Chapter 2

This chapter presents some background material that is relevant to the contents of the thesis. The first part of the chapter describes the various types of nanoclays, their classification and chemical structure. Further, the synthesis and applications of polymer nanoclay composites are also described. In the latter part of the chapter a brief introduction to conventional experimental techniques used for studying the microstructure of polymer nanoclay composite materials is provided. This includes x-ray diffraction, optical microscopy and transmission electron microscopy (TEM). Finally, a more detailed discussion on the rheology of complex fluids, in particular the rheology of filled systems, is provided.

2. 1. Clays

2. 1. 1. Phyllosilicates-structure and classification

Clays are ubiquitous minerals, which constitute a large part of the sediments, rocks and soils. Recent advances in polymer nanocomposites have rekindled interest in the smectite or phyllosilicates group of clays. [1-4] Phyllosilicates are aluminosilicates, which are 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 top of each other.

Aluminosilicate condensates in 2:1 ratio of tetrahedral Si sheets with an octahedral Al sheet are called as 2:1 phyllosilicates. Coupling of only one Si sheet to one Al sheet gives rise to 1:1 phyllosilicates called as 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. [1] Various groups of naturally occurring phyllosilicates are listed in Table 2.1.

**Table 2.1. Classification of Phyllosilicates**

<table>
<thead>
<tr>
<th>Mineral Group (Type)</th>
<th>Structural formula</th>
<th>Formula unit charge</th>
<th>Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite (1:1)</td>
<td>Al₂Si₂O₅(OH)₄</td>
<td>0</td>
<td>Dioctahedral</td>
</tr>
<tr>
<td>Serpentine (1:1)</td>
<td>Mg₃Si₂O₅(OH)₄</td>
<td>0</td>
<td>Triocathedral</td>
</tr>
<tr>
<td>Pyrophyllite (2:1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>Al₄Si₈O₂₀(OH)₄</td>
<td>0</td>
<td>Dioctahedral</td>
</tr>
<tr>
<td>Talc</td>
<td>Mg₆Si₈O₂₀(OH)₄</td>
<td>0</td>
<td>Triocathedral</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>Na₀.₂Ca₀.₁Al₂Si₄O₁₀ (OH)₂ (H₂O)₁₀</td>
<td>~0.25-0.6</td>
<td>Dioctahedral</td>
</tr>
<tr>
<td>Saponite</td>
<td>Ca₀.₁Na₀.₁Mg₂.₂₅Fe²⁺₀.₇₅ Si₃AlO₁₀(OH)₂ 4(H₂O)</td>
<td>~0.25-0.6</td>
<td>Triocathedral</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>Mg₁₈Fe²⁺₀.₆₅Al₄.₃SiO₁₀ (OH)₂ 4(H₂O)</td>
<td>~0.6-0.9</td>
<td>Dioctahedral</td>
</tr>
<tr>
<td>Illite</td>
<td>K₀.₆(H₂O)₀.₄Al₁.₃Mg₀.₃ Fe²⁺₀.₁Si₃.₅O₁₀(OH)₂ (H₂O)</td>
<td>~0.9</td>
<td>Dioctahedral</td>
</tr>
<tr>
<td>Mica (2:1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl₃Si₃O₁₀(OH)₂</td>
<td>~1.0</td>
<td>Dioctahedral</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>KMg₃AlSi₃O₁₀(OH)₂</td>
<td>~1.0</td>
<td>Triocathedral</td>
</tr>
</tbody>
</table>

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., Ca²⁺) or alkali metal ions (e.g., Na⁺). The unit cell of smectite clay comprises of eight silica tetrahedrons and six alumina octahedrons. [4] 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. [4,1]

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. [4,1] 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. [5,6]

2. 1. 2. Smectite Clays

2. 1. 2. 1. Montmorillonite

Montmorillonite is the most widely used clay for making polymer nanocomposites. This dioctahedral 2:1 phyllosilicate 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 aluminum octahedron. The aluminum octahedral sheet has Al\(^{3+}\) ion octahedrally coordinated to the hydroxyl groups. [5,6] Two third of the Al\(^{3+}\) ions are substituted by lower valency cations such as Mg\(^{2+}\) and Fe\(^{2+}\) in octahedral sites as shown in Figure 2.1.
Montmorillonite is further classified in 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$^{3+}$. [1,2] 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 as tactoids], as shown in Figure 2.2 (a). 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 color. 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. [7] These structural features endow montmorillonite with peculiar swelling properties and allow a wide range of moieties to be intercalated. For the study reported in this thesis, organically modified montmorillonites were used for making
polyolefin nanocomposites. A transmission electron microscope image (TEM) of montmorillonite is shown in Figure 2.2 (b).

