This chapter presents a survey of the contribution of various researches towards synthesis, characterization, processing and rheology of polymer layered silicate (PLS) nanocomposite materials. The purpose of the chapter is not to summarize all of the literature in this area, which is growing at an enormous rate. Rather, the discussion is restricted to only those topics that are of immediate relevance to the work described in this thesis. This survey includes only the literature published in various scientific journals. A compilation and discussion of the nearly 400 patents filed in last three decades for the various commercially important PLS nanocomposites, is out of the scope of this thesis.

3.1. Synthesis of PLS nanocomposites

The synthesis of polymers such as polystyrene [1,2] and polyacrylic acid [3] in the interlayer spacing of montmorillonite has been reported as early as in the 1960’s. The technological potential of these materials was realized after the pioneering efforts of the research group in Toyota Motor Co.

PLS nanocomposites can be synthesized by in-situ polymerization, solution blending and melt intercalation as discussed in chapter 2. Usuki et. al. reported the synthesis of nylon 6-clay hybrid by in-situ polymerization of $\varepsilon$-caprolactum in the interlayer layer space of montmorillonite, the surface of which was modified by $\omega$-amino acid. [4] The carboxyl acid end group of the amino acid initiated the polymerization of $\varepsilon$-caprolactum. TEM and XRD analysis of these hybrids showed an exfoliated microstructure. Polymers like poly $\varepsilon$-caprolactone (PCL), [5] polycarbonate (PC), [6,7] epoxy, [8-11] polyethylene (PE), [12-14] polypropylene (PP), [13,15,16] polyethylene terephthalate (PET), [17] polydimethyl siloxane (PDMS), [18] polyamide [19-22] and polyimide [23] have also been reported to give exfoliated hybrids by in-situ polymerization of the respective monomers in the interlayer spacing of the clays. Thus it may be inferred that in-situ polymerization often leads to exfoliated nanocomposites. However, the exact reason behind this phenomenon remains elusive.
There are extensive reports of exfoliated nanocomposites synthesized by in-situ polymerization method where the catalyst is anchored on the clay surface. PLS nanocomposites synthesized by this route has a portion of polymer chains tethered to the clay surface. [12,24-27]

PE nanocomposites have been synthesized by using a wide range of catalysts like Zirconocene based metallocene catalysts, [24,15] Ziegler-Natta Titanium based catalysts [27,26] and late transition metal based catalysts like Palladium (Pd), and Nickel (Ni). [28,12] Various types of clays like Flurohectorite, [28] montmorillonite [26] and Seiolite-palgorskite [27] have been used as the clay support. Jin et. al reported synthesis of PE nanoclay composites using Ti-based Ziegler-Natta catalyst, anchored to the silicate layers of montmorillonite. [26] The montmorillonite surface was modified using intercalation agents containing hydroxyl groups. Heinemann et. al synthesized HDPE, LLDPE and LDPE nanoclay composites by both melt extrusion and in-situ homo and copolymerization of ethylene, in the presence of methylaluminoxane (MAO) activated metallocene catalyst and late transition metal based catalyst like Ni and Pd and found that PLS-nanocomposite prepared by in-situ polymerization are better exfoliated. [12]

PLS nanocomposites can also be synthesized by using the sol-gel method, as discussed in chapter 2. Polymethylmethacrylate (PMMA) nanocomposites are commonly synthesized by the sol-gel method. [29-32] Seckin et. al synthesized PPMA nanoclay composite using bentonite clay. FTIR and XRD analysis showed that the polymer was linked to clay via hydrogen bonding. [30] Huang et. al synthesized PLS nanocomposites by using different functionalized viz., trialkoxysilyl, hydroxyl and unfunctionalized methyl acrylic polymers by the sol-gel method. [32] The trialkoxysilyl functionalized PMMA was found to be best suited, since it exhibited maximum property improvement.

Polymer clay hybrids can be synthesized by solution blending (i.e., intercalation of polymer from solution). PLS nanocomposites based on polymers like PCL, [33] polylactide (PLA), [34] polyethylene oxide (PEO), [35] syndiotactic-polystyrene (s-PS), [36] PMMA [37] and PE [38] have been synthesized by solution blending. Jeon et. al have reported the synthesis of HDPE nanoclay composites by solution blending. [38] TEM analysis revealed the formation of intercalated nanocomposites. However, the
presence of fairly large clay tactoids indicated very poor dispersion of clay in the polymer matrix.

