruder - Micro 27, Leistritz, Germany (L/D = 36). A screw diameter of 27 mm and a screw rotational speed of 200 rpm were used to generate a mass flow rate of 10 kg/hr. The barrel was programmed at 190 °C, 200°C, 210°C, 210°C, 200°C, 190°C, 190°C, 190°C and was equipped with vacuum degassing. The extruded strands were water cooled over a distance of 100 cm and were strand pelletized. The extruded pellets were melt-pressed into thin sheets of 2 mm thickness in a Carver hydraulic press at 150°C and specimen of
desired dimensions were cut out of the sheet for rheological testing. It was observed during melt pressing that with increasing incorporation of fusabond, the material adheres strongly to the polyester sheet used to melt press the compound. However, addition of clay eliminates the stickiness indicating that the clay acts as a releasing aid. This could be related to Hatzikiriakos et al., (2005) who reported that organically modified nanoclays at small concentrations well dispersed in a polyethylene matrix act as processing aids eliminating instabilities such as melt fracture. However, significant changes or trends in die pressure or torque with respect to exfoliation as reported by Gopakumar et al. (2002) were not noticed. Small variations were within the experimental error margins.

Table 4.1: Compounds of nanoclay-polyethylene compounds prepared using twin screw extrusion.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Exact 0201 (%)</th>
<th>Fusabond EMB226-DE (%)</th>
<th>Nanomer I.44P (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E0201</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A1</td>
<td>96</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>A2</td>
<td>98</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>A3</td>
<td>99.9</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>H1</td>
<td>90</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>H2</td>
<td>86</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>H3</td>
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<td>10</td>
<td>2</td>
</tr>
<tr>
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</tr>
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<td>70</td>
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</tr>
<tr>
<td>D2</td>
<td>66</td>
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<tr>
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</tr>
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<tr>
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<tr>
<td>B3</td>
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<td>99.9</td>
<td>0.1</td>
</tr>
</tbody>
</table>

-35-
4.3 X-Ray Diffraction

X-ray diffraction (XRD) is a non-destructive analytical technique for identification and quantitative determination of long-range order in various crystalline compounds. X-rays are electromagnetic radiation generated when an electron beam accelerated through a high voltage field hits a metal, which acts as an anode. The wavelength ($\lambda$) of x-rays is characteristic of the target anode material used and is given by

$$\lambda = \frac{hc}{E}$$

where, $h$ is the Planck’s constant, $c$ is the velocity of light and $E$ is the energy of the photon.

The wavelength of X-ray is comparable to the size of atoms, therefore they can be effectively used to measure the structural arrangement of atoms in materials. In laboratory instruments X-rays are produced in tubes having copper or molybdenum anodes, which emit X-rays corresponding to wavelengths of 1.54 $\text{Å}$ and 0.8 $\text{Å}$, respectively. In recent years synchrotron facilities have been widely used for x-ray diffraction measurements. Electrons or positrons travelling at near light speed in a circular storage ring are used to produce synchrotron radiation. These radiations are thousands to millions of times more intense than laboratory X-ray tubes and are very useful for structural investigations at very low incident X-ray angles.

X-rays interact with electrons in atoms. When X-rays collide with electrons, some X-rays from the incident beam are deflected away from the incident direction. If the wavelengths of these scattered X-rays remain unchanged, the process is called an elastic scattering (Thompson Scattering) in that only momentum is transferred during collision. These are the X-rays that are measured in diffraction experiments. They carry information about the electron distribution in materials. On the other hand, during inelastic collision (Compton Scattering), X-rays transfer some of their energy to the electrons and so the scattered X-rays will have different wavelength than the incident X-rays.

X-rays diffracted from different atoms interfere with each other. If the atoms are arranged in a periodic fashion, as in the case of crystals, the peaks in the interference
pattern will correspond to the distribution of atoms. The peaks in an X-ray diffraction pattern are directly related to atomic distances by Bragg's law

\[ n\lambda = 2d\sin\theta \]  

(4.2)

where, \( \lambda \) is the wavelength of X-ray, \( d \) is the inter-planar distance, \( \theta \) is the scattering angle and \( n \) an integer representing the order of the diffraction peak.

XRD data can be collected by using either reflection or transmission geometry. The reflected X-rays interfere with each other such that in the diffractogram, intense peaks are obtained at corresponding \( d \) values, according to the Bragg's law. The peak position, intensity and shape provide important information about the long-range order in the material. In the transmission mode, an area detector detects the X-rays transmitted through the sample. A circular cone of transmitted rays is incident on the detector, giving a circular ring like pattern. The radius of the circular ring corresponds to the inter-planar distance. The intensity along the circumference of the circle gives the intensity along the azimuthal angle (\( \chi \)), which gives information about orientation of the scattering entities in the sample. XRD can be very effectively used for intercalated composites, containing silicate layers arranged in a periodic spacing of a few nanometers. However, XRD has limited use in completely disordered exfoliated state, where the layered structure is completely lost. Hence, it should always be followed by TEM to detect XRD silent structures which is the case in exfoliated nanocomposites.

X-ray scattering at ambient temperature was used to characterize the microstructure of the compounds in this work. Experiments were performed on Rigaku MultiFlex X-ray diffractometer with Cu anode radiation generated at 40 kV and 20 mA and 20 range of 1 to 50 degrees with a sampling width of 0.02 degree at a scanning speed of 2 degrees per minute.

4.4 Transmission Electron Microscopy

Conventional optical microscopes can investigate structure to the resolution of few micrometers. But much higher resolution is required to study the fine structural details of the polymer nanoclay composites. A transmission electron microscope (TEM) is used to observe the fine scale structure. A TEM functions exactly as its optical
counterpart except that it uses a focused beam of electrons instead of visible light to “image” the specimen and gain insight about the structure and composition.

The four basic operations involved are: 1) A stream of electrons is formed and accelerated towards the specimen using a positive electrical potential, 2) This stream is confined and focused using a metal aperture and magnetic lenses into a thin, monochromatic beam, (magnetic lenses are circular electro-magnets capable of projecting a precise circular magnetic field in a specified region), 3) The focused beam is impinged on the sample by a magnetic lens, 4) The energetic electrons then interact with the irradiated sample. These interactions and effects are detected and transformed into an image.

TEM is used to directly observe the state of dispersion of clay in the polymer matrix. Normally nanocomposites constitute a blend of intercalated and exfoliated structures. No formulation can be a perfect structure of either of them. While XRD remains silent with exfoliated structures, TEM helps visualise the exact nature of such blend of composites.

Samples were sectioned into 70 nm thick slices using a Diatome diamond knife of 35 degrees at a cutting speed of 1 mm/s in a Leica Ultracut UCT, cryo-ultramicrotome equipped with EMFCS cryo-unit at -120°C. Samples were glued to a slotted pin mount with a superglue and further supported with non-reactive Tissue-Tek OCT gel that solidifies at low temperature to provide mechanical support. Sections were placed on 400 mesh carbon coated copper grids. FEI Tecnai 20 transmission electron microscope at an operating voltage of 200 kV was used to characterize the structure and the images were captured using Gatan dual-view CCD camera.

4.5 Tensile Testing Machine

A tensile testing machine was used to examine the effect of nanoclay incorporation (exfoliation or intercalation) on the mechanical properties of the extruded samples. A schematic of COM-TEN tensile testing equipment used is shown in Figure 4.1. This instrument comprises of a motor drive with adjustable speed, two interchangeable load cells of 20 N and 200 N, a Digital Monitor Controller (DMC) and the Data Acquisition System (DAS). The sample is placed and held with the clamps, the
upper clamp is fixed at the shaft activated by the motor. The sample is then stretched at a constant speed until it fails. The load cell senses the force applied by the sample and sends it to the DAS via the DMC.

A schematic of a typical stress-strain curve obtained for a semicrystalline polymer is shown in Figure 4.2 along with different stages of ductile deformation of a tensile specimen (Schultz, 1974). Initially, the stress ($\sigma$) increases linearly with strain ($\gamma$) and the slope of this linear part of the graph gives the Young's modulus ($E$) of the sample. After a critical stress the material yield; the stress passes through a maximum and then slightly decreases. The yield stress corresponds to the beginning of the process of necking in the gauge length. Necking continues with elongation in the sample and in this region the stress increases only slightly with increasing strain. The upsweep in the curve is called strain hardening. At still higher strain the specimen finally breaks. The area under the curve is called the toughness of the sample. Some polymers exhibit brittle fracture, i.e., the tensile sample breaks at the maximum applied load, without necking.

![Data Acquisition System](image)

**Figure 4.1:** A schematic of COM-TEN tensile testing equipment
4.6 Rheological Experiments

4.6.1 Rheology

Rheology is the study of deformation and flow of matter. Its techniques are among the most sensitive tools to monitor microstructural developments and intercrystallite interactions in a material with time either under quiescent or under shear and extensional conditions.

Detailed literature upon rheology is available in many references (Nakajima et al, 1977; Bailey et al, 1992; Macosko, 1994; Kim and Han, 1994; Han et al, 1995). Polymers are complex fluids that exhibit both elastic and viscous behaviour and are hence considered to be viscoelastic in nature (Macosko, 1994). Linear viscoelastic regime is the region below a critical deformation where the material response can be expressed as a linear combination of Hookean elastic and Newtonian viscous responses. At higher strains, the response deviates from linearity possibly due to orientation of chains. A dynamic strain sweep determines the critical strain that delineates between the linear and non-linear response regimes for a particular polymer. These tests can best be performed by means of a parallel plate rheometer, discussed below.

Figure 4.2: Schematic of the typical mechanical behaviour of a semicrystalline polymer
4.6.2 Parallel plate rheometer

Parallel plate rheometer shown in Figure 4.3 is one of the most versatile rheometers available for rheological analysis. In this rheometer, two plates are mounted on a common axis of symmetry, and the sample is inserted in the space between them. The upper plate is rotated at a specified angular velocity $\dot{\omega}(t)$ and as a result the sample is subjected to shear. The motion of the upper plate is programmed, and the resulting torque, $M$, is measured (so called constant strain rheometers). Another mode of operation is fixing the torque and measuring the displacement (constant-stress rheometers).

Most polymeric materials are said to be rheologically viscoelastic, i.e. a combination of viscous (representing liquid – loss of energy) and elastic (representing solid – storage of energy) components. If sufficiently large strain is applied, it is possible to break the structure or elastic component of the material, resulting in purely viscous flow. This is the simplest type of test possible on this rheometer, leading to determination of bulk viscosity of the sample or its characterization in terms of one of the several non-Newtonian flow models.

![Fig 4.3: Parallel plate rheometer](image)

The real power of this instrument lies in its ability to apply very small amount of deformations in dynamic or oscillatory fashion, without breaking the elastic structure of the sample. This is known as linear viscoelastic characterization of the material and provides very useful information about the morphology of the material.

Many utilities in using the parallel plate geometry make it a very versatile experimental tool and a preferred geometry for viscous melts for small strain material
functions. Sample preparation and loading are very simple for very viscous materials and soft solids such as polymers. One can vary shear rate (and shear strain) independently by varying the rotation rate $\Omega$ (and $\theta$) or by changing the gap $h$, thus permitting an increased range with a given experimental set up. One can also determine wall slip by taking measurements at two gaps. One of the common problems with polyolefins, edge failure due to higher shear rates in the steady shear experiments can be delayed by decreasing gap during an experiment without having to change the cone angle as is required in a cone & plate geometry. One can also measure normal stress data, $N_2$ when used with cone and plate thrust data.

Since the Oscillatory Linear Viscoelastic Characterization is the most important and useful test, a brief overview of it is presented here. In this test, a very small shear strain is applied to the sample sinusoidally – this is similar to vibrating the sample within its linear elastic range, and the stress response of the sample is observed.

Since viscoelastic sample is composed of viscous and elastic component, the elastic or solid component is expected to follow Hook’s law, where stress is directly proportional to strain – leading to stress responses ‘in phase’ with the applied sinusoidal strain. The viscous or liquid component on the other hand, tends to follow Newton’s law, where stress is directly proportional to shear rate and not strain – leading to stress
responses completely 'out of phase' to the applied strain. This is explained schematically in Figure 4.4.

In practice, most materials are a combination of viscous and elastic components and so the measured phase angle (\(\delta\)) will be somewhere between 0 and 90°. Since in this test, stress and strain are constantly changing, the viscoelastic properties are described in terms of Elastic (storage) Modulus (\(G'\)) and Viscous (Loss) Modulus (\(G''\)) defined below. The applied sinusoidal strain can be represented as:

\[
\gamma(t) = \gamma_0 \sin(\omega t) \quad (4.3)
\]

where \(\gamma_0\) is the strain amplitude and \(\omega\) is the frequency. The stress response can be shown to have the following form:

\[
\sigma(t) = \sigma_0 \sin(\omega t + \delta) \quad (4.4)
\]

where \(\sigma_0\) is the stress amplitude and \(\delta\) is a phase angle shift in the response. Using a trigonometric identity, one can rewrite Equation (4.4) in the following form:

\[
\sigma(t) = \frac{\sigma_0}{\gamma_0} \sin(\omega t + \delta) \quad (4.5)
\]

With,

\[
G' = \frac{\sigma_0}{\gamma_0} \cos(\delta) \quad \text{and} \quad G'' = \frac{\sigma_0}{\gamma_0} \sin(\delta)
\]

There are other two parameters, frequently used to present the test results. These are complex modulus (\(G^*\)) and complex viscosity (\(\eta^*\)), defined below.

\[
G^* = G' + iG'' \quad (4.6)
\]

\[
\eta^* = \eta' - i\eta'' \quad (4.7)
\]

where,

\[
\eta' = \frac{G'}{\omega} \quad \text{and} \quad \eta'' = \frac{G''}{\omega}
\]

As mentioned earlier, the oscillatory tests are very sensitive to the molecular structure of the polymer sample. Figure 4.5 (Dealy and Wissbrun, 1990) shows a typical plot of storage modulus for three samples of a linear polymer. It may be observed that at high frequencies, glassy behaviour is exhibited and the response is independent of the molecular weight. At smaller frequencies, molecular rearrangement becomes possible and there is a transition zone. For the low molecular weight materials (A) such transition
zone does not exist and we move to the terminal zone directly. For the higher MW sample (B), we have a plateaue zone. The plateaue zone is not clear for polydisperse material (C).