![Figure 2.2. (a) Schematic of a montmorillonite tactoid (b) Transmission Electron Micrograph (TEM) of montmorillonite [8]](image)

2.1.2.2. Other nano clays

Apart from montmorillonite, other types of layered silicates both naturally occurring (e.g., vermiculite) and synthetic clays (e.g., hectorite, Trade name: Laponite RD, manufactured by Rockwood additives Ltd.) have been used for making polyolefin nanoclay composites. [9-11] Tjong et. al. have used vermiculites for preparing polypropylene (PP) nanocomposites. [10] Vermiculite is a dioctahedral smectite clay. The Al$^{3+}$ and Si$^{4+}$ ions are partially substituted by Fe$^{2+}$ and Mg$^{2+}$ respectively. The extent of this isomorphic substitution is greater compared to montmorillonite, and much of this substitution occurs in the Si tetrahedral sheet.

Tudor et. al. have prepared PP-nanocomposites, using Laponite RD {structural formula: \((\text{Na}_{0.46}\text{Mg}_{5.45}\text{L}_{0.46}\text{Si}_{8}\text{(OH)}_{4}\text{O}_{20})\)} by in-situ polymerization method. [11] 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 Li$^+$ for Mg$^{2+}$. [9]
Except for a few such examples, organically modified montmorillonite is the most commonly used clay in commercial polyolefin nanocomposites due to its easy availability and lower cost.

2. 1. 3. Advantages of layered silicates

Any physical mixture of a polymer and an inorganic material (such as clay) does not form a nanocomposite. Conventional polymer composites that are prepared by reinforcing a polymer matrix with inorganic materials like reinforcing fibers 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. [5,6,12] Table 2.2 shows a comparison of the physical properties of nanocomposites and conventional composites of polyamide.

Table 2.2. Comparison of physical properties of Nylon nanocomposites and conventional composites

<table>
<thead>
<tr>
<th></th>
<th>Pristine polymer</th>
<th>3-5% Organo clay</th>
<th>30% Mineral</th>
<th>30% Glass fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength, Psi</td>
<td>7250</td>
<td>11800</td>
<td>8000</td>
<td>23000</td>
</tr>
<tr>
<td>Flexural Modulus, Psi*</td>
<td>120</td>
<td>500</td>
<td>650</td>
<td>1000</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Notched Izod impact</td>
<td>1.2</td>
<td>1.2</td>
<td>1.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Strength</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat Distortion</td>
<td>66</td>
<td>110</td>
<td>120</td>
<td>194</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.3</td>
<td>1.14</td>
<td>1.36</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Source: RTP Co.
It is observed that in contrast to conventional composites, significant property enhancement is still achieved at much lower filler loading for nanoclays. 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. First, 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. [12,5] Second, 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 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. [12,5,6]

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. [13] This is possible for the instance in the case of exfoliated composites wherein the clay platelets are oriented with their surface normal parallel to the direction of incident 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 inter gallery distance (~ 2-3 nm) of the organo clays approximately matches the typical persistence length of flexible polymers, thus making the diffusion of polymer chains more easy.
Incorporation of nano-clays 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 as shown in the Figure 2.3. [14,15]

![Figure 2.3. Schematic of diffusion barrier by silicate platelets (l_o>>l)](image)

To sum up, polymer nanoclay composites exhibit unique thermomechanical, barrier and optical properties not shared by conventional filled composites.

2. 2. **Synthesis of polymer nanoclay composites**

Polymer nanoclay composites can be synthesized by four methods:

1. **Sol-gel process:** The sol-gel process involves hydrolysis and polycondensation of metal alkoxides \( \{M(OR)\_n\} \) in aqueous acid or base, to form an inorganic gel network in an organic polymer matrix as shown in e. q. 2.1 and 2.2. [16,17]

\[
\begin{align*}
\text{Si-OR} + \text{H}_2\text{O} \quad &\xrightarrow{H-/OH^+} \quad \text{Si-OH} + \text{R-OH} \quad (2.1) \\
\text{Si-OH} + \text{HO-Si} \quad &\xrightarrow{H^-/OH^+} \quad \text{Si-}O\text{-Si} + \text{H}_2\text{O} \quad (2.2)
\end{align*}
\]

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. [16] 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. [17]

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. [18]

2. In-situ Polymerization: In this method, first 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 as illustrated in the schematic in Figure 2.4. Polycaprolactone [19] and nylon [20] 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 limit the commercialization of this method. [6]

![Figure 2.4. Schematic of nanocomposite synthesis by in-situ polymerization](image)

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 [21] and polylactide [22] 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. [5]

4. Melt Intercalation: This method involves the mixing of polymer with clay above the polymer glass transition or melt temperature. At higher temperatures polymer chains are sufficiently mobile to diffuse into the galleries of the clay. [23-27] Vaia et. al. 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. [23,26] Cho et. al. 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. [24]

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 sonication [28] and micellar intercalation. [29]

2.3. Morphologies of polymer nanocomposites

In general, the microstructures of polymer-layered silicate nanocomposites are classified in two idealized morphologies viz., intercalated and exfoliated. [5,6,30,31]