PLS nanocomposites of polymers like PEO, [39] polystyrene (PS) [40] and PMMA [41-43] have been synthesized by conventional techniques like emulsion and suspension polymerization. For example, Noh et. al. reported on the synthesis of PS nanocomposite synthesis by emulsion polymerization using Na⁺-montmorillonite, which demonstrated fine dispersion of clay in the polymer matrix and improved mechanical properties. [40]

Giannelis et. al. proposed the more versatile and environmental friendly method for nanocomposite synthesis namely, melt intercalation, which involves melt mixing the polymer and clay. [44] Vaia et. al. found improved intercalation through the aid of conventional processing techniques like extrusion. [45-47] Cho et. al. have shown twin-screw extrusion to be more effective for exfoliation and dispersion of the clay layers compared to single screw extrusion due to more extensive shear. Furthermore, for optimally compatibilized polymer-organoclay systems twin-screw extrusion leads to composite properties comparable to those produced by in-situ polymerization. [48]

Fornes et. al. have suggested that during melt compounding the shear stress, dictates the final morphology of the hybrid. [49,50] It was suggested that in the initial stages of extrusion the stress would break up the organoclay particles into smaller tactoids. Further during the extrusion, individual platelets of these tactoids would be peeled apart by combined effect of shear and diffusion of polymer chains in the gallery as illustrated in the Figure 3.1.

![Figure 3.1. Stepwise mechanism of clay exfoliation during the melt mixing of nanocomposites](image-url)
Dennis et. al. have reported on the effects of the melt processing conditions on the exfoliation of PLS nanocomposites. [51] They observed that factors like the residence time in the extruder and the intensity of shear play a crucial role in determining the dispersion of clay in the polymer matrix. They found that the degree of clay dispersion was maximized by the backmixing in a co-rotating twin-screw extruder. [51]


In the case of many commercially important polymers, the solution intercalation or the in-situ polymerization techniques are difficult to implement on an industrial scale, because a suitable solvent–polymer system is not always available and also an additional step of solvent removal is involved. [59,60] Ecofriendly and cost-effective melt intercalation shifts the synthesis of the nanocomposites down stream to the polymer processing industry.

Vaia et. al. have shown that the d spacing in PEO/Na⁺ montmorillonite hybrids prepared by melt intercalation at 80°C matches with those of the PEO hybrids prepared by solution intercalation. [47] Thus under suitably chosen processing conditions the morphology of hybrids obtained by melt intercalation can be comparable with that in hybrids prepared by other synthetic routes.

Organic modifiers play a crucial role in the synthesis of PLS nanocomposites. Layered silicates, montmorillonite in particular, are hydrophilic in the pristine form. The clay surface can be rendered organophilic by exchanging the mobile Na⁺ with suitable cationic surfactants. Such organoclays have lower surface energy compared to pristine clay and are more compatible with the polymer matrix. [44,45] Vaia et. al. found that PS does not intercalate in pristine Na⁺-montmorillonite, however the intercalation does take place with organosilicates. [45] Usuki et. al. synthesized nylon-6 nanocomposite using the Na⁺ - montmorillonite modified with various ω-amino acids \( \{H_3N'(CH_2)_{n-1}COOH, n = 2-8, 11, 12 and 18\} \). [22] XRD results showed that amino
acids were stretched with longitudinal axes perpendicular to the silicate layer in the interlayer gallery. Among the different amino acids used, 12-aminolauric acid was found to be the most appropriate modifier for nylon nanocomposites.