![Indicative plot of G'(\omega) for three samples of a linear polymer. (A) is monodisperse with low MW, (B) is monodisperse with high MW, and (c) is polydisperse with high MW.](image)

Figure 4.5: Indicative plot of G'(\omega) for three samples of a linear polymer. (A) is monodisperse with low MW, (B) is monodisperse with high MW, and (c) is polydisperse with high MW.

It is generally long established that linear viscoelastic oscillatory test for LLDPE sample shows an ideal behaviour wherein at small frequencies (terminal zone), $G'$ tends to become proportional to $\omega^2$ (slope of $\sim 2$) whereas $G''$ tends become proportional to $\omega$ (slope of $\sim 1$). It is also established that for LLDPE, at low frequency, $G'' > G'$, implying a rubbery or liquid like behaviour. At higher frequency, a crossover takes place indicating a rigid, glassy or solid like behaviour (Kazatchkov et al, 2000).

Several empirical relationships between molecular structure and linear viscoelastic properties have been proposed for linear polymers. No such relationships have been proposed for branched polymers because of the difficulty of seperating the effects of the degree and the type of branching from that of molecular weight distribution (Dealy and Wissbrun, 1990).

In addition, the rheometer (parallel plate or cone-and-plate) can also carry out creep analysis (slow deformation of material, measured under constant stress) and stress relaxation (stress response of the material under constant strain). Creep analysis is useful for predicting effects such as sedimentation, sagging and levelling. The stress relaxation
is mainly used as a quality control tool. Specific reasons for stress relaxation and creep experiments in the case of nanocomposites are to identify the critical viscous and elastic transitions with respect to microstructure and morphology of the nanocomposites, which are dependent upon the intercalation or exfoliation phenomena. Creep experiments in particular aid in thermodynamic interpretation of exfoliation (Galgali, 2003).

4.6.3 Capillary Rheometer

Flow of molten polymer through a tube or a channel under pressure is commonly encountered in polymer processing, for example in an extrusion die or in the runner feeding of an injection mold. A capillary rheometer simulates this type of flow behaviour. In the present research work, capillary rheometer is primarily used to extrude nanoclay composites to study the effect of clays in eliminating/postponing the appearance of melt fracture at a given shear rate. The extrudates obtained were visually examined to see the sharkskin and gross melt fracture taking place at the surface of extrudate.

A typical schematic of capillary rheometer is shown in Figure 4.6, followed by an overview of its underlying principles.

![Figure 4.6: Schematic of a capillary rheometer (Baird and Collias, 1995).](image-url)
Capillary rheometers are also used widely to determine the viscosities in the shear rate range of 5 to 5000 s\(^{-1}\) (Dealy and Wissburn, 1990). Reproducibility of capillary rheometer experiments is typically ± 5%.

The capillary rheometer consists of a melt reservoir or barrel, for melting the polymer and a plunger or piston that causes the melt to flow through the capillary die of known diameter, \(D\), and length, \(L\). The quantities normally measured are the flow rate, \(Q\), (related to the piston speed) and the driving pressure, \(P_d\), (related to force on the piston that is measured by means of a load cell). The measured piston force, \(F_d\), is related to \(P_d\) as follows:

\[
P_d = \frac{F_d}{\pi R_b^2}
\]

where \(R_b\) is the radius of the barrel or reservoir. Alternatively, \(P_d\) can be measured by mounting a pressure transducer directly in the barrel.

4.6.3.1 Rheometer fitted with capillary die

To calculate the viscosity, it is necessary to know the wall shear stress and the wall shear rate, and it is therefore necessary to have reliable techniques for evaluating these basic rheological quantities on the basis of experimental data. For steady-state, fully-developed flow of an incompressible Newtonian fluid, the wall shear stress, \(\sigma_w\), can be calculated as:

\[
\sigma_w = \frac{\Delta P D}{4L}
\]

where \(\Delta P\) is the total pressure drop along the capillary. The magnitude of the wall shear rate, \(\dot{\gamma}_w\), for a Newtonian fluid can be calculated as:

\[
\dot{\gamma}_w = \frac{32Q}{\pi D^3}
\]

For the case of a non-Newtonian fluid, this quantity is called the apparent wall shear rate, \(\dot{\gamma}_A\), that is the rate that a Newtonian fluid would have at the same volumetric flow rate \(Q\):

\[
\dot{\gamma}_A = \frac{32Q}{\pi D^3}
\]
Capillary flow of a Newtonian fluid is a controllable flow which means that the flow kinematics does not depend on the nature of the fluid. Capillary flow of molten polymers, however, is only a partially controllable flow. This means that the velocity distribution in this flow is governed not only by the boundary conditions but also depends on the nature of the fluid. To account for this, at least two corrections should be applied to the experimental data. First, the velocity profile in the flow of a polymeric fluid is nonparabolic, and one must correct the wall shear rate, \( \dot{\gamma}_w \), defined by Equation (4.10). This correction, generally known as the Rabinowitch correction, can be calculated as (Dealy and Wissbrun, 1990):

\[
\dot{\gamma}_w = \left( \frac{3 + b}{4} \right) \dot{\gamma}_A
\]  

(4.13)

A power-law fluid is defined as

\[
\sigma = K\dot{\gamma}^n
\]  

(4.14)

where \( \sigma \) is the shear stress, \( \dot{\gamma} \) is the shear rate, \( K \) is the consistency index, and \( n \) is the power law exponent. It can be shown that the wall shear rate for a power law fluid can be expressed as:

\[
\dot{\gamma}_w = \left( \frac{3 + 1/n}{4} \right) \dot{\gamma}_A
\]  

(4.15)

Thus, it can be seen from Equations (4.13) and (4.15) that the Rabinowitch correction is equal to \( 1/n \) for a power law fluid and 1 for a Newtonian fluid. It mainly represents deviation from Newtonian behavior. Second, the pressure drop must be corrected for the additional pressure required for the melt to pass through the contraction between the barrel and the capillary. The wall pressure distribution actually observed for capillary flow of molten polymers is sketched in Figure 4.7.
It can be seen that the pressure drop, $P_d$, is clearly not the pressure drop that one would observe for fully developed flow in a capillary of a length $L$. There is a significant pressure drop near the entrance of the die, $\Delta P_{\text{ent}}$. There may also be residual pressure at the die exit, called the exit pressure, $\Delta P_{\text{ex}}$, but it is quite small compared to $\Delta P_{\text{ent}}$. The total pressure correction for exit and entrance regions is called the end pressure, $\Delta P_{\text{end}}$, that is,

$$\Delta P_{\text{end}} = \Delta P_{\text{ex}} + \Delta P_{\text{ent}}$$

(4.16)

The true wall shear stress is then obtained as:

$$\sigma_w = \frac{(\Delta P - \Delta P_{\text{end}})}{4(L/D)}$$

(4.17)

The pressure correction, $\Delta P_{\text{end}}$, or the Bagley end correction can be determined by use of a scheme proposed by Bagley (1957). He suggested to measure the driving pressure, $P_d$, at various values of the flow rate, $Q$, using a variety of capillaries having different lengths. For each value of the apparent wall shear rate, he then plotted driving pressure versus $L/D$ and drew a straight line through the points as shown in Figure 4.8. Extrapolating the lines to the $P_d=0$ axis, he then obtained an end correction, $e$. 

---

*Figure 4.7: Wall pressure distribution for capillary flow (Dealy, 1982)*
Thus, the true wall shear stress can then be calculated as follows:

\[
\sigma_W = \frac{P_d}{4(L/D + e)}
\]  

(4.18)

An alternative way to determine the end correction is to use orifice capillaries with \( L/D = 0 \). This will directly measure \( \Delta P_{end} \) and thus equation (4.17) can be used directly to infer the wall shear stress.

In our work, a capillary die with diameter of 0.048 in, length of 0.7480 in with an L/D ratio of 15.58 and \( 2\alpha \) of 180 degrees is used in a barrel of diameter 0.375 in.

4.6.4 Sliding Plate Rheometer

The main advantages of sliding plate geometry are that there are no effects of pressure on measurements and that the edge effects can be eliminated by measuring the shear stress locally using a flush-mounted shear stress transducer. It can be also very useful to study orientation effects for example, in glass fiber reinforced plastics.

The laboratory procedure that most closely approximates simple shear is to place a thin layer of fluid between two flat plates, clamp one of the plates in place, and move the second plate at a constant velocity, \( u \), as shown in Figure 4.9.
Under no-slip conditions (Figure 2.9 a),

Shear strain, \( \gamma(t) = \frac{\Delta x}{h} \) (4.19)

Shear rate, \( \dot{\gamma}(t) = \frac{u}{h} \) (4.20)

Shear stress, \( \sigma = \frac{F}{A} \) (4.21)

If one assumes that the no-slip boundary assumption is valid, then the actual shear rate, \( \dot{\gamma} \), is equal to the nominal shear rate, \( \dot{\gamma}_n \). When slip is present, the actual shear rate is less than the nominal shear rate and these two cases are shown schematically in Figure 4.10.

In fact \( \dot{\gamma} \) and \( \dot{\gamma}_n \) under slip condition are related through the following expression

\[
\dot{\gamma}_n = \dot{\gamma} + \frac{2u_s}{h}
\] (4.22)
where $u_s$ is the slip velocity.

The sliding plate rheometer designed by Interlaken consists of two stainless steel plates that are located within a temperature controlled oven. The first plate is a fixed plate and is fastened into a rigid position by eight bolts. The second plate is a sliding plate which can be moved vertically in both directions by a high pressure pump. The movement of the sliding plate is controlled by a computer software program also developed by Interlaken. The unit has temperature sensors for the air inside the oven as well as on the stationary plate. The shear stress transducer is located in the center of the fixed plate and is flush mounted (Giacomin et al, 1989). The basic features of the transducer are shown in Figure 4.11. An end plate is acted on by the shear stress generated by the fluid and transmits the resulting moment to the cantilever beam. To avoid melt penetration into the gap around the end plate, the deflection of the latter must be limited to very small levels. That is why a capacitance system is used, where a capacitor is formed by the probe acting as one of the plates and the beam as the second plate.

![Figure 4.11: Schematic of shear stress transducer assembly in a sliding plate rheometer.](image)

There are many advantages associated with the direct measurement of the shear stress:

- Uncontrolled flow at the edges of the sample does not affect the determination of the shear stress, allowing tests with large and rapid deformation to be carried out
• Degradation occurring as a result of contact between the exposed edges of the sample and the environment does not affect the measurement
• The exact size and shape of the sample need not be known and this greatly simplifies sample loading
• Tests can be carried out with only a few grams of sample
• Bearing friction has no effect on the measured shear stress, as long as it does not introduce mechanical noise.
• The accuracy of the sliding plate rheometer data is typically between 3 and 8%.

4.6.5 Extensional Rheometer

Extensional flow or deformation that involves the stretching of a viscous material, is the dominant type of deformation in converging and squeezing flows that occur in typical polymer processing operations. When the true strain rate of extension, also referred to as the Hencky strain rate, is constant, simple extension is said to be a “strong flow” in the sense that it can generate a much higher degree of molecular orientation and stretching than flows in simple shear. As a consequence, elongational flows are very sensitive to crystallinity and macrostructural effects such as long-chain branching and as such can be far more descriptive with regard to polymer characterization than other types of bulk rheological measurement. All the extensional measurements in this work have been carried out using the Sentmanat Extensional Rheometer Universal Testing Platform, which is described below (Sentmanat, 2004).

The rheometer consists of paired master, A, and slave, B, wind-up drums mounted on bearings, C, housed within a chassis, E, and mechanically coupled via intermeshing gears, D, as shown in Figure 4.12. Rotation of the drive shaft, F, results in a rotation of the affixed master drum, A, and an equal but opposite rotation of the slave drum, B, which causes the ends of the sample, H, that are secured to the drums by means of securing clamps, I, to be wound up onto the drums resulting in the sample being stretched over an unsupported length, L_o. For a constant drive shaft rotation ratio, Ω, the Hencky strain rate applied to the sample specimen can be expressed as:

\[ \dot{\varepsilon}_H = \frac{2\Omega R}{L_o} \]  

(4.23)
where $R$ is the radius of the equal dimension wind-up drums, and $L_0$ is the fixed, unsupported length of the specimen sample being stretched which is equal to the centerline distance between the master and slave drums.