In an immiscible composite or an unmixed system the polymer does not penetrate inside the galleries between the clay layers and hence the pristine gallery distance is maintained in the composite. In intercalated structures however, polymer chains penetrate
inside the galleries and effectively expand the silicate layers. [31] Such structures consist of ordered, alternating polymer–silicate layers with repeat distance of a few nanometers. The equilibrium gallery height is determined by entropic and energetic factors. When the gallery distance, (h) is less than the radius of gyration, (Rₜ), of the polymer chains, the configurational entropic penalty of polymer chain confinement may be compensated by increased conformational freedom of the tethered surfactant chain. When h > Rₜ, the entropy change is almost zero. [30]

An ideal exfoliated state refers to a structure, where the polymer extensively penetrates in the silicate galleries so as to completely delaminate the layered structure. In the exfoliated state the average gallery height is determined by clay loading. This class of microstructure can be further classified based on the relative change in the separation between platelets with silicate volume fraction. Low silicate loadings result in disordered exfoliated nanocomposites in which single clay platelets are randomly suspended in the polymer matrix and are typically separated by an average distance of > 10 nm. Above a critical clay loading, the platelets start arranging in an ordered fashion and this is called the ordered exfoliated nanocomposites, as shown in Figure 2.5. [31]

However, real nanoclay composites exhibit morphologies, which are combinations of these idealized morphologies.

The state of dispersion of clay in polymer is in general dictated by the polymer-silicate interactions, aspect ratio of silicate, method of manufacturing (melt, solution, in-situ polymerization) and possible orientation of layers during processing.
2. 4. Applications of polymer nanocomposites

Polymer nanoclay composites caught the attention of the technologist after nylon nanocomposite made a market debut in Toyota Motor Company's car model in the late 1980's. Since then nanocomposites are gradually gaining acceptance in mainstream polymer industry finding applications in automotive to packaging sectors. [6,7,12,32]

Polymer nanoclay composites have huge potential as they can achieve the same properties, e.g., increased tensile strength, improved heat deflection temperature and impact strength, with typically 3 – 5 wt% of the filler compared to 30-wt% for conventional composites, as shown in Table 2.2. Such improvements in the thermo-mechanical properties make nanocomposites a potential candidate for many automotive products such as mirror housings, door handles, engine covers and timing belt covers. General industrial applications currently being considered include usage as impellers and blades for vacuum cleaners, power tool housings, etc. [12]
Nanocomposites offer 25% weight reduction over conventional composites and as much as 80% over steel. Reduced weight helps to increase fuel efficiency. Further, such improvements can be achieved with very little increase in fabrication cost and material cost. General Motors and Montell have jointly developed olefin (TPO) clay nanocomposite for an exterior step assist for the 2002 Astra and Safari vans. Mitsubishi used a nanocomposite in the engine cover for its GDI engines. [12]

A recent study in UBE Industries revealed significant reductions in diffusive fuel loss through polyamide–6/66 polymers by using nanoclay as filler. This is due to the enhanced barrier properties of polymer nanoclay composites as discussed earlier in section 2.1.3. As a result, considerable interest is now being shown in these materials as both fuel tank and fuel line components for cars. [33]

Honeywell Inc. claims that incorporation of just 2 % nano-clays improves the oxygen barrier (OTR) three times than that of pristine nylon 6 films. [33] Owing to the excellent barrier properties, nanocomposite films can be used in food packaging like pet foods, boil-in bags and vacuum packs. Bayer and Nanocor are aiming nylon 6 nanocomposites cast film for multi-layer packaging, protective films for medical and corrosion-prone items.

Kabelwerk Eupen of Belgium claims to be on the way to commercialize EVA nanocomposites for wire and cable compounds. [33] Calorimeter tests for these materials show decline in heat release at relatively low (3 - 5 wt%) loadings. Nano-EVAs also exhibit superior mechanical properties, chemical resistance and thermal stability. Showa Denko of Japan recently started commercial production of nylon 66 nanocomposites. They show improved flame retardancy and rigidity. [33] Table 2.3 lists the current suppliers of polymer nanoclay composites.

In addition to these already commercialized nanocomposites various industries and academic research groups are investigating nanocomposites of other polymers like polycarbonate, biodegradable polylactic acid (PLA) and polyaniline. It will not be a surprise to see many of them in the market soon.
### Table 2.3. List of nanocomposite suppliers and targeted applications