The hybrids of polymers like nylon [49,50] and PS [44,45] can be prepared by melt intercalation with organosilicate. However, for non-polar polymers like PP [53,54, 61-68] and PE [52] very often an additional compatibilizer is required. The backbone of the compatibilizer is typically miscible with the polymer matrix, while the polar group interacts with silicates as illustrated in the Figure 3.2. Polyethylene grafted with maleic anhydride (PE-g-MA) [52] and polypropylene grafted with maleic anhydride (PP-g-MA) [53] respectively, are widely used for making PE and PP nanocomposites by melt intercalation. Kawasumi et. al. suggested that PP-g-MA could intercalate in the interlayer space through hydrogen bonding with polar OH group of silicates. [53] Addition of such modifiers may help to enhance certain desired properties of the hybrids. For instance, Liu et. al. have shown that addition of PP-g-MA in nylon-6 PLS nanocomposite further reduces the water absorption of the composite. [69]

![Figure 3.2. Schematic of compatibilizer action with clay and polymer](image)

Functionalization of the polymer matrix can also aid the synthesis of nanoclay composites by melt intercalation. Chrisholm et. al. have prepared PBT nanocomposites by sodium sulfonate functionalization (-SO$_3$Na) of PBT, which helps to achieve better exfoliation compared to pristine PBT. [57] The exfoliation does increase with concentration of (-SO$_3$Na) group and so do the mechanical properties.
The addition of modifier and clay has been reported to enhance the rate of crystallization of PLS nanocomposites. [64,70,71] Ma et. al. observed isothermal crystallization of PP nanocomposites and reported that the crystallinity of PP-nanocomposites decreased with increasing clay concentration. On the other hand, the crystallization rate increased dramatically with clay content. [70] Similarly Maiti et. al. found that clay acts as a nucleating agent and observed reduction in the spherulite dimensions with increasing clay content. [71] Kodigre et. al. found that the PP nanocomposites could be crystallized at higher temperature than pristine PP. They also reported significantly different crystalline morphology of PP at high temp (T = 122°C). [64]

Apart from the synthesis of homopolymer PLS nanocomposites, the intercalation of copolymers like polystyrene-acrylonitrile, [72] Acrylonitrile-Butadiene-Styrene (ABS) [73] and polystyrene-polyisoprene (PS-PI) block copolymers [74-76] has also been studied. Ren et. al. reported that while pristine polyisoprene (PI) could not be intercalated into organoclay, the same could be achieved by copolymerising PI with PS. [76]

Apart from the three main methods of synthesis mentioned above the PLS nanocomposites can also be synthesized by different methods like ultasonication, [77] photo-polymerization [78] and UV curing. [79]

Thus PLS nanocomposites have been synthesized by many different methods. Generally the surface of the clay is suitably tailored to facilitate the clay-polymer interaction. All the efforts in the synthesis of these materials are focused on finding ways to delaminate the layered structure of silicates, which is critically required for maximum property enhancement. [80-82]

3. 2. Characterization and properties of PLS nanocomposites

As discussed in chapter 2, the state of dispersion of clay in PLS nanocomposites may be classified in two idealized class of morphologies: (1) Intercalated, in which the polymer expands the interlayer distance resulting in an ordered, alternating multilayered polymer - clay layer structure, and (2) Exfoliated, where the polymer chains completely delaminate the layered clay structure. However, real nanocomposites exhibit
morphologies, which are combinations of these two idealized cases as discussed in several researches summarized below. [83-85]

Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and x-ray diffraction (XRD) are techniques that are often used to directly quantify the structure of PLS nanocomposites. [86] XRD is the most obvious technique to study the periodic structure of clays in case of intercalated PLS nanocomposites. However, XRD cannot be used very effectively for exfoliated PLS nanocomposite systems. In addition to XRD, TEM can be used effectively to characterize the hybrid structure. Figure 2.10 shows TEM of PP - nanoclay composite. [82] The dark lines in the micrograph are the silicate layers, dispersed in the polymer matrix. The separated dark lines correspond to the exfoliated clay, while the small clustered dark lines are for the intercalated clay tactoids. Thus the two idealized morphologies coexist in the PLS nanocomposites.

XRD has also been extensively used to study polymorphism in PLS nanocomposites, and the effect of clay on polymorphism. [87-91] It has been reported that clay induces the $\gamma$ phase of nylon-6 in nylon-6/PLS nanocomposites. [89,90] Similarly for nylon-66 PLS nanocomposites, the $\gamma$ phase of nylon-66 is favored and the crystalline phase transition was lowered by 20°C. [87,88] Tseng et. al. reported that in s-PS nanocomposites, in the presence of clay facilitated the formation of $\beta$ phase of s-PS. [91]

Spectroscopic techniques like Fourier Transform Infrared spectroscopy (FTIR) [92] and Nuclear magnetic resonance (NMR) [93-95] are also being employed to probe the interlayer structure of the clay.