![Figure 4.12: Schematic view of the Sentmanat extensional rheometer (SER) during operation. Inside squares: A Master drum, B slave drum, C bearings, D intermeshing gears, E chassis, F drive shaft, G torque shaft, H sample, I securing clamps. Other symbols: $L_0$ unsupported length, $\Omega$ drive shaft rotation rate, $T$ torque, $F$ tangential force (adopted from Sentmanat, 2004)](image)

The material’s resistance to stretch is manifested as a tangential force, $F$, acting on both the master, A, and slave, B, drums. In the case of a rotational rheometer host system with a de-coupled drive motor (motor mount attached to drive shaft, F) and torque transducer (transducer mount attached to torque shaft, G), the stretching force acting on the master drum is borne by the drive shaft, F, and subsequently by the drive motor and contributes nothing to the resultant torque, $T$, borne by the chassis, E, and torque shaft, G. Ultimately the resultant torque, $T$, which is measured by the torque transducer, results only from the tangential stretching force acting on the slave drum, B (Sentmanat, 2004).

If there is no deviation between the nominal and actual strain rates, the instantaneous cross-sectional area, $A(t)$, of the stretched specimen changes exponentially with time, $t$, for a constant Hencky strain rate experiment and can be expressed as:

$$A(t) = A_0 \exp \left[ -\dot{\varepsilon}_H t \right]$$

(4.24)
where \( A_0 \) is the initial cross-sectional area of the unstretched specimen. For melt rheology experiments however, polymer samples exhibit a decrease in density upon melting, manifested as a volumetric expansion of the specimen span while loaded on the SER. In order to account for this dimensional expansion the following expression was used to calculate the cross-sectional area of the molten polymer specimen:

\[
A(t) = A_0 \left( \frac{\rho_s}{\rho_m} \right)^{2/3} \exp[-\dot{\varepsilon}_H t]
\]  

(4.25)

where \( A_0 \) is the cross-sectional area of the specimen in the solid state, \( \rho_s \) is the solid-state density and \( \rho_m \) the melt density of the polymer. It is to be noted that the expansion in the unsupported span length of the polymer is observed as a slight lag in the torque response that can be accounted for with a slight time offset in the recorded time data.

Thus, for a constant Hencky strain rate, the tensile stress growth function, \( \eta^*_E(t) \), of the stretched sample can then be expressed as:

\[
\eta^*_E(t) = \frac{F(t)}{\dot{\varepsilon}_H A(t)}
\]

(4.26)

where \( F(t) \) is the instantaneous extensional force at time \( t \) exerted by the sample as it resists stretch as determined from the measured torque signal, \( T \) and radius, \( R \).
CHAPTER 5
RESULTS AND DISCUSSION

Several rheological techniques have been used during the course of this work to verify theories. A continuously increasing strain is imposed at a constant shear rate to determine the effect of clay and graft modification on the transition between the well defined linear viscoelastic (LVE) regime and the non-linear viscoelastic regime. In the LVE regime, oscillatory shear experiments with an advancing shear rate at a constant strain describe the radical influence of clay and graft modification on the exfoliation phenomena in the matrix over various shear regimes. Complex viscosity, cross-over of viscous and elastic moduli are analysed to interpret the rheological significance. Zero shear viscosity is predicted to assess the substantial changes in the complex viscosity. Relaxation Spectra are predicted to analyse the relaxation behaviour of the nanocomposites. Extensional and sliding plate rheometers were used to study the extensional properties and non-linear rheological behaviour of the nanocomposites respectively. Morphology of extrudates is used to examine clay’s role as a processing aid. Intercalation and exfoliation were characterized by XRD and TEM. Tensile properties were determined using Comten tensile testing instrument.

This chapter presents the various experimental results and their analysis. Firstly, characterization of nanocomposites using XRD and TEM are discussed. Secondly, linear viscoelastic properties of the nanocomposites are discussed followed by non-linear and extensional rheological behaviour. Capillary extrusion results indicating the influence of clay on the processability of polyethylene are discussed next and the chapter concludes by presenting the mechanical properties of the nanocomposites.

5.1. XRD Measurements

All XRD experiments were conducted at room temperature. Intensity of diffraction peak in XRD is an indication of interlayer distance and thus could be effectively considered to be an indication of intercalation or exfoliation of silicate layers in the composite matrix.
Figure 5.1 shows the characteristic XRD peaks exhibited by the pure components in the study. Diffraction beginning at zero angle grazes over the surface and shows up as a sudden huge peak that's erroneous. Virgin polymer and pure fusabond being semi-crystalline polyolefins exhibit three distinct peaks characteristic of polyethylenes near 19, 21 and 23 degrees. Fusabond belongs to a subgroup of polyethylene and hence, characteristic peaks are not expected to be seen at diffraction angles other than those for pure polyethylene, however, they do show a difference in the intensity. Fusabond exhibits a much higher intensity in its characteristic peaks compared to pure polyethylene possibly due to the high number of grafts that may induce higher crystallinity even in quiescent state at room temperature. Organically modified clay exhibits three distinct characteristic peaks at 3.5, 7.16 and 19.74 degrees with heights of 4340, 599 and 2030 cps respectively. Figure 5.2 indicates that addition of 4 wt% nanoclay brings down the first (2522 to 2185 units) and second (15316 to 11318 units) characteristic peaks in the case of fusabond as well as first (2885 to 2524 units) and third (2100 to 1535 units) characteristic peaks in case of pure polyethylene. While one can reason that the addition of clay decreases the semi-amorphous state of polyethylene and fusabond, the difference in peak numbers is not well reasoned.

![Figure 5.1: Characteristic peak report for pure components](image-url)
Figure 5.2: Addition of clay brings down the intensity of the characteristic peaks of the pure polymers.

Figure 5.3: Fusabond being a polyethylene doesn't affect the characteristic peaks of pure polyethylene.
The characteristic peaks are particular to each polymer depending upon its crystallinity and hence have no relevance to intercalation or exfoliation phenomena other than the variable solid content by incorporation of clay. Hence, we consider only the initial response (0 – 10 degrees) of XRD data as a measure of $d$-spacings in the silicate structures. Figure 5.3 illustrates that increasing fusabond content has virtually no effect on XRD data of polyethylene at low angles of diffraction.

Figure 5.4: XRD response curves of nanocomposites with 4 wt% clay clearly distinguish the phase separated and intercalated morphologies. Intensities of peaks diminish and broaden out indicating increasing intercalation with fusabond fraction.

X-ray diffraction data shown in Figure 5.4 indicates the influence of fusabond on the dispersion of clay in polyethylene matrix. The XRD responses of nanocomposites with varying proportions of fusabond and a constant weight percent of clay (4 wt%) are compared with those of the pure components. Addition of clay into the polyethylene matrix is shown to have resulted in very high intensity peaks exceeding those of the pure
clay. A shift in the basal reflection peak towards lower 2θ angles is noted. It is clearly an indication of a phase separated system formed in the absence of fusabond. Broadening of the peak and diminishing intensity with respect to increasing fusabond concentration indicate intercalation in the compound. The second peak that is observed in the compound of pure polyethylene with only clay (no fusabond) gradually disappears with the addition of increasing amounts of fusabond while the first peak decreases in its intensity considerably with increasing intercalation. These findings imply larger $d$-spacings of galleries at higher fusabond fractions. However, XRD is not a conclusive tool to differentiate between intercalated and exfoliated morphologies since the microstructural interpretations of X-ray diffraction patterns in polymer layered silicate (PLS) nanocomposites can be inaccurate (Eckel et al, 2004).

Figure 5.5: Blending clay with polyethylene without fusabond results in a phase separated system.

Figure 5.5 is a classic example of a phase separated system wherein the blocks of clay aggregated at 4 wt% inside polyethylene diffract at very low angles and very high intensities. Since the polymer is reluctant to squeeze inside the silicate galleries, it may
probably compress the aggregate as a whole that may yield high intensities and low d-spacings characterized by a considerable shift in the first diffraction peak to a lower angle. Dilution of clay proportion from 4 wt% to 2 wt% leads to an additional shift in the second diffraction peak to a lower angle. While 0.1 wt% clay could be considered insignificant proportion to be detected by XRD range under consideration, it could also be observed that there still are indications of peaks and the response is not flat in agreement with pure polyethylene.

Figure 5.6: Addition of even 10% fusabond helps to initiate phase miscibility.

Addition of fusabond helps to make the polyethylene-clay system more compatible and open to intercalation. Figure 5.6 shows that 10% fusabond into the system reduces both diffraction peaks dramatically. The intensity at the first diffraction angle decreasing below that of nanoclay is a clear indication of silicates letting the polymer inside their interlayer spaces. As a result of entry of polymer, the silicate layers swell and grow apart from each other. Figures 5.7 to 5.10 present individual examples of XRD characterization with decreasing clay concentration. Each figure corresponds to a
different fusabond concentration. The baseline correction has not been applied to the data, hence all the graphs indicate a typical baseline of the silicate-polymer matrix remarkably at lower angles. The figures show a trend of increasing intercalation with increasing fusabond concentration and decreasing clay concentration. The second peak evidently disappears with higher fusabond while the clay content is characterised by a characteristic slope in place of first peak. At a constant fusabond concentration, better intercalation could be achieved with lesser amounts of clay which is demonstrated by the broad response curves. The overall effect of fusabond is strikingly evident in Figures 5.9 and 5.10 where the second peak completely vanishes. The consistent failure in all the indicative graphs to pick up any generic result with 0.1% clay clearly demonstrates the phenomena of XRD silence (a case where XRD fails to pick up wide distances of dispersions due to the limitations in diffraction angles) and hence, the need for a more powerful visualization/microscopic technique such as TEM for an accurate representation of nanolevel dispersions in matrices.

<table>
<thead>
<tr>
<th>Compound</th>
<th>PE</th>
<th>Fusabond</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>70</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>D2</td>
<td>66</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>D3</td>
<td>68</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>D4</td>
<td>69.9</td>
<td>30</td>
<td>0.1</td>
</tr>
<tr>
<td>L.44 P</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 5.7: X-ray diffraction in nanocomposites with 30% compatibilized PE compared with response from pure silicate nanomer, L.44 P. Increased broadening of peaks relative to Figure 5.6 is observed that indicates the gallered structure of silicates is breaking down with decreasing weight proportion of clay more rapidly with higher incorporation of graft modification.
**Figure 5.8:** Increased broadening of peaks with 50% fusabond over 30% fusabond is observed that indicates better and more rapid intercalation with decreasing weight proportion of clay with higher incorporation of graft modification. Better intercalation is also achieved with lesser clay.

<table>
<thead>
<tr>
<th>Compound</th>
<th>PE</th>
<th>Fusabond</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>50</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>F2</td>
<td>46</td>
<td>50</td>
<td>4</td>
</tr>
<tr>
<td>F3</td>
<td>48</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>F4</td>
<td>49.9</td>
<td>50</td>
<td>0.1</td>
</tr>
<tr>
<td>1.44 P</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

**Figure 5.9:** Increased broadening of peaks with 70% fusabond over 50% fusabond is observed that indicates better and more rapid intercalation with decreasing weight proportion of clay with higher incorporation of graft modification. Better intercalation is also achieved with lesser clay.
Figure 5.10: X-ray diffraction in nanocomposites with 100% compatibilized PE compared with response from pure silicate nanomer, 1.44 P. The first and the second peaks have completely vanished while showing just a baseline for the silicate content. The XRD for 0.1% compound while expected to be exfoliated is found to be XRD silent.

5.2 TEM Characterization

Figures 5.11 to 5.17 are TEM pictures of various nanocomposites at different magnifications. Figures 5.11 to 5.15 visualize a regular increase in the intergallery distance between the nanolayers in a layered tactoid structure of silicates inside the polyethylene matrix with increase in fusabond concentration at a given concentration of clay (4 wt%). Figures 5.16 and 5.17 illustrate an increasingly well-distributed matrix with further dilution of clay concentration at a given amount of fusabond (70 wt%). Best exfoliation is observed in the polyethylene nanoclay composite with 0.1% clay and 70% fusabond. TEM is the most reliable technique to adequately visualize and quantify the degree of intercalation or exfoliation that cannot be measured by rheological or diffraction techniques alone.
Figure 5.11: TEM image of a polyethylene compound with 10% fusabond and 4% clay.

Figure 5.12: TEM image of a polyethylene compound with 30% fusabond and 4% clay.

Figure 5.13: TEM image of a polyethylene compound with 50% fusabond and 4% clay.
Figure 5.14: TEM image of a polyethylene compound with 70% fusabond and 4% clay.

Figure 5.15: TEM image of 96% fusabond compound with 4% clay

Figure 5.16: TEM image of a polyethylene compound with 70% fusabond and 2% clay.
5.3. Rheological measurements

5.3.1 Strain Sweep Interpretation

Figure 5.18 plots strain sweep experiments for blends with the same amount of fusabond and varying amounts of clay. An inverse scaling relation of \( \gamma_c \) (critical strain percent where non-linearities begin to appear) with clay concentration is observed as given by the following expression:

\[
\gamma_c \propto \phi^{-1}
\]  

(5.1)

where \( \phi \) is the volume fraction of clay. Aubry et al., (2005) reported a similar behaviour with increasing solid volume in polyamide-12 silicate nanocomposites. It is noted that \( \gamma_c \) for 0.1 wt% clay compound is identical to that of 0 wt% clay compound as it might be very difficult to pick up such small effects experimentally.

The appearance of nonlinearities in the viscoelastic response of nanocomposites at a critical strain \( \gamma_c \) can be fallout of breaking down of intercalated network. If \( \gamma_c \) is considered to be the work required to initiate such break-up, it could effectively be concluded that minimum energy required to initiate rupture in a polyethylene nanoclay composite should then be dependent on the concentrations of both clay and fusabond. In other words, graft modification and silicate volume cast a synergistic influence on the yield behaviour of the nanocomposites since they affect the elastic energy stored in the system. Strong interactions between the organic intergallery anions and the maleic
anhydride functionalyzed graft chains result in increased entropy and consequently increased enthalpy in the system that directly influences exfoliation phenomena.