<table>
<thead>
<tr>
<th>Supplier &amp; Tradename</th>
<th>Matrix Resin</th>
<th>Target Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayer AG (Durethan LPDU)</td>
<td>Nylon 6</td>
<td>Barrier films</td>
</tr>
<tr>
<td>Clariant</td>
<td>PP</td>
<td>Packaging</td>
</tr>
<tr>
<td>Creanova (Vestamid)</td>
<td>Nylon 12</td>
<td>Electrically conductive</td>
</tr>
<tr>
<td>GE Plastics (Noryl GTX)</td>
<td>PPO/Nylon</td>
<td>Automotive painted parts</td>
</tr>
<tr>
<td>Honeywell (Aegis)</td>
<td>Nylon 6, Barrier Nylon</td>
<td>Multi-purpose bottles and film</td>
</tr>
<tr>
<td>Hyperion</td>
<td>PETG, PBT, PPS, PC, PP</td>
<td>Electrically conductive</td>
</tr>
<tr>
<td>Kabelwerk Eupen of Belgium</td>
<td>EVA</td>
<td>Wire &amp; cable</td>
</tr>
<tr>
<td>Nanocor (Imperm)</td>
<td>Nylon 6, PP Nylon MDX6</td>
<td>Multi-purpose molding PET beer bottles</td>
</tr>
<tr>
<td>Polymeric Supply</td>
<td>Unsaturated polyester</td>
<td>Marine, transportation</td>
</tr>
<tr>
<td>RTP</td>
<td>Nylon 6, PP</td>
<td>Multi-purpose, electrically conductive</td>
</tr>
<tr>
<td>Showa Denko (Systemer)</td>
<td>Nylon 6, Acetal</td>
<td>Flame retardance, Multi-purpose</td>
</tr>
<tr>
<td>Ube (Ecobesta)</td>
<td>Nylon 6, 12, Nylon 6, 66</td>
<td>Multi-purpose Auto fuel systems</td>
</tr>
<tr>
<td>Unitika</td>
<td>Nylon 6</td>
<td>Multi-purpose</td>
</tr>
<tr>
<td>Yantai Haili Ind., Commerce of China</td>
<td>UHMWPE</td>
<td>Earthquake-resistant pipe</td>
</tr>
</tbody>
</table>

Source: Bins & Associates, Sheyboygan, U.S.A.
2. 5. Experimental characterization techniques

Analytical techniques like x-ray diffraction (XRD), optical microscopy (OPM) and transmission electron microscopy (TEM) are very often used to elucidate the structure of polymer nanoclay composites.

2. 5. 1. X-ray Diffraction (XRD)

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 [34,35]

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

(2.3)

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 (Cu) or molybdenum (Mo) anodes, which emit x-rays corresponding to wavelengths of 1.54 Å and 0.8 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. [34]

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 the atomic distances by Bragg's law [34,35]

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

(2.4)

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, as shown in Figure 2.6.

![Figure 2.6. Schematic for Bragg's law](image)

X-ray diffraction data can be collected by using either reflection or transmission geometry as shown in Figure 2.7. In the reflection mode, x-rays scattered or reflected from the sample are detected as shown in Figure 2.7 (a). 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.
Figure 2.7. Schematic of x-ray diffraction geometries (a) reflection mode
(b) transmission mode

The peak position, intensity, and shape provide important information about the long-range order in the material. For example, the apparent crystal size (L) can be quantitatively calculated by Scherrer’s formula. [34]

\[ L = \frac{0.9 \lambda}{\beta_0 \cos \theta} \]  

(2.5)

where, \( \beta_0 \) is the half width of the crystalline peak in radians.

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 as shown in the Figure 2.7 (b). 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. The x-ray diffraction technique has been extensively used to investigate the structure of polyolefin-nanoclay composites in this thesis.
2. 5. 2. Optical Microscopy (OPM)

Optical microscopy is a technique in which visible light transmitted through the bulk of or reflected from the surface of a sample is collected and magnified to enable visualization of the structural features in the sample. [34] In this thesis we will be concerned with observing cross-polarized light transmitted through the sample. When light passes through any material, it interacts with the molecules of the material. Depending upon these interactions, light is partly absorbed, partly transmitted and partly reflected. These interactions often slightly reduce the velocity of light passing through it. The extent of reduction in velocity of light can be measured as the refractive index.

In general, the optical character of any specimen can be described by three orthogonal refractive indices, \((n_1, n_2, n_3)\). The three indices would be equal for an unoriented sample, while the refractive indices parallel and perpendicular to the direction of orientation would be different for an orientated sample. The birefringence may be expressed as [34]

\[ \Delta n = n_1 - n_2 \]  

(2.6)

Thus the magnitude of \(\Delta n\) measured using an optical microscope depends on the degree of orientation and the optical anisotropy of the material. Birefringent structures upto a few microns (~1-4 microns) can be studied by using optical microscopy. Thus polymer crystalline entities such as spherulites and primary clay particles can be observed by OPM.

A schematic of an optical microscope is illustrated in Figure 2.8. As shown in the schematic, light is first passed through a polarizer, which allows the rays vibrating in only one direction to pass through. Polarized light is then passed through the sample followed by an analyzer before reaching the observer. [34]
2.5.3. Transmission Electron Microscopy (TEM)

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. [34] 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 [34]: 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. A schematic of a TEM is illustrated in Figure 2.9.
Figure 2.9. Schematic of transmission electron microscope (TEM)

In the present work TEM has been used occasionally to directly observe the state of dispersion of clay in the polymer matrix. A TEM of polypropylene nanocomposites is illustrated in Figure 2.10

Figure 2.10. TEM of polypropylene nanoclay composites [12]
2. 6. Rheology

2. 6. 1. General introduction

The term ‘Rheology’ means the study of deformation and flow of matter. The science of rheology deals with the study of stress - deformation relationships of materials that are more complex in behavior than ordinary liquids and solids. [36-41]

Consider the case of simple shear deformation, where the material is sheared in between two parallel plates, held distance (h) apart, with the lower plate stationary and the upper plate moving with velocity (V), exerting shear force (F) on area (A), and displacing the material by a finite distance (V) in time (dt) as illustrated in Figure 2.11.