Analytical techniques like differential scanning calorimetric (DSC), dynamical mechanical analysis (DMA) and thermogravimetric analysis (TGA) can provide indirect but useful evidence of structural attributes. For instance, Vaia et. al. have used DSC to study the kinetics of PEO/clay hybrid formation. [47] Pristine PEO is a crystalline material. At time t = 0 hr, it showed a distinct endotherm corresponding to the crystalline PEO. However, as the intercalation progressed, more and more PEO chains were intercalated and consequently the area of the endotherm corresponding to the crystalline PEO reduced. At time t = 6 hrs, this transition had largely vanished, indicating that all of the PEO had intercalated. Similarly for PS-nanocomposites, Vaia et. al. have shown that
the DSC thermograms of pristine PS, physical mixture of PS - organoclay and intercalated PS – organoclay are qualitatively different. [46] Both the pristine polymer and the physical mixture of PS with organoclay exhibited characteristic glass transition at 96°C, while the intercalated hybrid did not show any such transition. These results complimented the results obtained by high temperature x-ray analysis, which showed that with annealing time the clay peak shifted to higher d spacing.

PLS Nanocomposites exhibit improved thermo mechanical properties, reduced gas permeability and improved solvent resistance. [86] Kojima et. al. have shown that the modulus of nylon-6 PLS nanocomposite increases by 100%, impact strength by 25%, flexural modulus by 100% and heat distortion temperature (HDT) increases by 125%. These improvements in the properties were achieved by the addition of just 4.5 wt% of clay. [21] Usuki et. al. have tested the mechanical properties of nylon-6 clay hybrid using four different types of clays viz., montmorillonite, aconite and synthetic clays like limonite and mica. These clays were modified using 12-aminolauric acid. [22] They found that the mechanical properties for the hybrid synthesized by using montmorillonite were superior to other clay hybrids. Using NMR measurements they attributed this property enhancement to greater ion bonding between the montmorillonite and nylon-6 as compared to that in the other the types of clays. [12,93] Lan et. al. have shown that exfoliated epoxy clay nanocomposites have higher modulus than the intercalated epoxy clay composites. [80]

Fornes et. al. studied the structure, mechanical properties and rheological properties of nylon-6 PLS nanocomposites prepared from nylon of three different molecular weights by melt intercalation. [49,50] The mechanical properties enhanced with increasing molecular weight. These results were in agreement with TEM results, which showed greater extent of exfoliation with increasing molecular weight. The PLS nanocomposites based on lower molecular weight polymer had significant amounts of intercalated clay tactoids. Akkapeddi et. al. compared the barrier and mechanical properties of cast and biaxially oriented nylon nanoclay composites films. [96,97] The biaxially oriented composite film showed markedly improved properties compared to the cast films.
Thus the mechanical property enhancement was found to be dependent on many factors such as the concentration and aspect ratio of the silicate layers, [20] interactions between clay and polymer [97] and orientation of clay and polymer. [98,99]

Yano et. al. have shown that incorporation of nano-clays in polyimide matrix increases 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. [100] Interestingly, Merkel et. al. have shown that dispersion of nanoparticles of fumed silica increases the permeability of glassy amorphous poly(4-methyl-2-pentyne) membranes due to disruption of chain packing and a subsequent increase in the free volume. [101]

3. 3. Thermodynamics of PLS nanocomposites

Vaia et. al. proposed a mean-field, lattice-based model of polymer melt intercalation in organically-modified layered silicates (OLS). In general, an interplay of entropic and energetic factors determines the outcome of polymer intercalation. 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 (\( R_g \))]. This requires very favourable polymer-OLS interactions to overcome the polymer - polymer and clay - clay interaction. [102,103] 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. [102-106] For polar polymers like nylons an 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. [53,64,62]

2. Decrease the interaction between the surfactant and OLS, which effectively makes the polymer-OLS interaction dominant. Manias et. al have claimed to reduce the alkylammonium surfactant-montmorillonite interaction by fluorinating the surfactant. [61]

3. 4. Rheology of PLS nanocomposites

Rheology of PLS nanocomposites is important because on the one hand it relates to the microstructure of the nanocomposite and on the other, it provides information about the processibility of the material. Rheology is highly sensitive to the microstructure and can be effectively used as a characterization tool that complements the traditional methods of structure determination like XRD and TEM.