![Graph showing strain and complex viscosity](image)

**Figure 5.18:** The critical strain, \( \gamma_c \), for the onset of nonlinear viscoelasticity at a given fusabond concentration and varying clay fraction exhibits inverse scaling relation with clay fraction.

5.3.2 Oscillatory Shear Experiments

Figures 5.19 and 5.20 depict the complex viscosity of various blends under study. The effect of clay addition up to 4 wt\%, on complex viscosity is negligible on its own. The effect of fusabond on complex viscosity is noticeable in Figure 5.19, but it is still insignificant. However, as seen from Figure 5.20, the effect of clay on complex viscosity in the presence of fusabond is significant and increases with increasing amount of fusabond. In fact, complex viscosity increases up to one order of magnitude with the highest percentage of fusabond. It is also indicative of mixed intercalation and exfoliation of silicate galleries in the matrix as also supported by XRD measurements and decisively demonstrated by TEM measurements. The highest silicate loading used is 4 wt\% and there is no disappearance of Newtonian plateau at the accessible lower shear
anhydride functionalized graft chains result in increased entropy and consequently increased enthalpy in the system that directly influences exfoliation phenomena.

Figure 5.18: The critical strain, $\gamma_c$, for the onset of nonlinear viscoelasticity at a given fusabond concentration and varying clay fraction exhibits inverse scaling relation with clay fraction.

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rates which has been reported by some researchers for clay levels above 5 wt% (Gopakumar et al., 2002). At higher shear rates, regardless of graft modification or silicate content, all compounds approach matrix-like behaviour where the nanocomposites exhibit the shear thinning behaviour of the base polymer. Yield-like behaviour attributed to nanofiller content is only observed at low shear rates. Such a transition exhibits the dual flow behaviour of the nanocomposites; a region at low shear rates dominated by the dispersed clay in a mesoscopic structure and a region at high shear rates completely resembling the rheological qualities of the host matrix. It should be noted here that the polyethylene and graft modified polyethylene used in this study share common rheological properties i.e. close complex viscosity material functions. The effect of graft modified polyethylene is only pronounced in the presence of nanofiller. One interesting fact to report is the reduction in viscosity of compound below that of the virgin polymer when the clay concentration is diluted from 4 wt% to 0.1 wt%. Possible explanation to this observation could be that the clay tactoids are exfoliated into individual nanometer scale platelets and these platelets by virtue of their highly anisotropic nature orient themselves in the flow direction thus decreasing the entanglement density of the matrix.

![Figure 5.19: The complex viscosity of blends of Exact 0201 with Fusabond EMB226-DE. The overall effect is relatively insignificant.](image)

- 68 -
Figure 5.20: The complex viscosity of blends of Exact 0201 with Fusabond EMB226-DE and 4% clay. Viscosity significantly increases with fusabond fraction. Sharp transition from constant viscosity to power law relation is seen. Shear thinning behaviour of the matrix is pronounced.

Figure 5.21 showing an effect on torque generated with respect to clay fraction bolsters such an explanation. It is evident from the viscosity measurements that the system is a percolated network. An alternate approach would be to analyse it from a processing perspective where clay as a processing aid possibly causes polymer to slip at the wall rather than decreasing the bulk viscosity of the resin. Role of surfactant molecules in the organically modified clay in causing slip can be dismissed given a negligible concentration at 0.1% clay. A similar analogy was reported by Yip et al. (2000) for certain platelike boron nitride particles with high aspect ratios that act as processing aids in the extrusion of polyethylene. In fact, they have shown that although hexagonal boron nitride particles can enhance processability, only platelike morphology may promote about 12% pressure reduction in extrusion experiments of polyethylene loaded with only 0.1% boron nitride.
Figure 5.21: Torque at 0.1% clay is less than that at 0% clay over the entire frequency range.

Figure 5.22 shows an interesting behaviour for the crossover frequency i.e. the frequency where the two viscoelastic moduli intersect. While there is absolutely no effect on this transition with fusabond incorporation at a clay loading of 0.1%, such transitions are seen to happen at lower frequencies at a clay loading of 2% or higher. Such changes are substantial at a fusabond proportion of 70% or higher in the compound. Note the drop of almost three orders of magnitude in the crossover frequency when the fusabond concentration changes from 50 to 70%. Obviously, fusabond introduces higher elasticity into the nanocomposites even at very low shear rates, however, only above a critical percentage of clay and likewise, it could also be interpreted as an effect of clay only above a critical percentage of fusabond. Such observations demonstrate the synergistic role played by the organically modified silicate galleries and the graft modified resin on the mechanical properties of the nanocomposites.
5.3.3 Zero-shear viscosity of nanocomposites

As already discussed, there exists a power law dependency of complex viscosity in nanocomposites at higher shear rates just as the base polymers. At sufficiently low shear rates, the viscosity tends to become independent of shear rate and plateaus out to a limiting value, called zero-shear viscosity, $\eta_0$. In many cases, one cannot determine $\eta_0$ experimentally because rheological instruments cannot reach these extremely low shear rates. An alternative way is to fit an appropriate model to the empirical data and obtain $\eta_0$ as a model parameter.

Earliest proposal to approach the limiting viscosity at very low shear rates while also showing the high shear rate behaviour was an empirical power law to describe the dependence of viscosity, $\eta$, on shear rate, $\dot{\gamma}$, as

$$\eta = K\dot{\gamma}^{n-1}$$  \hspace{1cm} (5.2)
The shear stress was given by

\[ \sigma = K\dot{\gamma}^n \tag{5.3} \]

For a Newtonian fluid, \( n = 1 \) and \( K \) becomes equal to the viscosity. The awkward features were eliminated by using a new form:

\[ \eta = \eta_0 \left| \lambda \dot{\gamma} \right|^{n-1} \tag{5.4} \]

where \( \lambda \) is a characteristic time constant of the material or more specifically, the reciprocal of the shear rate at which the calculated value of \( \eta \) becomes equal to \( \eta_0 \). To overcome undesirable feature, Cross (1968) had proposed to predict an approach to a constant viscosity at low shear rates by a relationship:

\[ \eta = \eta_0 \left[ 1 + \left| \lambda \dot{\gamma} \right|^m \right]^{-1} \tag{5.5} \]

where \( m \) is related to the power law index as follows:

\[ m = 1 - n \tag{5.6} \]

Carreau (1969) generalized this with a power law equation:

\[ \eta = \eta_0 \left[ 1 + (\lambda \dot{\gamma})^\mu \right]^{-\nu} \tag{5.7} \]

Yasuda et al., (1981) had introduced flexibility into Carreau’s model with an additional constant to predict an approach to a constant viscosity at low shear rates as follows:

\[ \eta = \eta_0 \left[ 1 + (\lambda \dot{\gamma})^a \right]^{(\nu-1)/a} \tag{5.8} \]

Zero-shear viscosity values calculated by means of Eq. (5.8) are shown as a function of varying fusabond percentage in Figure 5.23. An exponential fit describes increase in \( \eta_0 \) with respect to fusabond fraction in nanocomposites quite well. A composite of clay in fusabond is shown to exhibit an increase of an order of magnitude in complex viscosity over that in pure polyethylene. While this huge effect is pronounced in a composite with clay above 2 wt%, there is virtually no enhancement in rheological properties at 0.1 wt% of clay, which is believed to be the best exfoliated amongst all.
Note the steady decrease in values of exponents with respect to decreasing clay concentration. It should be noted that the negative exponent in the 0.1% clay compound clearly shows the decrease in viscosity at small loadings of clay.

![Graph](image)

**Figure 5.23:** The zero shear viscosity of nanocomposites can be described quite well as a function of fusabond fraction by means of an exponential relation.

Linear polymers with narrow molecular weight distribution have distinct regions of essentially constant viscosity and a well-defined power law region with a sharp transition between these two regions. On the other hand, polydisperse polymers with broad molecular weight distribution and significant long-chain branching attain constant plateau viscosity at extremely low shear rates that are inaccessible by standard commercial rheometers and the transition to power law dependent zone happens over a broad range of shear rates (Dealy and Wissbrun, 1990). Virgin polyethylene copolymer and maleated polyethylene used in this study have significant short chain branching and low polydispersity index; hence, a behaviour shown in Figure 5.19 is expected. With the addition of clay and in particular along with higher volumes of fusabond, it is observed
that the power law zone at higher shear rates becomes a free fall zone tending towards an absolute straight line at the highest incorporation of fusabond and clay (see Figure 5.20). Furthermore, it is also evident that the transition from constant viscosity region to power law region becomes more distinct with higher graft modification and silicate solid volume fraction. Figure 5.20 depicts this dramatic change or variation in slope of viscosity curve with respect to fusabond fraction. It is strikingly notable from this study that nanocomposites with higher degree of exfoliation or intercalation behave increasingly monodispersed even with highest levels of graft modification inside them. This finding challenges insight into physical and fundamental interpretation of relation between flow phenomena and microstructural changes in exfoliation facilitated by graft modified polyethylene. What is intriguing here is that fusabond alone or clay alone has little influence on such change. It only happens when they are compounded together.

5.3.4 Moduli and Time-Temperature Superposition studies

Storage and loss moduli are plotted as a function of frequency in the linear viscoelastic region in Figures 5.24 to 5.27. A power law dependency of $G'$ and $G''$ with frequency in the terminal zone is seen only for the pure components as in Figures 5.24 and 5.25. The results demonstrate that the terminal zone for nanocomposites ($G' \propto \omega^2, G'' \propto \omega$) is shifted to even smaller values of frequencies not accessible by our instrument and such effects are more dominant in $G'$ than in $G''$. Ayyer and Leonov (2004) reported such effects at very low nanofiller concentrations in polyamide nanocomposites. Dissipation or damping coefficient or $\tan \delta = \frac{G''}{G'}$ could be a clear indication of relative response of elastic and viscous parts. Figures 5.28-5.30 show that with increasing proportions of either fusabond or clay, dissipation diminishes to values below 1 at low shear rates and then re-approaches the plateau at 1 at higher shear rates. This signals increasing elastic response thus substantially deviating from the terminal behaviour. While they certainly indicate a complex behaviour in the polymer-nanoclay network, it is yet to be confirmed whether it is a consequence of chemical gelation or just a pseudo solid-like behaviour attributed to the formation of a percolated network. Experiments at very low frequency ranges may help to determine the critical difference.
Figure 5.24: No significant change in $G'$ is observed in blends of fusabond and polyethylene. Parsimonious model describes the data well.

Figure 5.25: No significant change in $G''$ is observed in blends of fusabond and polyethylene. Parsimonious model describes the data well.
Figure 5.26: Graft modification enhances significantly the value of elastic modulus in nanocomposites. Parsimonious model describes the data well.

Figure 5.27: Graft modification enhances significantly the value of loss modulus in nanocomposites. Parsimonious model describes the data well.
Figure 5.28: Damping coefficient remains above 1 at low shear rates in blends without clay.

Figure 5.29: When fusabond is added along with clay in polyethylene, its effect is demonstrated with damping coefficient dropping below unity.
The rheological behaviour of the compounds undergoes a strong variation with respect to different temperatures used (130°C, 163°C and 200°C) quantitatively but not qualitatively. Time-temperature superposition was applied to shift the data horizontally to a mastercurve at a reference temperature. All compounds under study were found to be thermorheologically simple. The glass transition temperatures $T_g$ for both the polyethylenes being used are below -100°C; test temperatures are far above $T_g$ and hence the Arrhenius equation was found to adequately describe the available data:

$$a_T = \exp \left[ \frac{E_a}{R \left( \frac{1}{T} - \frac{1}{T_{ref}} \right)} \right]$$

(5.9)

where $E_a$ is the flow activation energy, $R$ is the universal gas constant and $T_{ref}$ is the reference temperature. Figure 5.31 shows the shift factor, $a_T$, as a function of temperature and amount of clay content for exfoliated compounds. It is conclusive from Figure 5.21 that the flow energy of activation, $E_a$ varies with respect to the clay

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**Figure 5.30**: Lowering the clay content results in a low damping coefficient.
concentration. Given that a high fusabond concentration is incorporated (70% in this case), it is observed that the higher the clay content, the lower is the flow energy of activation that means that the material behaves more elastic or in other words, increasingly solid-like. In the example shown in Figure 5.31, $E_a$ reduces from 64,456 kJ/kmol for PE/fusabond (30/70) to 50,894 kJ/kmol (21% reduction) with the addition of 4% clay, which is significant. Interestingly, at a given clay concentration (4% in the figure shown), increasing the amount of fusabond steadily increases the shift factor as shown in Figure 5.32. Flow activation energy, $E_a$ increases from 39,479 kJ/kmol for PE/clay to 50,894 kJ/kmol (22.4% enhancement) with addition of 70% fusabond. This can most likely be attributed to the high flow activation energy of fusabond (67,957 kJ/kmol) compared to that of pure polyethylene (36,164 kJ/kmol), which is comparable to the values reported in earlier literature for metallocene LLDPE’s (Hatzikiriakos, 2000).

![Figure 5.31: Horizontal shift factors ($a_T$) of nanocomposites at various clay fractions follow the Arrhenius equation.](image-url)
5.3.5 Relaxation Spectra of Nanocomposites

In an effort to understand the network structure inside the nanocomposites, relaxation behaviour is investigated. For linear flexible polymers, the entanglement molecular weight can be calculated from plateau modulus (Larson, 1990; Krevelen, 1991).

\[
M_e = g_N \frac{\rho RT}{G_0^N}
\]  \hspace{1cm} (5.10)

where \(g_N\) is a numerical factor (close to 1 for flexible polymers), \(\rho\) is the polymer density and \(G_0^N\) is the plateau modulus.