Then, shear stress (σ), shear rate (γ') are defined as

Shear stress (σ) = F/A = Force/Area (dyne/cm²)
Shear Strain (γ) = V/h = Displacement/spacing (dimensionless)
Shear rate (γ') = (dV/dt)/h (s⁻¹)

(Hookean solid: For a perfectly Hookean elastic solid, the applied stress (σ) is proportional to the strain (γ).) [36]

\[ σ = Gγ \]  (2.8)

where, the proportionality constant, G is called as the shear modulus. The modulus of the material is a measure of its stiffness or ability to resist the deformation.

Newtonian liquid: For a perfectly viscous liquid, the applied stress (σ) is proportional to the strain rate (γ')

\[ σ = ηγ' \]  (2.9)
where, \( \eta \) is the coefficient of viscosity. A liquid is said to be Newtonian if the viscosity does not depend upon the strain rate.

Hookean solids and Newtonian liquids are idealized cases representing perfectly elastic and viscous materials, respectively. A perfectly elastic material stores all the deformational energy and regains its original shape after the deforming forces are removed, while a perfectly viscous material dissipates all the deformational energy through flow. In reality however, the response of all materials, especially those of complex fluids such as polymers, to the applied deformation is a combination of both viscous and elastic behavior. Such combined behavior is termed as viscoelastic behaviour. [37]

### 2. 6. 2. Linear viscoelasticity

Linear viscoelasticity refers to the behaviour of complex fluids which can be expressed as a linear combination of a Newtonian viscous and a Hookean elastic response. Thus, the modulus and viscosity of the material remains constant over the range of deformation or stresses applied. The stress in a viscoelastic fluid depends on not only the present deformation but also on the history of deformation. A fading memory function, which is typically an exponential decay, describes how much of the past deformation contributes to the present stress state. [38,40] A viscoelastic fluid has a characteristic time scale over which the stress relaxes. A dimensionless number, the Deborah number (\( D_e \)) may be defined as the ratio of the material relaxation time (\( \lambda \)) to process time (\( t_p \)).

\[
D_e = \frac{\lambda}{t_p} \tag{2.10}
\]

For a steady state process a similar dimensionless number viz., the Weissenberg number (\( W_e \)), may be defined as,

\[
W_e = \dot{\gamma}\lambda \tag{2.11}
\]

where, \( \dot{\gamma} \) is the steady rate deformation rate. At short times, i.e., large \( D_e \) or \( W_e \), the material response is elastic, while at long times, i.e., small \( D_e \) or \( W_e \), the material response is viscous.
Typically linear viscoelastic behaviour is exhibited over a limited range of small deformation or stress. Several linear viscoelastic material functions, which quantify the response of the fluid, can be obtained from rheological experiments. Those that are used in this work are described in the following:

**Stress relaxation after step strain:** In this experiment, a small strain ($\gamma_0$) is instantaneously imposed on the material and held constant, while the stress ($\sigma$) is measured as a function of time. Typical response of a Hookean elastic solid, a Newtonian viscous liquid and a linear viscoelastic fluid are shown in Figure 2.12. (b). [40]

![Stress Relaxation Diagram](image)

**Figure 2.12. Stress relaxation experiment a) step in shear strain with time b) typical response of viscous, elastic, viscoelastic materials**

When $\gamma$ is small, then stress relaxation modulus $G(t)$ is defined as

$$G(t) = \frac{\sigma(t)}{\gamma_0} \quad (2.12)$$

**Creep Experiment:** In a shear creep experiment, a constant shear stress ($\sigma_0$) is imposed and the shear strain $\gamma(t)$ is monitored as a function of time. For polymeric liquids the strain rapidly increases initially like an elastic solid and then continues to increase more slowly with time until at long times a linear increase with time (i.e., constant $\dot{\gamma}$) is observed. Creep behaviour of typical polymer is shown in Figure 2.13. [37]

Data usually is expressed in terms of the creep compliance, $J(t)$ given as

$$J(t) = \frac{\gamma(t)}{\sigma_0} \quad (2.13)$$

As indicated in the figure steady state creep compliance ($J^0$) is defined by the extrapolation of the limiting slope to $t = 0$. For a Newtonian liquid ($J^0$) would be zero. A
non-zero value for $J_e^0$ is clear indication of viscoelastic nature. [38] An ideal Hookean solid will not creep or flow under stress with time and for Newtonian liquid creep compliance will vary linearly with time. [40]

![Graph showing Creep and Recovery](image)

**Figure 2.13. Creep experiment a) stress with time b) compliance with time**

The slope of the compliance curve at long time gives the inverse of zero shear viscosity ($\eta_0$). At long times the creep compliance can be written as [37,39,40]

$$J(t) = J_e^0 + \frac{t}{\eta_0}$$

(2.14)

Another type of experiment often done in conjunction with creep is creep recovery, which is the measurement of the recoil of strain after the stress is removed. Recoverable creep compliance is given as [35]

$$J_r = \frac{\gamma_r(t)}{\sigma_0}$$

(2.15)

where, $\sigma_0$ is the stress before recovery starts.