Linear viscoelastic properties: The linear viscoelastic properties of several intercalated and exfoliated nanocomposites such as those made from polystyrene-polyisoprene (PS-PI) block copolymer, [74-76,107-109] PCL, [110-112] polyamide, [113,114] PS, [115-117] PDMS [94] and polypropylene (PP) [62,66,67,118] have been studied.

The characteristic rheological signatures of PLS nanocomposites in the linear region, in the above-mentioned reports can be summarized as:

1. A solid-like response ($G', G'' \rightarrow \omega$) at very low frequency above a certain clay loading. [75]
2. Dynamic data \((G', G'' vs \omega)\) can be shifted by the time-temperature superposition even for the PLS nanocomposites to obtain master curves. The temperature dependence of the frequency shift factors \((a_T)\) is comparable to that of the pristine polymer matrix. The values of frequency shift factors \((a_T)\) are found to be independent of silicate loading. \([75]\) This indicates that the fraction of polymer chains tethered to the clay surfaces are not responsible for solid-like behaviour exhibited by PLS nanocomposites. \([75]\)

Ren et. al. attributed the solid-like behaviour to the existence of a percolating network of the clay tactoids. \([75]\) Such a percolation network is formed even at very low clay concentration, due to the anisotropy of the tactoids. A three dimensional network is formed when the clay tactoids are close enough to interact hydrodynamically with each other, as illustrated in the Figure 3.3. Ren et. al. have related the weight fraction of layered silicates at percolation \((w_{sil, per})\) to the average number of silicate layers per tactoid \((n_{per})\) as \([75]\)

\[
n_{per} \equiv \frac{4}{3 \phi_{per}} \left[ \frac{w_{sil, per} \rho_{org}}{w_{sil, per} \rho_{org} + (1 - w_{sil, per}) \rho_{sil}} \right] \frac{R_h}{h_{sil}}
\]

where, \(\rho_{org}\) and \(\rho_{sil}\) are the densities of the organic phase (i.e., polymer matrix) and silicates, respectively. \(R_h, h_{sil}\) are the hydrodynamic radius and the thickness of the
layered silicate, respectively and $\phi_{pc}$ is the volume fraction at percolation threshold for of spheres in 3-D space reported to be $\sim 0.30$. [75]

Krishnamoorti et. al. reported the dynamic and steady state flow of PDMS nanocomposites, containing 8 - 15 wt% clay. [94] At low shear rates, they observed viscosity enhancement, which increased monotonically with increasing silicate loading. Furthermore at the lower shear rates, where a Newtonian plateau was observed for the PDMS matrix, the nanocomposite exhibited shear thinning.

Lee et. al. showed that hydrogen bonding between the polymer and silicate can have dramatic effects on the rheology of PLS nanocomposites. [74] Nanocomposite of polystyrene-block-hydroxylated polyisoprene (SIOH diblock) and polystyrene-block-polyisoprene (SI diblock) with clay were prepared. It was observed that PLS nanocomposites using SIOH diblock showed increase in the $G'$ and $\eta'$ with temperature, while $G'$ and $\eta'$ decreased with increasing temperature for PLS nanocomposites based on SI diblock. FTIR analysis suggested that the Si-OH – nanocomposite had hydrogen bonding even at higher temperature, which might be contributing to the observed increase in the modulus. [74]

Krishnamoorti et. al. have also reported the solid-like behaviour at low oscillatory frequencies for end-tethered polymer chains in poly$\varepsilon$-caprolactone nanocomposites. [110] Hoffmann et. al. showed that tethering has an effect on the degree of dispersion and rheology of PLS nanocomposites. [116] Two types of PS based nanoclay composites were prepared. The first containing phenyl ethylamine as a modifier was of intercalated type, while the second, containing amine terminated - PS tethered to the clay surface was of exfoliated nature. The plots of $G'$ vs. shifted frequency ($\omega a_T$) of both PS and intercalated PLS nanocomposites nearly superposed on each other, while the exfoliated nanocomposites showed a significantly higher $G'$ compared to matrix polymer, particularly at the lower frequencies. [116]

**Non-linear rheological properties:** The strain amplitude sensitivity of PP [62,66,67] and PS - PI copolymer [74-76,107-109] nanoclay composites have been reported. [119] It was observed that $G'$ and $G''$ begins to decrease at strain amplitudes
significantly smaller than those for the pristine polymer matrix. Additionally, the strain amplitude defining the onset of softening decreased with increasing silicate loading.