Because of the difficulty in measuring plateau modulus and the highest possibility of experimental error, an alternative way was proposed by Baumgaertel et al. (1990) by...
making use of the empirical BSW-relaxation time spectrum. The relaxation spectrum of linear flexible polymers with molecules of (nearly) uniform length can be very well represented as

\[
H(\lambda) = n_e G_N^0 \left[ \left( \frac{\lambda}{\lambda_c} \right)^{-n_e} + n_g G_N^0 \left( \frac{\lambda}{\lambda_c} \right)^{-n_g} \right], \text{for } \lambda \leq \lambda_{\text{max}} 
\]

\[
H(\lambda) = 0 \text{ for } \lambda > \lambda_{\text{max}} 
\]

(5.11)

where \(\lambda_{\text{max}}\) is the longest relaxation time, \(n_e\) and \(n_g\) are the slopes of the spectrum in the entanglement and glass transition zones respectively and \(\lambda_c\) is the cross-over time to the glass transition. The first term in the brackets represents the high frequency glass transition region, while the second term describes the entanglement and flow region.

Later, Baumgaertel and Winter (1992) modified this spectrum to suit broadly distributed polymers by replacing the abrupt cut-off at the longest relaxation time with a stretched exponential cut-off as follows:

\[
H(\lambda) = \left[ H_e \left( \frac{\lambda}{\lambda_c} \right)^{-n_e} + n_e G_N^0 \left( \frac{\lambda}{\lambda_c} \right)^{-n_e} \right] \times \exp \left( -\frac{\lambda}{\lambda_{\text{max}}} \right)^{\beta}, \text{for } M_w \gg M_c 
\]

(5.12)

where \(M_c\) is the critical molecular weight. Due to the exponential term, this equation provides an improved representation of the relaxation spectrum compared to Eq. (5.11), in particular in the terminal region. Equation (5.12) tends closer to Eq. (5.11) with increasing \(\beta\). In addition, using Eq. (5.12) to fit the spectrum of polymers yields directly the maximum relaxation time, \(\lambda_{\text{max}}\). One can calculate the parameters of the spectrum \(H(\lambda)\) by fitting the contribution of the flow region to experimental points in the terminal zone by means of the following formulae:

\[
G'(\omega) = \int_0^{\lambda_{\text{max}}} H(\lambda) \frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} \frac{d\lambda}{\lambda} 
\]

(5.13)
In general, the continuous relaxation spectrum can be expressed in a discrete form in terms of Maxwell modes \((\lambda_i, g_i), i = 1,\ldots, N\) where \(\lambda_i\) is the \(i\)-th relaxation time, \(g_i\) is the \(i\)-th relaxation strength and \(N\) is the number of Maxwell modes. The dynamic moduli can be re-written as

\[
G'(\omega) = \sum_{i=1}^{N} g_i \left(\frac{\omega \lambda_i}{1 + (\omega \lambda_i)^2}\right)^2
\]

(5.15)

\[
G''(\omega) = \sum_{i=1}^{N} g_i \frac{\omega \lambda_i}{1 + (\omega \lambda_i)^2}
\]

(5.16)

The parameters of a discrete relaxation spectrum are found by fitting Eq. (5.15) and Eq. (5.16) to experimental data by means of a suitable minimization technique. As the criterion for minimization, the average square deviation between predicted and measured values of \(G'\) and \(G''\) was chosen:

\[
\frac{1}{M} \sum_{i=1}^{N} \left[ \left(\frac{G'(\omega_j)}{G'_j} - 1\right)^2 + \left(\frac{G''(\omega_j)}{G''_j} - 1\right)^2 \right] = \min
\]

(5.17)

where \(G'_j, G''_j\) are the measured data at \(M\) frequencies \(\omega_j\) and \(G', G''\) are the calculated values from Eqs. (5.15) and (5.16). The values of \(\lambda_i, g_i\) and \(N\) are freely adjusted during minimization. This method is called "parsimonious modelling" (Baumgaertel and Winter, 1989), since it attempts to find the spectrum with the minimum number of Maxwell modes that still represents the data well within the experimental error margin. Figures 5.24 – 5.27 show the parsimonious fit (PM fit) applied to our experimental data.

Predicted relaxation moduli, \((g_i, \lambda_i)\) in Figure 5.33 and Figure 5.34, exhibit power law relation with relaxation time, which indicates that stress can relax to zero even if it takes a very long time. It can be seen from Figure 5.33 that the spectrum decays sharply and does not change for the various compounds in the absence of clay. It seems that with the addition of clay and with increasing intercalation/exfoliation, the spectrum extends significantly towards higher relaxation times (Figure 5.34). It is also evident that the behaviour of spectrum deviates from power-law behaviour at higher fusabond contents where the degree of exfoliation increases significantly.
Figure 5.33: Parsimonious spectra for blends of polyethylene and fusabond without clay. A power law relation is observed for all concentrations of fusabond.

Figure 5.34: Parsimonious spectra for blends of polyethylene and fusabond without clay. A power law relation is observed except at high fusabond concentrations.
5.3.6 Non-linear measurements

Steady shear experiments were carried out using a sliding plate rheometer at shear rates ranging from 0.5 s\(^{-1}\) to 200 s\(^{-1}\). Start-up or transient regions presented below indicate that the non-linear stress growth coefficients are similar to their linear counterpart predicted from a generalised Maxwell model. Cox and Merz observed that curves of \(\eta(\dot{\gamma})\) are often nearly identical to curves of \(|\eta'|\) versus \(\omega\). Thus, the Cox-Merz rule is expressed as:

\[
\eta(\dot{\gamma}) = |\eta'(\omega)| \quad \text{for} \quad \omega = \dot{\gamma}
\]  

(5.18)

This rule has been applied and the linear and non-linear data are plotted together in Figures 5.35 and 5.36. It is commonly observed that even the flexible linear polymers disagree with this rule at larger shear rates because of the large reductions in entanglement densities in non-linear zones. However, as shown in Figures 5.35 and 5.36, at low shear rates, while the pure components and those nanocomposites that do not contain fusabond are in agreement with the Cox-Merz rule, the rule fails completely for nanocomposites with fusabond over the entire range of shear rates. Cox-Merz rule can be tested for detecting the energetic intermolecular interactions (Arendt and Kulicke, 1998). Such failures in Cox-Merz rule were reported by Larson (1999) for mesostructured materials, Ren and Krishnamoorti (2003) for styrene based nanocomposites, Park et al. (2001) for PHB/PEO blends, Kalika and Denn (1987) for branched polyethylene and Schulken et al. (1980) for rigid molecules. Hence, the failure in nanocomposites could be due to the increased interactions between the grafts of fusabond and the exfoliated silicate layers resulting in highly anisotropic system at the application of even small shear rates. Complex viscosity is observed to be higher than the shear viscosity for these nanocomposites, the difference being more with higher clay concentration and less with increasing shear rate. This suggests the formation of a mesoscale structure. So, one cannot use empirical Cox-Merz rule to predict \(\eta(\dot{\gamma})\) from \(\eta'(\omega)\) in case of polyethylene nanocomposites consisting of graft modification.
Figure 5.35: Complex viscosity and shear viscosity plotted together according to Cox-Merz empirical rule. The rule holds good for polyethylene and its compounds with clay.

Figure 5.36: Cox Merz rule fails for nanoclay composites in the presence of fusabond. Complex viscosity exceeds the shear viscosity, the difference being more evident at lower shear rates and higher with increasing clay concentration.
Start-up of steady shear is a method for studying non-linear viscoelasticity (Dealy and Wissbrun, 1990). A sample initially at rest is subjected to a steady shear rate, \( \dot{\gamma} \) and the shear stress is monitored as a function of time. The relevant material function is the shear stress growth coefficient:

\[
\eta^*(t, \dot{\gamma}) = \frac{\sigma(t)}{\dot{\gamma}}
\]  

(5.19)

At low shear rates, the non-linear shear stress growth coefficient is expected to become equal to its linear counterpart:

\[
\lim_{\dot{\gamma} \to 0} \eta^*(t, \dot{\gamma}) = \eta^+(t)
\]  

(5.20)

which can be expressed in terms of the parameters of the generalized Maxwell model as:

\[
\eta^+(t) = \sum_{i=1}^{N} G_i \lambda_i \left(1 - e^{-t/\lambda_i}\right)
\]  

(5.21)

At large times \( \eta^* \) becomes \( \eta_0 \).

Non-linear studies have been carried out by performing experiments in a sliding plate rheometer for shear rates ranging from 0.5 s\(^{-1}\) to 200 s\(^{-1}\). Figures 5.37 to 5.39 represent experimental start up steady shear response for polyethylene-clay compounds and Figures 5.40 and 5.42 depict the experimental curves fusabond-clay compounds respectively. Non-linear shear stress growth coefficient approaches the limiting behaviour of the linear shear stress growth coefficient (calculated from Eq. 5.21) generally at shear rates less than 10 s\(^{-1}\). Agreements are similar for pure components as well as at 4\%, 2\% and 0.1\% clay concentrations. Typically there are start-up overshoots at higher shear rates and they become smaller at lower shear rates. It is noticed that overshoots are more visible and deviate significantly in the case of fusabond-clay compounds than polyethylene-clay compounds at higher shear rates perhaps due to the high elastic storage in fusabond.
Figure 5.37: Start-up steady shear data for pure Exact 0201. At small shear rates, non-linear shear stress growth coefficient becomes equal to its linear counterpart.

Figure 5.38: Start-up steady shear data for blend of polyethylene and 2% clay. At small shear rates, non-linear shear stress growth coefficient becomes equal to its linear counterpart.
Figure 5.39: Start-up steady shear data for blend of polyethylene and 4% clay. At small shear rates, non-linear shear stress growth coefficient becomes equal to its linear counterpart.

Figure 5.40: Start-up steady shear data for pure Fusabond EMB226DE. At small shear rates, non-linear shear stress growth coefficient becomes equal to its linear counterpart. Higher overshoots are observed.
Figure 5.41: Start-up steady shear data for blend of fusabond and 2% clay. At small shear rates, non-linear shear stress growth coefficient becomes equal to its linear counterpart.

Figure 5.42: Start-up steady shear data for blend of fusabond and clay. At small shear rates, non-linear shear stress growth coefficient becomes equal to its linear counterpart.
Figure 5.43 plots the steady state values of $\eta^*$ as a function of shear rate for nanoclay loaded polyethylene composites in the absence of fusabond and indicates that there is no rheological effect of clay on pure polyethylene even at very high shear rates. Pronounced effect of clay is observed on pure fusabond as seen in Figure 5.44. Such effect diminishes at 2% clay and gradually disappears at higher shear rates above 5 s$^{-1}$, which probably is an indication that intercalated silicate nano layers orient themselves in the flow direction at high shear rates and do not contribute to stress growth. Thus, in intercalated or exfoliated states, nanofillers do not alter the flow behaviour of polyethylene in the composite at small concentrations and high shear rates. Figure 5.45 illustrates a peculiar correlation where fusabond-4% clay compound shows similar shear stress as that of polyethylene-clay compounds at very high shear rates that were not accessible by oscillatory rheometers. Further, the shear stress of fusabond and its compounds with lower amounts of clay generate less shear stress values than those of polyethylene-clay composites perhaps indicating breakdown of network structures in fusabond-clay composites.

![Figure 5.43: Steady shear stress is identical for different polyethylene-clay blends over a wide range of shear rates.](image)
**Figure 5.44:** Fusabond with clay shows a significant increase in steady shear stress at 4% clay concentration. But at 2% clay concentration, the difference vanishes at higher shear rates.

**Figure 5.45:** Fusabond-clay composites generate lesser or equal shear stresses at very high shear rates relative to polyethylene blends.
5.3.7 Extensional rheological behaviour of nanocomposite melts

Extensional rheological experiments simulate the melt stretching that a polymer undergoes while being processed and hence is a versatile tool to determine the deformation and tensile growth behaviour of the molten polymer. The nanoclay composites under study have been observed to behave solid-like at low shear rates and liquid-like at higher shear rates in oscillatory shear experiments. They have also been found to exhibit a marginal but consistent decrease in complex viscosity. They shear stress at 0.1 wt% clay loading. Unlike simple shear flow, extensional flow can generate a strongly oriented flow and hence will be a credible measure of performance of molecular structure of the composite with respect to its viscoelastic nature. As a result, it will also be a sensitive indication of effects of nanodispersions of silicate structures and graft modifications of compatibilizing polyethylene.

The extensional flow experiments were performed in a Sentmanat extension rheometer (fitted on a Bohlin VOR rheometer) whose performance and governing equations for constant Hencky strain rate and tensile stress growth function have been described in detail in chapter 4 of this thesis. Small strips were cut out from melt pressed samples of the composites to avoid any orientational history. Sample dimensions were approximately 20 mm X 0.6 mm X 3.5 mm. All experiments were conducted at different Hencky shear rates between 0.113 s\(^{-1}\) to 22.6 s\(^{-1}\) at 130°C.

It is to be noted that the tensile stress growth data are able to capture the plateau viscosity corresponding to three times the zero-shear viscosity of the polymer melt corresponding to the terminal relaxation zone of linear viscoelasticity. Such superposition is an indication of excellent reproducibility and hence the credibility of the experimental results.