**Oscillatory experiments:** An oscillatory shear experiment is the most commonly used method for determining the linear viscoelastic properties of polymers. In a typical oscillatory shear experiment a sinusodally varying small amplitude stress or strain is applied to the sample, and the response, i.e., either sinusodally varying strain or stress, respectively, is measured. This kind of deformation is achieved in parallel plate or cone-plate geometries (discussed in the next section) by rotating the cone or the plate about its axis. The strain oscillates sinusoidally as given by

$$\gamma(t) = \gamma_o \sin(\omega t)$$

(2.16)
where, $\omega$ is the frequency of oscillations. For viscoelastic materials the response is qualitatively illustrated in the Figure 2.14. [36]

![Graph showing oscillatory shear strain and stress response](image)

**Figure 2.14. Oscillatory shear strain, shear stress in small amplitude oscillatory shear**

The strain amplitude ($\gamma_o$) is so chosen as to ensure that the material deformation is in the linear viscoelastic regime. For an elastic solid, since the stress is directly proportional to the strain, it will be *in phase* with the applied strain. In case of viscous liquids the stress response is *out of phase* with the applied strain. The polymer response is typically in between these two limits as illustrated in Figure 2.15 with some phase shift ($\delta$). In general, the sinusoidally varying stress can be represented as [36,41]

$$\sigma(t) = \gamma_o [G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)]$$

(2.17)

where, the term $G'(\omega)$ is *in phase with the strain* ($\gamma$) and is called the *storage modulus*. It represents the stored elastic energy. The term $G''(\omega)$ is in phase with the rate of strain ($\dot{\gamma}$) and is called the *loss modulus*. It represents the viscous dissipation of stored energy. The ratio $G''/G'$ is called the *loss tangent* ($\tan \delta$). A higher value ($>>1$) of loss tangent indicates liquid like response of the material and lower value ($<<1$) indicates a solid like behavior. The complex modulus $(G^*)$ is given as

$$G^* = G' + iG''$$

(2.18)

where, $G'$ is the real part and $G''$ is the imaginary part. Similarly, a complex viscosity is defined as

$$\eta^* = \eta' + i\eta''$$

(2.19)

where, $\eta'$ is the real part and $\eta''$ is the imaginary part.
Figure 2.15 shows a schematic variation of the complex modulus ($G^*$) with frequency ($\omega$) for a flexible, entangled polymer melt.

![Schematic of complex modulus variation as a function of frequency for a typical polymer](image)

**Figure 2.15. Schematic of complex modulus variation as a function of frequency for a typical polymer [39]**

At low frequencies, i.e., in the terminal region of relaxation, the material response is mainly liquid-like and $G'' > G'$ in this region. The slopes of $G''$ and $G'$ are 1 and 2, respectively. Both $G''$ and $G'$ increase in this region till a crossover point at some frequency ($\omega_c$). [39] The reciprocal of crossover frequency gives the characteristic relaxation time of the material. In the terminal regime $G'$ and $G''$ data can be fit to a multimode Maxwell model given by [36]

$$
G' = \sum_i g_i \frac{(\omega \lambda_i)^2}{1 + (\omega \lambda_i)^2}, \quad G'' = \sum_i g_i \frac{(\omega \lambda_i)}{1 + (\omega \lambda_i)^2}
$$

(2.20)

where, $g_i$ and $\lambda_i$ are the modulus and relaxation time of mode $i$.

After crossover, at intermediate frequencies, i.e., in the plateau region, $G'$ reaches a constant value ($G' \approx G_N^*$). The **plateau modulus** ($G_N^*$) is independent of the molecular weight and depends only on the chemical nature of the polymer. Correspondingly in this region $G''$ passes through a minimum.