PLS nanocomposites exhibit significant decrease in the viscoelastic moduli under large amplitude oscillatory shear. Kim et. al. reported the ability of large amplitude oscillatory shear to orient short glass fibers in glass reinforced polymer composites. [120] PLS nanocomposites show similar orientation when an external shear field is applied. PLS nanocomposites demonstrate liquid-like behaviour, under the application of large amplitude oscillatory shear, even in the cases where the silicate loading is well above the percolation threshold. [75]

Krishnamoorti et. al. reported the nonlinear dynamic response of end-tethered poly ε-caprolactone nanocomposites to large amplitude oscillatory shear. [112] PLS nanocomposites exhibit shear thinning at higher shear rates, however, these materials exhibited a strain hardening beyond certain critical strain amplitude. This critical strain amplitude was found to be a function of silicate loading. The observed strain hardening was attributed to the stretching of the tethered polymer chains beyond a critical displacement and is considered unique to the high surface grafting density melt - brush systems. [112]

Krishnamoorti et. al. reported that at higher shear rates, the viscosity of the hybrids is comparable to the matrix viscosity, [109] suggesting that the application of shear flow aligns the clay tactoids, which is reminiscent of conventional filled composites [120] and highly filled clay suspensions. [121,122]

The elasticity, as measured by the first normal stress difference, when compared at constant shear stress was found to be independent of silicate loading and was the same as that of the polymer matrix. This unique combination of matrix like viscosity and elasticity for the PLS nanocomposites is ascribed to the alignment of the clay tactoids in the flow direction resulting in a minimal contribution by the clay tactoids to both viscosity and the elasticity of the hybrids. [109]

The empirical Cox-Merz rule (e. q. 2.20), which is obeyed by the polymer matrix, fails for PLS nanocomposites and especially for the case of hybrids with silicate loading greater than percolation threshold, as reported by Krishnamoorti et. al. [109] and Fornes et. al. [49,50] Typically, the complex viscosity \( \eta^* \) measured in the linear viscoelastic
regime in the case of PLS nanocomposites, exceeds the steady shear viscosity $[\eta(\dot{\gamma})]$. Furthermore, a comparison of the steady shear viscosity $\eta(\dot{\gamma})$ with aligned state viscosity ($\eta_{al}^*$) shows that $\eta(\dot{\gamma}) \geq \eta_{al}^*$. These results indicated that even at low shear rates, the application of steady shear results in at least some alignment of the silicate layers.

Failures of the Cox-Mars rule have been observed in other systems like polymer-polymer blends, [123] particle filled polymers, [124] liquid crystalline polymers, [125] and fiber reinforced polymer composites. [120,126] Nakajima et. al. observed for rubber composite filled with particulate carbon black that $\eta(\dot{\gamma})$ obtained by capillary rheometry was significantly lower than the $\eta^*$ obtained by dynamic measurements. This was ascribed to the strain hardening in dynamic measurements. [124] Bailey et. al. demonstrated that glass reinforced nylon-6 and polypropylene composites do not obey Cox-Merz rule due to significant fiber orientation in capillary under high shear rates. [126]

Solomon et. al. studied the linear and non-linear rheological properties of PP nanocomposites by using flow reversal experiments. [62,118] The transient flow reversal stress response exhibited a stress overshoot, the magnitude of which was found to increase with the quiescent annealing time between the flow reversals. The stress overshoot varied linearly with the concentration of clay and scaled with the strain. These results indicate that microstructure of PLS nanocomposite evolved with annealing time and that the rheological measurements were sensitive to these changes.