Figure 5.46 depicts the extensional behaviour of virgin Exact 0201 at 130°C at various Hencky strain rates. Being a linear low density polyethylene copolymer resin with low polydispersity index, Exact 0201 consists of very small chain branches and hence bulk of the extensional or tensile stresses are borne directly by the main chain of the copolymer and hence a brittle failure is noticed. Figures 5.47 and 5.48 plot the extensional growth functions for polyethylene-clay composites and the decrease in growth coefficient and time for rupture is insignificant. McLeish and Larson (1998)
suggested that the energy borne by the chain backbone upon initiation of high extensional flow rates is dissipated somewhat by the associative flow and deformation behaviour of long-chain branching and subsequently contributes to backbone stretch. Such stress can contribute to a tensile retardation mechanism that may delay propagation of melt rupture of branched polymers particularly sharkskin melt fracture. Figure 5.49 demonstrates that upon introduction of 30 wt% of graft modified polyethylene, pure polyethylene sustains higher tensile stresses for a longer time which can be treated as endurance or toughness. Also noticeable is the trace of strain hardening which is generally attributed to long chain branching and high molecular weight. One possible reason could be the higher yield properties of fusabond attributed to its high level of grafts that may be able to hold the elastic stresses for a longer period and sustain higher deformations.

Figure 5.46: The extensional behaviour of Exact 0201 at 130°C. It can be seen that brittle failure occurs during melt extension of virgin Exact 0201 resin.
Figure 5.47: Introduction of 0.1 wt% clay into pure exact has insignificant effects on the extensional behaviour of polyethylene at all Hencky strain rates.

Figure 5.48: The effect of clay on polyethylene alone up to percentage incorporation of 4% can be considered insignificant.
However, Fusabond EMB226DE being a graft polymer with maleic anhydride cross chains, is able to hold higher stresses that are borne by the extensive branched structure and are slowly transferred on the backbone of the polymer. Figure 5.50 shows a prolonged ductile failure of fusabond at several Hencky strain rates. It can also be seen that the tensile stress function is much higher than the linear viscoelastic envelope thanks to long chain branches in fusabond. Due to the presence of long branches, the mode of failure is ductile. This significant difference in the predicted tensile stress growth from linear viscoelastic data and the experimentally measured elongational stress growth is found to be unique to fusabond and its compound with 0.1 wt% clay (Figure 5.51). This difference is eliminated either by adding 4 wt% of clay (Figure 5.55) or by adding 30 wt% of polyethylene (Figure 5.52). Introduction of 30 wt% polyethylene into the fusabond also brings down its capacity for tensile stress, however, introduces significantly higher endurance to sustain the imposed tensile stress over a longer duration (Figure 5.52). This is followed by a less prolonged brittle-like failure.
Figure 5.50: The extensional behaviour of Fusabond EMB226DE at 130°C. Ductile failure during melt extension of virgin Fusabond EMB226DE resin without strain hardening is obtained. Tensile growth function lies above the linear loop indicating a small strain hardening effect.

Figure 5.51: Introduction of 0.1% 1.44 P into pure fusabond certainly decreases the tensile stress growth however it also results in earlier tensile failure.
Figure 5.52: Introduction of 30% Exact 0201 into fusabond contributes to brittle mode of failure and less tensile growth but longer rupture times as well.

Figure 5.53: Addition of 0.1% clay significantly decreases the failure time as well as the tensile growth coefficient with the exception of the slowest Hencky strain rate used.
Figure 5.53 indicates that minute clay loading of 0.1 wt% results in lesser extensional forces earlier failures unless stretched at very low shear rates when clay particles probably have enough time to orient themselves in the stretching direction, thus gaining some tenacity. Figure 5.54 clearly demonstrates that introduction of higher amounts (4 wt%) of clay contributes to extended failure times and failure zones and strain hardening at low Hencky strain rates. Evidently such increased tensile stress growth and strain hardening at higher clay loading is only noticed in the presence of pure polyethylene and not in graft modified polyethylene alone (Figure 5.55). Fusabond retains its ductile behaviour even at the highest percentage of clay loading used, however, looses it upon addition of virgin polyethylene. Hence, from Figure 5.52 and 5.55, one can conclude that combination of Exact 0201 and Fusabond EMB226DE with the 4 wt% clay loading provides the best combination among the ones tested for delaying fracture in strongly oriented flows. Low amounts of clay (0.1 wt%) introduced into pure polyethylene shows no definite trends (Figure 5.47) and that into pure fusabond does decrease the tensile stress coefficient, however decreasing the fracture time.

Figure 5.54: Higher amounts of clay (4%) introduces strain hardening at lower strain rates. The trend of lower clay implying lesser stress and earlier failure is again demonstrated.
Though the tensile stresses are higher for pure fusabond with 4 wt% clay, at Hencky strain rates lower than 4.5 s\(^{-1}\), they tend to fail earlier than the one with 30% Exact 0201 that seems to facilitate strain hardening and hence a higher stress growth coefficient and strain hardening resulting in brittle failure.

In conclusion, addition of appropriate amounts of clay in nanocomposites retards high extensional rates and deformations and inhibits the rate of stress growth to an extent. Extensional stretching of the thin film may induce some crystallinity into the ordered matrix and hence slight deviations from linear viscoelastic predictions in certain cases. A physical probability could be the transfer of extensional stresses from the chain network of entanglements onto the nanosilicates with high surface areas to dissipate the energy.

When highly entangled polymer chains are rapidly stretched in the entrance region of the capillary die, then high extensional stresses are generated as a result of the storage of elastic energy. When these become higher than the load which can be supported by the entanglements at certain surfaces, then the material fails catastrophically (Joshi and Denn, 2003). However, in the presence of nanoclays, the levels of tensile stresses are suppressed and the failure of the polymer occurs mildly at longer extensional strains. Tensile retardation mechanism delays propagation of melt rupture of branched polymers particularly sharkskin melt fracture (Sentmanat and Hatzikiriakos, 2004; Hatzikiriakos et al., 2005).
5.3.8 Capillary extrusion

The primary aim of capillary rheometry is to assess the performance of clay as a processing additive or aid in the extrusion of polyethylene and the influence of graft modified polyethylene on the outcome. It was reported by Hatzikiriakos et al (2005) that organoclays can act as polymer processing aids in postponing the melt instabilities of polyolefins reviewed in chapter 2 of this thesis. The specifications for barrel and the die used are also described in the experimental section of this thesis. A wide range of shear rates from 10 s$^{-1}$ to 3000 s$^{-1}$ were used.

Figure 5.56 depicts the flow curves (wall shear stress versus apparent shear rates) for a variety of polymer blends containing various amounts of fusabond in polyethylene. The corresponding apparent shear viscosities as a function of apparent shear rates are plotted in Figures 5.57. Similar trend was observed with increasing fusabond concentration in the presence of minute clay loading of 0.1 wt% (Figures 5.58 and 5.59). Figure 5.60 captures an increase in apparent shear stress with clay loading at low shear rates which begins to decrease at higher shear rates. Correspondingly, there is an increase in apparent shear viscosity with clay loading at low shear rates that reverses its trend to decrease with clay loading at higher shear rates (Figure 5.61). However, it’s observed that the viscosity of 0.1% clay loaded compound remains below that of the pure component compound.

These results in this section are an indication that addition of fusabond casts a positive effect in retarding the stress generated and hence in postponing the melt instabilities. As discussed in extensional rheological studies in the previous section, fusabond, by virtue of its branching can introduce higher surface area and strain hardening assisted by ductile failure that can delay surface fracture. However, no clear effects of fusabond alone on the melt instabilities are observed. Clay supposedly does not act favourably at low shear rates in eliminating melt instabilities but can be effective at higher shear rates. Synergistically, clay and fusabond together can act as processing aid to polyethylene resins and delay appearance of sharkskin.
Figure 5.56: Apparent shear stress decreases with fusabond concentration.

Figure 5.57: Apparent shear viscosity decreases with increasing fusabond concentration.
Figure 5.58: Apparent shear viscosity decreases with increasing fusabond concentration.

Figure 5.59: Apparent shear viscosity decreases with increasing fusabond concentration.
Figure 5.60: Apparent shear viscosity increases at low shear rates with clay loading.

Figure 5.61: Apparent shear viscosity increases with clay loading at low shear rates.
Table 5.1 lists the critical shear rates for the onset of sharkskin melt fracture and the onset of gross melt fracture in the mixture of pure polyethylene and pure fusabond. It seems that effect of fusabond addition on processability is negligible. Table 5.2 shows the effect of clay concentration on the processability of nanocomposites at a given concentration of fusabond (70%). It is observed that clay has no significant effect on polyethylene processing. More experiments at the recognized shear regions might lead to absolute critical shear rates resulting in melt instabilities.

Table 5.1: Fusabond doesn’t affect the processibility of polyethylene

<table>
<thead>
<tr>
<th>Compound</th>
<th>Critical shear rate for onset of Shark Skin (s⁻¹)</th>
<th>Critical shear rate for onset of Gross Melt Fracture (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Exact 0201</td>
<td>200</td>
<td>500</td>
</tr>
<tr>
<td>90% Exact 0201 + 10% Fusabond EMB226 DE</td>
<td>200</td>
<td>500-600</td>
</tr>
<tr>
<td>70% Exact 0201 + 30% Fusabond EMB226DE</td>
<td>200</td>
<td>500-600</td>
</tr>
<tr>
<td>50% Exact 0201 + 50% Fusabond EMB226DE</td>
<td>200</td>
<td>500-600</td>
</tr>
<tr>
<td>30% Exact 0201 + 70% Fusabond EMB226DE</td>
<td>200</td>
<td>500-600</td>
</tr>
<tr>
<td>100% Fusabond EMB226DE</td>
<td>200</td>
<td>500</td>
</tr>
</tbody>
</table>

Table 5.2: Increasing clay content doesn’t have a significant effect on melt fracture

<table>
<thead>
<tr>
<th>Compound</th>
<th>Critical shear rate for onset of Shark Skin (s⁻¹)</th>
<th>Critical shear rate for onset of Gross Melt Fracture (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% Exact 0201 + 70% Fusabond EMB226DE</td>
<td>200</td>
<td>500-600</td>
</tr>
<tr>
<td>29.9% Exact 0201 + 70% Fusabond EMB226DE + 0.1% Nanomer 1.44 P</td>
<td>200-300</td>
<td>600-700</td>
</tr>
<tr>
<td>28% Exact 0201 + 70% Fusabond EMB226DE + 2% Nanomer 1.44 P</td>
<td>300</td>
<td>600-700</td>
</tr>
<tr>
<td>26% Exact 0201 + 70% Fusabond EMB226DE + 4% Nanomer 1.44 P</td>
<td>200-300</td>
<td>600</td>
</tr>
</tbody>
</table>

Table 5.3 shows the effect of clay at a very dilute concentration of 0.1% on the processability of nanocomposites. The critical shear rate for the onset of sharkskin melt fracture is found to increase from 200 s⁻¹ to 500 s⁻¹ and the gross melt fracture is also found to have been put off roughly by 200 to 300 s⁻¹. However, there hasn’t been similar
effect on the nanoclay composites of mixtures of fusabond and polyethylene. It seems that when exfoliated or intercalated, clays do not exhibit an effect on processibility.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Critical shear rate for onset of Shark Skin (s⁻¹)</th>
<th>Critical shear rate for onset of Gross Melt Fracture (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.9% Exact 0201 + 0.1% Nanomer I.44 P</td>
<td>500</td>
<td>700-800</td>
</tr>
<tr>
<td>89.9% Exact 0201 + 10% Fusabond EMB226DE + 0.1% Nanomer I.44 P</td>
<td>200-300</td>
<td>700-800</td>
</tr>
<tr>
<td>69.9% Exact 0201 + 30% Fusabond EMB226DE + 0.1% Nanomer I.44 P</td>
<td>200-300</td>
<td>600-700</td>
</tr>
<tr>
<td>49.9% Exact 0201 + 50% Fusabond EMB226DE + 0.1% Nanomer I.44 P</td>
<td>200-300</td>
<td>600-700</td>
</tr>
<tr>
<td>29.9% Exact 0201 + 70% Fusabond EMB226DE + 0.1% Nanomer I.44 P</td>
<td>200-300</td>
<td>600-700</td>
</tr>
<tr>
<td>99.9% Fusabond EMB226DE + 0.1% Nanomer I.44 P</td>
<td>200-300</td>
<td>600-700</td>
</tr>
</tbody>
</table>

Table 5.3: 0.1 % clay postpones shark skin and gross melt fracture in pure polyethylene.

These effects of clay on polyethylene are visualized in the pictures shown in Figure 5.62. The pictures were captured using a Olympus Mic-D microscope. The results are in agreement with Hatzikiriakos et al (2005) who reported that organoclay helps in putting off the melt instabilities.
0.1 wt% of nanoclay is found to be effective in postponing shark skin and gross melt fracture in nanocomposites.

Figure 5.62: 0.1 wt% of nanoclay is found to be effective in postponing shark skin and gross melt fracture in nanocomposites.
5.3.9: Mechanical properties of nanocomposites

The tensile properties of thermoplastics are normally reported at break point and those for elastomers are reported for a given percentage elongation depending on the elasticity of the material and the extensional limits of the instrument. The tensile properties are measured between two points in the gauge length between the dumbbell grips of a standard specimen. However, in this work, we have used the filament stretching machine available in our laboratory. Tensile properties are strongly dependent on the orientation and hence, they are reported perpendicular to the direction of injection moulding for a thermoplastic. Elastomers are pressed and dumbbell standard dimension samples are cut out of the flat sheets for testing.