Both $G''$ and $G'$ increase again at higher frequencies. At such higher frequencies or small time scales only the response of small parts of the polymers (i.e., few monomeric
units) can be probed. The glassy modulus \( (G_g) \) measured at much higher frequency is of the same order of magnitude for all polymers \( (G_g \sim 10^9 \text{ Pa}) \). [39]

**Time-temperature superposition:** The viscoelastic material functions are strong functions of temperature. Also, the \( G(t), G' \) and \( G'' \) span many orders of magnitude in time or frequency scale. No single experiment can cover the entire span. Fortunately most of the polymeric melts obey the principle of time-temperature superposition. Consequently a change in temperature shifts the viscoelastic functions along the time (or frequency) scales without changing their shapes. [34,37]

Thus, from e. q. 2.20 and neglecting the weak temperature dependence of \( g_{ig} \),

\[
G'(T) = G'(T_o)
\]

if

\[
[\omega \lambda]_T = [\omega \lambda]_{T_o}
\]  (2.21)

The dependence of the relaxation time on temperature is given by either the WLF e. q.

\[
\ln a_T = \ln \frac{\lambda(T)}{\lambda(T_o)} = -\frac{C_i(T - T_o)}{C_2 + T - T_o}
\]  (2.22)

or by the Arsenics e. q.

\[
\ln a_T = \ln \frac{\lambda(T)}{\lambda(T_o)} = \frac{\Delta E_o}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right)
\]  (2.23)

where, \( E_o \) is the flow activation energy and \( a_T \) is called the horizontal shift factor. Thus we get,

\[
\ln \omega_T = \ln \omega_{T_o} + \ln a_T
\]  (2.24)

which implies a horizontal shift by an amount \( \ln a_T \) on \( \ln \omega \) axis.

**2.6.3. Non-Linear viscoelasticity**

At high strains the viscoelastic response of polymeric fluids deviate from linearity. The non-linear response is typically caused by orientation of the microstructure (e.g., chain orientation). Usually \( G(t), G' \) and \( G'' \) decrease with increasing strain. A dynamic amplitude sweep test is done to delineate the linear and non-linear viscoelastic regimes. Figure 2.16 shows a schematic of a strain amplitude sweep test.
In the non-linear regime the relaxation modulus $G(t)$ becomes a function of time and strain. Equation 2.12 is then modified to

$$G_{nl}(t, \gamma) = \sigma(t, \gamma)/\gamma_o = G(t)h(\gamma)$$

(2.25)

where, $G(t)$ is the relaxation modulus in the linear regime (e.g. 2.12) and $h(\gamma)$ is called the damping function. Equation 2.25 shows an important property of viscoelastic fluids viz., time-strain factorability, which is observed for polymer melts above a certain time scale.

**Figure 2.16. Schematic of a strain amplitude sweep**

**Steady shear:** In this experiment, a constant shear rate is applied and steady shear stress and normal stresses are measured. Measurements are typically made over a wide range of shear rates to study shear rate dependence of the sample. At low shear rates a Newtonian plateau is seen, whereas the viscosity often decreases with increasing shear rates at high shear, as illustrated in Figure 2.17. The shear thinning or thickening response can be described by a simple empirical inelastic constitutive model viz. the power law equation given by

$$\eta_{app} = m\gamma^{n-1}$$

(2.26)

where, $\eta_{app}$ is the apparent viscosity, $n$ is power law index and $m$ is the consistency index. The material is shear thinning when $n < 1$ and shear thickening when $n > 1$. 

33
Figure 2.17. Viscosity dependence of Newtonian and Non-Newtonian materials

**Cox-Merz rule:** Generally for many polymer melts and solutions, the shear viscosity as a function of shear rate, \( \eta(\dot{\gamma}) \), is almost identical to the complex viscosity as a function of frequency. [35]

\[
\eta(\dot{\gamma}) = \eta^*(\omega), \text{ for } \dot{\gamma} = \omega.
\] (2.27)

This is the empirical Cox-Merz rule and is frequently used to estimate shear-viscosity curves from linear viscoelastic data. However, fluids having complex structure such as liquid crystalline polymers do not obey this law.

**Plastic behaviour:** Certain materials show no deformation up to certain level of stress, referred to as the yield stress. Above the yield stress the material flows readily, as illustrated in the Figure 2.18. [37]

Figure 2.18. Bingham plastic behaviour
Various flow models have been proposed to explain the viscoplastic behaviour of such fluids. [38]

Bingham model:

\[ \sigma = \sigma_y + \eta \dot{\gamma} \]  

(2.28)

Herschel-Bulkely:

(HB-1) \( \sigma = G_0 \dot{\gamma} \) for \( \sigma < \sigma_y \); (HB-2) \( \sigma = \sigma_y + m \dot{\gamma}^n \) for \( \sigma > \sigma_y \)  

(2.29)

Casson Model:

\[ \dot{\gamma} = 0 \text{ for } \sigma < \sigma_y ; \quad \sigma^{\frac{1}{2}} = \sigma_y^{\frac{1}{2}} + (\eta \dot{\gamma})^{\frac{1}{2}} \text{ for } \sigma > \sigma_y \]  

(2.30)

Papanastasiou's modification:

\[ \sigma = \left\{ \eta + \frac{\sigma_y (1 - \exp(-a \dot{\gamma}))}{\dot{\gamma}} \right\} \dot{\gamma} \]  

(2.31)

The above models qualitatively predict the plastic behaviour of the material. These models will be discussed in more detail in chapter 8.

2.6.4. Rheometers and test geometries

The rheological characterization reported in this thesis has been performed using both stress-controlled and strain-controlled rheometers. A stress-controlled rheometer consists of a constant torque motor. [36-41] The software converts the applied value of torque to a shear stress, and by monitoring the change of strain as a function of time the shear rate is obtained. The strain-controlled rheometer consists of a constant speed motor with a torque detection system. The software converts the measured torque to shear stress value.

**Test geometries:** Parallel plate geometry is used for the melt rheological experiments at lower shear rates. The material is held in between two parallel plates as shown in the schematic in Figure 2.19. [36]
Figure 2.19. Schematic of a) parallel plate geometry b) capillary rheometer

One of the discs is rotated with an angular velocity ($\omega$). The shear rate ($\dot{\gamma}$) is given by

$$\dot{\gamma} = \frac{\omega R}{H}$$  \hspace{1cm} (2.32)

where, $R$ is the radius of the plate.

The viscosity ($\eta$) is given as

$$\eta = \frac{2\pi R^3 \left[ 3 + \frac{d \ln(T/2\pi R^3)}{d \ln \dot{\gamma}_R} \right]}{\dot{\gamma}_R}$$  \hspace{1cm} (2.33)

where, $\dot{\gamma}_R$ is the shear rate at the edge of plate.

A small quantity of sample is required for the analysis. The parallel plate geometry can be used only over a limited range of shear rates. For higher shear rates, a capillary rheometer is used. In this rheometer the melt in the barrel is forced through a capillary by a piston moving with a velocity ($V$) as shown in the schematic in Figure 2.19 (b).

The shear stress at the wall ($\tau_w$) is given by

$$\tau_w = \frac{\Delta P R}{2L}$$  \hspace{1cm} (2.34)

where, $\Delta P$ is the pressure drop across the capillary, $R$ is the radius of capillary and $L$ is length of the capillary. The shear rate at wall ($\dot{\gamma}_w$) is given by the Weissenberg - Rabinowitsch equation as [38]
\[ \dot{\gamma}_w = \frac{1}{\tau_w^2} \frac{d}{d\tau_w} \left[ \tau_w^3 \frac{Q}{\pi R^3} \right] \]  

(2.35)

where, \( Q \) is the flow rate of the material. The apparent viscosity \( \eta_{app} \) is then calculated from eq. (2.9).

2.6.5. Rheology of filled polymers

The low shear viscosity of a dilute suspension is given by the Einstein equation as [40]

\[ \eta_o = \eta_{os} (1 + K_E \phi) \]  

(2.36)

where, \( \eta_{os} \) is viscosity of the matrix fluid, \( \eta_o \) 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 for very low filler loading \( (\phi \leq 0.03) \). When the filler loading increases, the filler particles get close enough that 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 \( (\phi \leq 0.10) \) is given by

\[ \frac{\eta_o}{\eta_{os}} = 1 + 2.5\phi + 6.2\phi^2 \]  

(2.37)

At still higher filler concentration, the viscosity of the suspension increases dramatically with the filler loading and may be modeled by an exponential function as shown in the Figure 2.20.

\[ \eta_o = \eta_{os} \exp(\phi) \]  

(2.38)
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 \([40]\)

\[
P_e = \frac{\eta_0 \dot{\gamma} a^3}{k_B T} \propto \dot{\gamma}_D
\]

(2.39)

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

\[
t_D \approx \frac{6\pi \eta_0 a^3}{k_B T}
\]

(2.40)

\( k_B \) 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 \([40]\)

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

(2.41)

where, \( f(\phi, t) \) is the fraction of particles oriented at an angle \( (\phi) \) at time \( (t) \), and \( (\Theta) \) is the rotational diffusion coefficient. From e. q. (2.40) the orientation is expected to decay in an exponential manner given by

\[
f = f_0 e^{-\Theta t}
\]

(2.42)
For an ellipsoidal particle the rotational diffusivity is related to particle dimensions and to matrix viscosity ($\eta_{\text{matrix}}$) by [42]

$$\Theta = \frac{3k_B T}{16\pi\eta_{\text{matrix}} a^3} \left[ 2 \ln \left( \frac{2a}{b} - 1 \right) \right]$$

(2.43)

where, $a$ and $b$ are the major and minor axes of the ellipsoidal particle. For such asymmetric particles the Peclet number may be defined as

$$P_c = \frac{\dot{\gamma}}{\Theta}$$

(2.44)

### 2.6.6. Mechanical behaviour of semicrystalline polymers

This discussion of mechanical properties is restricted to only tensile properties of semicrystalline polymers in the context of the work reported in chapter 9 of this thesis. The schematic of stress-strain curve for a typical semicrystalline is shown in the Figure 2.21 along with different stages of ductile deformation of a tensile specimen [43]

![Figure 2.21. Schematic of the mechanical behaviour of the semicrystalline polymer](image)

Figure 2.21. Schematic of the mechanical behaviour of the semicrystalline polymer
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 yields; 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 as 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.

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