In this work, we have cut stripes of specimen from melt pressed sheets of nanocomposites that are thermoplastics. We haven’t used the standard dumbbell shaped tensile specimen dimensions prescribed in ASTM/ISO standards and haven’t used the standard injection moulded oriented samples to measure uniaxial tensile strength. However, the following results should be a fair comparative indication of tensile properties of various nanocomposite compounds with respect to their compositions. The elongational properties of all the samples tested were beyond the elongational limitations of the instrument and hence ultimate strength and elongation at break could not be measured. So, tensile properties at 300%, 500% and 600% (that are used for elastomers by ASTM/ISO) are reported. A stress-strain curve typical to all the compounds and the corresponding terms have been described in the literature section. It is to be noticed that stress-strain data obtained at a constant strain rate follow the same trend for all pure components and the nanocomposites irrespective of their clay or fusabond content. All of them exhibit elastic-plastic deformation behaviour, including an initial viscoelastic region followed by yielding, strain softening and strain hardening. Hsieh et al. (2004) report a similar behaviour in the compression behaviour of polycarbonate nanoclay composites but observe a tensile response dependent on clay content. All the nanocomposites and pure components under study exhibit a soft and tough behaviour. Gopakumar et al. (2002) and Galgali (2003) have reported a steady increase in tensile moduli of compatibilized polyethylene and polypropylene nanocomposites respectively.
Figure 5.63 plots various tensile strengths measured. A steady increase in tensile stress with respect to increasing fusabond concentration can be observed. What is noticeable here is the significant decrease in tensile strength for 50% fusabond compounds regardless of clay concentration. We do not have a valid explanation for this. Extensional data for these compounds haven't been obtained and they could be crucial in understanding this behaviour. A possible reason could be that the grafted modified polyethylene and the pure polyethylene in equal proportions may form a unique chain structure that is fragile and prone to earlier failure under high extensional stresses.

![Figure 5.63: Tensile strength of 50% fusabond compound shows a unique dip and couldn't be explained with available data.](image)

Figure 5.64 describes the tensile behaviour of nanocomposites with respect to the clay concentration. A noticeable dip in the tensile stress at 0.1 wt% of clay signifies the slight decrease in linear viscoelastic properties observed earlier in this thesis at similar concentrations of clay. A steady increase in tensile stress with respect to clay concentration is observed. 4 wt% of clay is seems to be the threshold or critical concentration required compensate for loss of tensile strength and to match it with that of pure polyethylene.
Figure 5.64: Tensile strength decreases at 0.1 wt% clay and then steadily increases, however, there is hardly any enhancement in the tensile stress with respect to clay.

Figure 5.65 illustrates the yield strength exhibited by the nanocomposites at room temperature. It can be seen that pure polyethylene has the highest yield strength and hence the highest resistance to plastic deformation. Addition of fusabond into pure polyethylene has an inverse effect on the plastic resistance of polyethylene. Addition of 4 wt% clay into compatibilized polyethylene matrix further reduces the yield strength of the nanocomposite. A peculiar pattern of crossover is observed at a fusabond concentration of above 70 wt% wherein addition of 4 wt% of clay overcomes the yield loss due to addition of fusabond. An progressively increasing trend in yield strength with increasing amounts of fusabond at a fixed clay concentration of 4 wt% clay indicates the dramatic change in mesostructure formed due to highly intercalated or exfoliated structures. An appropriate reasoning would be that the yield strength increases with intercalation and increases beyond that of the pure blend in case of exfoliation. Figure 5.66 illustrates the increasing yield strength of one such well exfoliated nanocomposite with respect to clay concentration at a fixed fusabond concentration of 70 wt%.
Figure 5.65: Pure Exact 0201 has the highest resistance to plastic deformation. Addition of fusabond decreases the elastic deformation limits of the composite. However, 4 wt% clay reinstills part of the elasticity.

Figure 5.66: Clay decreases the elastic resistance of the nanocomposite; higher quantities of clay try to recover the resistance but 4 wt% is not quite enough.
Figures 5.67 and 5.68 illustrate the steady increase in the elastic modulus with higher amounts of fusabond and clay respectively. The effect is seen to be more pronounced in their combination at the highest concentrations incorporated. This explains for the loss of stiffness at 0.1 wt% clay and attainment of higher stiffness in well intercalated compatibilized nanocomposites.

![Figure 5.67: Stiffness or toughness of the nanocomposites increases with increasing fusabond concentration; material with clay are stiffer.](image1)

![Figure 5.68: 0.1% clay decreases stiffness of the nanocomposites; however, higher proportions of clay recover and attain higher toughness levels.](image2)
CHAPTER 6

CONCLUSIONS

This thesis presents interesting consequences of graft modification in the formation and properties of nanoclay polyethylene composites. The nanocomposites were studied in the absence and variable presence of fusabond and with varying proportions of organically modified nanoclay. All compounds were prepared by melt mixing in a twin screw extruder and no significant effects on torques exerted during processing were observed. All specimen for testing were prepared by a melt pressing procedure that facilitates the isotropic distribution of fillers.

X-ray diffraction is a technique chiefly aimed at detecting crystalline structures by means of diffraction of incident X-rays. This technique was applied on nanocomposites to detect the d-spacings between silicate galleries with a logic that increasing spacings indicate separating layers that indicate intercalation of polymer inside the silicate nanolayers. Such microstructural changes are picked up to a certain extent by the X-ray response curves that indicate the phase separated morphologies in the absence of fusabond and intercalated morphologies in the presence of increasing quantity of fusabond and decreasing quantity of clay. They are indicated by broadening and diminishing of intensity peaks. However, the results do not adequately distinguish exfoliation morphologies due to the limitations of XRD and this phenomenon of XRD silence is noticed.

Powerful TEM images visualize exfoliation aided by graft modification of polyethylene and dilution of clay concentration. Significant influence of fusabond in aiding exfoliation with decreasing clay concentration is picturised and presented.

Fusabond and clay are found to cast a non-linear effect on the nanocomposites by shifting the critical strain $\gamma_c$ to lower values. A scaling relation of critical strain with clay volume ($\gamma_c \propto \phi^{-1}$) previously reported in the literature agrees with our experimental findings.

Oscillatory shear experiments demonstrate a dramatic increase in complex viscosity of nanoclay composites with higher concentrations of clay and fusabond, an
exception being at 0.1% clay concentration. A power law relation at higher shear rates and a constant viscosity at very low shear rates are observed. It is discussed how nanocomposites behave like their base polymer at high shear rates. Sharper transition from constant viscosity to power law dependency at a critical frequency with increasing graft modification in addition to increasing clay concentration is reasoned. Influence of high loadings of fusabond on the crossover frequency of elastic and loss moduli is correlated to the increasing elastic energy, pseudo solid-like behaviour and possible gelation in the entangled matrix. Deviation from terminal zone behaviour in nanocomposites is noted at least over the experimentally accessible range of frequencies. Zero shear viscosity, $\eta_0$, is determined by fitting the Yasuda model in the experimental results and an exponential relation with graft modification is shown. Variation of rheological properties with temperature was studied and all compounds used are found to be thermorheologically simple. Horizontal shift factor, $a_T$ at a reference temperature fits into an Arrhenius type of equation. Flow activation energy exhibits a decreasing trend with respect to increasing clay concentration and an increasing trend with respect to increasing fusabond concentration.

Discrete relaxation spectra are predicted using Parsimonious model and the experimental data are found to be in agreement with the model. Relaxation modulus and relaxation time predicted a power law relation in unexfoliated composite and a deviation in exfoliated matrix where the spectra are extended to higher relaxation time scales. It is also seen that the relaxation modulus increases with clay indicating greater entanglement density.

Non-linear experiments at extremely high shear rates and controlled deformations using sliding plate rheometer suggest that the nanocomposites with graft modification violate the Cox-Merz rule over the entire range of shear rates and hence the rule cannot be used to predict the shear viscosity of the nanocomposites through complex viscosity measurements. It is suggested that the rigid entanglements formed in the matrix due to grafts and dispersion of silicates contribute to energetic interactions and hence a disagreement with the Cox-Merz rule. Start up steady shear experiments reveal higher overshoots at higher shear rates in fusabond based compounds.
Extensional melt rheology suggests that fusabond contributes to higher tensile stress growth functions and introducing a ductile mode of failure to otherwise brittle failure natured polyethylene nanocomposites. The resulting ability to melt stretch the nanocomposites is reduced by the addition of higher proportions of clay and reasonable quantities of polyethylene. Such suppression of extensional growth coefficients in the presence of clay contributes to reduced failures. Strain hardening tendencies are occasionally observed in fusabond-clay composites.

Capillary extrusion experiments were carried out to study the influence of nanoclays on processibility of the nanocomposites. The flow curves indicate that addition of higher amounts of clay increase the shear stress developed to a small extent. However, 0.1% clay reduces the shear stress developed. Fusabond on the other hand also contributes to a slight reduction in the shear stress. No significant effect on the melt instabilities were evident from the extrudate appearances of the compatibilized nanoclay composites. However, the organically modified nanoclay does affect the onset of shark skin and gross melt fractures in pure polyethylene matrix as observed by the morphologies of extrudate surfaces.

The extensional studies were conveniently complemented by the study of mechanical properties. 0.1% clay composites were observed to be less stiffer and the loss of stiffness was made up for by incorporating higher amounts of clay. Fusabond with its high elastic modulus renders its compounds stiffer but decreases the plastic deformation limits overall. Organoclay enhances plastic deformation limits in the nanocomposites. It is also discovered that the tensile strength of the nanocomposites are hardly affected by the slight addition of clay and a minimum of 4% clay is required to prompt any considerable enhancement.

Overall, the study has resulted in some significant contributions to the field of polymer nanotechnology. While researching the fundamental flow rheology and applied processing behaviour of nanocomposites, the present work presents various optimized formulations with organically modified clay and a coupling agent - graft modified polyethylene for achieving desired properties in a polyethylene nanocomposite. An efficient polyethylene-nanoclay composite would be a very economic and efficient material for the future.
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APPENDIX

STUDY OF COMPOUNDS PREPARED BY SINGLE SCREW EXTRUSION

This section discusses the results obtained by melt compounding different polyethylene and different clays in our Killion single screw extruder using a conveying screw as well as a screw with a kneader. These experiments were carried out in different rheometers for optimizing the compounding formulations and materials. A few among them have been presented in this section as examples.

A.1 Oscillatory shear experiments

Fusabond EMB265D is a maleic anhydride graft modified HPDE resin with a melt flow rate of 123 dg/min at 190°C/2.16 kg (ASTM D1238, ISO 1133), melt point of 131°C (ASTM D3418, ISO 3146) and a typical density of 0.95 g/cc (ASTM D792).

All experiments were carried out at 200°C in a parallel plate rheometer. Figure A1.1 represents the reduction in complex viscosity of the pure polyethylene Exact 0201 with the addition of Fusabond EMB265D. This is due to the low viscosity of this fusabond compared to pure polyethylene. This must be an indication that the two polymers are perfectly miscible.

Figure A1.2 illustrates the similar behaviour discussed in the main part of the thesis wherein the clay increases the complex viscosity of the nanocomposite. What is noticeable here is that the increase over the virgin polyethylene is seen after the compensation for the loss of viscosity due to fusabond concentration. In the main part of the thesis, it has been discussed that the Newtonian plateau that is reported by Gopakumar et al. (2002) for clay concentrations above 5 wt% is not seen in our compounds at the accessible lowest frequency. However, this is clearly seen at 4 wt% and even 2 wt% clay composites in Figure A1.2. Furthermore, the dual flow behaviour wherein the nanocomposite flow approaches the shear thinning behaviour of the host polymer is reproduced in this combination.
Figure A1.1: Fusabond E MB265D being less viscous material is found to decrease the complex viscosity of the pure polyethylene.

Figure A1.2: The organically modified clay is found to increase the viscosity with higher concentrations. A distinct Newtonian plateau begins to appear with higher clay concentrations at low frequencies.
Polyone Inc., Ohio prepared 40 wt% and 4 wt% (nanoblend 2101) compound of nanomer 1.44 PA, 4 wt% compound of cloisite 10A, another organically modified clay and 4 wt% of cloisite Na+, an unmodified clay with LLDPE 1001.29 in a twin screw extruder. Cloisite clays are the products of Southern Clay Inc., Texas. These compounds were diluted in our single screw extruder to 4 wt%, 2 wt% and 0.1 wt% respectively. No modified polyethylene or fusabond was used in these studies.

Figures A1.3 to A1.5 show the complex viscosities of the nanocomposites of different clay concentrations of modified 1.44 PA, 10A and unmodified Na+ clays respectively. Gopakumar et al. (2004) reported that unmodified clays do not exhibit equivalent enhancement in complex viscosity and supported their inference from XRD analysis that unmodified clays do not exfoliate or intercalate. However, the single screw extrusion experiments in our case did not exhibit any noticeable difference between the unmodified clay composites and those with modified clay. Hence, a need for twin-screw extrusion was realized.

![Complex Viscosity Graph](image)

**Figure A1.3:** The 4 w% 1.44 PA nanocomposite exhibits an enhanced complex viscosity.
Figure A1.4: The 4 w% cloisite 10A nanocomposite exhibits an enhanced complex viscosity.

Figure A1.5: The 4 w% unmodified clay (cloisite Na+) nanocomposite exhibits similar enhancement.
Figures A1.6 to A1.8 illustrate the phenomenal deviation in terminal behaviour of the solid-like 4 wt% clay nanocomposites that were prepared from twin screw extrusion.

Figure A1.6: A huge deviation in terminal behaviour is observed in twin screw compounded 4wt% I.44 PA nanocomposite.

Figure A1.7: A huge deviation in terminal behaviour is observed in twin screw compounded 4wt% cloisite 10A nanocomposite.
Figure A1.8: A huge deviation in terminal behaviour is observed in twin screw compounded 4 wt% cloisite Na+ nanocomposite.

Nanomer I.44 PA, Cloisite 10A and Cloisite Na+ powders were also mixed together with polyethylene (Exact 3128) and compounded at 4 wt%, 2 wt% and 0.1 wt% in Killion single screw extruder. No coupling agent such as a grafted polyethylene was used. As seen from Figure A1.9, only nanocomposite with 4 wt% I.44 PA exhibits an enhancement in complex viscosity. It is also noted that in the absence of fusabond, the Newtonian plateau is not at all observed at low frequencies. This enhancement in viscosity could not be attributed to intercalation or exfoliation. The sharp slope at low frequencies supports such an argument. The enhancements observed in the cases of cloisite 10A and cloisite Na+ are insignificant. So, one can dismiss the dry mixing and single screw extrusion as plausible methods for nanocomposite preparation leading to intercalation. Figure A1.10 illustrates a comparison of storage and viscous moduli in the case of single screw extruded compounds and it could be clearly seen that only the 4 wt% I.44 PA nanocomposite shows a significant non-terminal behaviour in both the moduli while the rest of the compounds do not show any significant deviation.
Figure A1.9: Dry mixing and single screw extrusion do not seem to lead to intercalation of clay. 4 wt% 1.44 PA nanocomposite shows a significant enhancement in complex viscosity but the trend doesn’t support intercalation or exfoliation.

Figure A1.10: Moduli in case of 4 wt% 1.44 PA nanocomposite show non-terminal behaviour.
A.2 Capillary extrusion

All capillary extrusions were done in Bohlin Rosand capillary extruder without applying Rabinowitch correction factor. All the experiments were carried out at 200°C with a die of 1 mm diameter and L/D of 16 with an entrance angle of 180°. Some indicative examples are provided below.

Figure A2.1 illustrates that fusabond EMB265D contributes to a slight reduction in the apparent shear stress clearly due to its lower viscosity. Figure A2.2 illustrates that clay in fusabond based or intercalated composites plays almost no role in processing at any concentrations. Concentrations of 0.1 wt%, 2 wt% and 4 wt% are shown. Table A2.1 illustrates these findings. However, as explained in the main section of this thesis and reported by Hatzikiriakos et al. (2005), organically modified nanoclays in their pristine state do eliminate sharkskin and postpone gross melt fracture. This effect was observed in different concentrations of clay on pure polyethylene.

**Figure A2.1:** Moduli in case of 4 wt% L44 PA nanocomposite show non-terminal behaviour.
**Figure A2.2:** Moduli in case of 4 wt% I.44 PA nanocomposite show non-terminal behaviour.

**Table A2.1:** Nanoclays do not affect processability of intercalated polyethylene-fusabond nanocomposites.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Critical shear rate for onset of Shark Skin (s⁻¹)</th>
<th>Critical shear rate for onset of Gross Melt Fracture (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact 0201</td>
<td>200</td>
<td>500</td>
</tr>
<tr>
<td>90% Exact 0201 + 10% Fusabond EMB265D</td>
<td>300-400</td>
<td>500-600</td>
</tr>
<tr>
<td>80% Exact 0201 + 20% Fusabond EMB265D</td>
<td>300-400</td>
<td>600</td>
</tr>
<tr>
<td>70% Exact 0201 + 30% Fusabond EMB265D</td>
<td>300</td>
<td>600</td>
</tr>
<tr>
<td>69.9% Exact 0201 + 30% Fusabond EMB265D + 0.1% Nanomer I.44 P</td>
<td>400</td>
<td>600-700</td>
</tr>
<tr>
<td>68% Exact 0201 + 30% Fusabond EMB265D + 2% Nanomer I.44 P</td>
<td>300</td>
<td>700-800</td>
</tr>
<tr>
<td>66% Exact 0201 + 30% Fusabond EMB265D + 4% Nanomer I.44 P</td>
<td>300</td>
<td>700-800</td>
</tr>
<tr>
<td>48% Exact 0201 + 48% Fusabond EMB265D + 4% Nanomer I.44 P</td>
<td>400</td>
<td>700-800</td>
</tr>
<tr>
<td>49% Exact 0201 + 49% Fusabond EMB265D + 2% Nanomer I.44 P</td>
<td>400</td>
<td>700-800</td>
</tr>
<tr>
<td>49.95% Exact 0201 + 49.95% Fusabond EMB265D + 0.1% Nanomer I.44 P</td>
<td>400</td>
<td>600-700</td>
</tr>
</tbody>
</table>
A.3 Scanning Electron Microscopy

Some of the pictures taken in scanning electron microscopy (SEM) are shown below (Figure A3.1) to illustrate the effect of fusabond on better dispersion. These were better visualized in TEM pictures that are presented in the main section of this thesis.

Figure A3.1 SEM pictures of nanocomposites.

- PE 0201 + 4% I.44 PA
- PE 0201 + 10% Fusabond EMB226 + 4% I.44
- PE 0201 + 30% Fusabond EMB226 + 4% I.44
- PE 0201 + 50% Fusabond EMB226 + 4% I.44
- PE 0201 + 70% Fusabond EMB226 + 4% I.44
- Fusabond EMB226 + 4% I.44

Single screw extruded 30% fusabond EMB265D compounds with 4, 2 and 0.1 wt% I.44 PA respectively.
A.4 Surface Energy

Surface energy is defined as the energy required to form a unit area of surface and it also represents the interfacial tension of the solid in equilibrium with its vapor. It influences all physical interactions between different material surfaces. It is especially important in applications involving lubricants and release agents, adhesives, cleansing agents, paints and coatings.

Surface energy of a solid surface is most easily estimated from the contact angle of a liquid droplet placed on the given solid surface. This is because surface energy of solid and surface tension of liquid decide the contact angle and hence the wettability of liquid for a given surface. The contact angle is the angle formed by the solid/liquid interface and the liquid/vapor interface measured from the side of the liquid as shown in Figure 2.13. Liquids wet surfaces when the contact angle is less than 90 degrees. In fact, the contact angle for most liquid penetrants is very close to zero degrees.

To cite a practical example, the contact angle formed by a drop of ink on the paper determines the printing quality of ink. For good quality of paper, contact angle, should be between 90° and 110°. If contact angle is less than 90° then ink will spread on paper and if it is greater than 110° then breaks will occur while printing.

Interfacial force equilibrium of a liquid drop on a solid substrate, known as Young’s equation relates the interfacial forces shown in Figure A4-1 by the following equation.

\[ \gamma_{sv} = \gamma_{lv} \cos \theta + \gamma_{sl} \]  

(A4-1)

![Figure A4.1: Droplet of a liquid on a solid substrate at equilibrium](image)

In the above equation, suffix \( s \) stands for solid and \( l \) for the test liquid. The total surface energy or surface tension is divided into dispersive and polar components. Thus,
where $\gamma^D$ is the surface energy resulting from London dispersion forces. $\gamma^P$ is the surface energy resulting from dipole-dipole, induced dipole and hydrogen bonding interactions. Each of these surface energy components can be estimated by selecting two different test liquids – polar and non-polar ones for contact angle measurement.

The solid–liquid interfacial tension $\gamma_{sl}$ can be expressed by the Good and Girifalco's Geometric Mean approach, equation (A4-3) which assumes that only intermolecular force interactions are important in determining surface tension components between a liquid and a solid.

\[
\gamma_{sl} = \gamma_s + \gamma_l - \left[ 2\sqrt{\gamma_s^D \gamma_l^D} + 2\sqrt{\gamma_s^P \gamma_l^P} \right]
\]  

Combining equations (A4-1) and (A4-3), a single equation is obtained with two unknowns in the form of $\gamma_s^D$ and $\gamma_s^P$ (Girifalco and Good, 1957; Owens and Wendt, 1969).

\[
(1 + \cos \theta) = \frac{2}{\gamma_l} \left[ \sqrt{\gamma_s^D \gamma_l^D} + \sqrt{\gamma_s^P \gamma_l^P} \right]
\]  

Once the contact angle $\theta$, is estimated, equation (A4-4) can be used with two different test liquid with known surface tension to solve for the two unknowns: $\gamma_s^D$ and $\gamma_s^P$.

A.4.1 Contact Angle Measurement

The methods used for contact angle measurement can be categorized into direct and indirect methods. The direct methods involve direct observation of the liquid droplet placed on the solid surface. The image of the droplet can be photographed and magnified or can be directly viewed under a microscope fitted with angle calibrated eye piece (known as goniometry).

The indirect method of contact angle measurement estimates contact angle using the wettability of test liquid for a solid surface. It either measures the force/tension exerted on solid plate brought in contact with test liquid (known as tensiometry or Whilnely plate method) or measures the penetration rate of test liquid through a vertical bed of solid particles (known as Washburn's capillary rise method).
Goniometry and tensiometry are normally preferred for plane solid surfaces whereas capillary rise method is prevalent for solid particles and powders. Both methods have their own advantages and disadvantages. Advanced goniometry is expected to be highly accurate with an accuracy level within +/- 1° on flat solid surfaces and it is very easy to carry out the test. On the negative side, there is a possibility of human error in measuring the tangent and hence contact angle when the angle is measured manually. In addition, for porous surfaces, the major challenge in goniometry is to measure the contact angle before the liquid drop gets absorbed on the surface. This difficulty can be overcome by using high speed video images of the droplet and then analyzing the very first image of the droplet on the solid surface.

Although Washburn’s capillary rise method is normally preferred for porous surfaces and powders, there are several issues related to its accuracy and reproducibility. In the original method, the solid powder is packed in a capillary and brought in contact with the test liquid and the rising rate is measured. See Figure A4.2.

Penetration rate of the liquid through the bed of packed solid is then given by Washburn’s equation (A4-5).

\[
\frac{dh^2}{dt} = \frac{K \gamma \cos \theta}{2 \mu}
\]  

(A4-5)

\[ Condition \text{ with } \gamma_n, \mu, \theta, r, K, \nu, \phi \]

Figure A4.2: Schematic of original capillary rise method for contact angle measurement

where \( \gamma_n \) and \( \mu \) are the surface tension and viscosity of liquid, respectively, \( \theta \) is the liquid contact angle on the solid surface, \( r \) is the capillary radius, \( K \) is tortuosity constant, a property of packed solid bed, which depends on its porosity and its distribution in the bed.
For accurate measurement of the rate of liquid rise through the solid bed, equation (A4-5) is modified to measure the rate of liquid weight rise through the capillary, which can be measured using a sensitive weigh scale.

\[
\frac{d(\Delta w)^2}{dt} = \frac{K' \rho^2 \gamma_v \cos \theta}{2 \mu}
\]  

(A4-6)

The major disadvantage of the capillary rise method is the precise measurement of tortuosity constant, \( K' \). Measurement of \( K' \) is carried out by using a liquid that is considered to wet the given solid perfectly, so that the contact angle, \( \theta \), in the Washburn's equation can be assumed equal to 0. Secondly, since \( K' \) represents porosity and its distribution inside the packed bed, for reproducible results it is necessary to obtain the reproducible packing of the solid bed in terms of its porosity. This is a challenging task because it is observed that the packing is likely to get unevenly disturbed once the packing pressure is removed. It also develops fine hair cracks or capillaries as the liquid wets the bed, subsequently changing the rate of liquid rise for the remaining liquid.

![Figure A4.3: Clay-water interface](image1)

![Figure A4.4: Clay-bromonaphthalene interface](image2)

![Figure A4.5: Oven dried L44 PA - water interface](image3)

![Figure A4.6: Oven dried PGW clay – water interface](image4)
Figure A4.3 illustrates a drop of water on nanomer 1.44 P. Contact angle of water on nanomer 1.44 PA is 132.9° and non-dispersive surface energy, $\gamma_{ND}$, of nanomer 1.44 PA using water is 5.8 mJ/m². Contact angle of 1-bromonaphthalene on nanomer 1.44 PA is 30.8° and dispersive surface energy, $\gamma_{D}$, of nanomer 1.44 PA using 1-bromonaphthalene is 38.5 mJ/m².

Figure A4.4 illustrates a drop of bromonaphthalene on nanomer 1.44 P. Contact angle of water on PGV clay is 26.5° and non-dispersive surface energy, $\gamma_{ND}$, of PGV clay using water is 31.6 mJ/m². Contact angle of 1-bromonaphthalene on PGV clay is 32.4° and dispersive surface energy, $\gamma_{D}$, of PGV clay using 1-bromonaphthalene is 37.9 mJ/m².

Contact angle of water on PGW clay is 33.43° and non-dispersive surface energy, $\gamma_{ND}$, of PGW clay using water is 26.8 mJ/m². Contact angle of 1-bromonaphthalene on PGW clay is 34.67° and dispersive surface energy, $\gamma_{D}$, of PGW clay using 1-bromonaphthalene is 40.6 mJ/m². Figure A4.5 illustrates a drop of water on dried nanomer 1.44 P and Figure A4.6 illustrates a drop of water on dried PGW.

(Density of water is 1000 kg/m³ and density of 1-bromonaphthalene is 1483 kg/m³. Viscosity of water is 1.002 m Pa.s and viscosity of 1-bromonaphthalene is 4.8 m Pa.s)