3. 5. Yield behaviour of filled systems

The existence of structured fluid was intensely debated a decade ago, mainly due to the confusion over the precise definition of yield stress. [127-134] It was originally accepted that the yield stress of a solid is a stress from which if the applied stress were increased, the deforming solid would exhibit liquid-like behaviour i.e., continual deformation. Similarly in the context of structured fluids and liquids, it was understood that as the stress is decreased below the yield stress a solid-like behaviour is observed i.e., no continual deformation. [127]
However, with the increase in sophistication of experimental capabilities, it became clear firstly for solids and then for structured fluids that, although there is a small range of applied stress over which the viscosities change dramatically, which is usually referred to as the apparent yield stress, these materials show slow but continual steady deformation when stressed for a very long time even below yield stress level. [131-134] Thus yield behaviour of materials was understood to be a time dependent phenomenon.

The shear thinning, shear thickening, and apparent yield behaviour for filled suspensions and conventional polymer composites has been very well reported. [128-131] Krishnamoorti et. al. indicated the presence of an apparent yield stress for the PLS - nanocomposites. [109] They studied the shear rate dependence of steady shear viscosity for PS-PI nanocomposites, as a function of clay loading. The viscosity of PLS nanocomposites showed divergence with increasing silicate loading. The divergence was significant above the percolation threshold and was considered as being indicative of the existence of a finite yield stress for these materials.

3. 6. Flow orientation of PLS nanocomposites

The silicate layers can be oriented in response to an externally applied force field. [109, 110, 135] Zhang et. al. investigated the shear-induced morphological changes for PP nanocomposites by TEM and XRD analysis. [136] The intercalated structure changed to exfoliated under shear, due to the orientation of silicate clay platelets. The silicate layers were found to be oriented under shear while the polymer chains remained unoriented. This ability to orient the clay appears to control the viscoelastic properties of such materials. [109,110] Recent studies have demonstrated that along with the exfoliation, orientation of the clay platelets plays a crucial role in determining the property enhancement in PLS nanocomposites. [98,99,137-146] The three dimensional (3-D) orientation of clay platelets and unit cells in polymers in PLS nanocomposite have also been studied. [138-142] The orientation of silicate layers in PLS nanocomposites has been studied using various techniques like XRD, TEM, SAXS and SANS. [137-146]

Kojima et. al. have characterized the orientation of silicate layers in nylon-6 nanocomposites using XRD and TEM. [137] In an injection-molded bar they found three
different regions of orientations as a function of depth. At the center of the sample, where the shear forces are minimal, the silicate layers and polymer crystallites were found to be randomly oriented with the chain axes of the polymer crystallites always perpendicular to the silicate layers. Near the surface, where the shear stress would be very high the silicate layers and chain axes of the polymer crystallites were parallel to the bar surface. In the intermediate shear region, the clay layers, may due to their asymmetric nature, still orient parallel to the bar surface, but the chain axes of the polymer crystallites were perpendicular to the silicate layers. [137] Varlot et. al. also demonstrated that the polymer lamellae grow on the silicate sheet with chain axes parallel to the silicate layer. [138]

Rheological characterization coupled with other structural characterization offers a useful tool to directly investigate the rheology-microstructure linkages in the materials. Ex-situ analysis of clay orientation in PP-nanocomposites under biaxial and uniaxial extensional flow has been reported recently. [140,141] Okamoto et. al. observed strain induced hardening in an elongational flow for PP nanocomposite foam. [141] The strain hardening and time dependent shear thickening was attributed to the perpendicular alignment of the silicate layers in the stretching direction. [140] The TEM analysis showed that, the biaxial flow-induced alignment of clay particles along the cell boundaries, enhances the modulus of the foam. [141]

Several in-situ techniques like Rheo-SAXS, [142] Rheo-SANS, [143-148] Rheo-NMR, [149,150] Rheo-optics [151,152] and Rheo-WAXD [153] and have been used to investigate the flow-induced micro structural evolution in other structured fluids.

The effect of high strain on the crystallization of end-tethered nylon-6 nanocomposite was studied by Medallling-Rodriguez et. al. using rheo-SAXS analysis. They found that the silicate layers and the polymer chains are oriented in the flow direction even at relatively low shear and at temperatures just above the melting point. [142] The shear-induced orientation was found to increase with time. The clay platelets were found to be oriented even after cessation of shear, and this orientation remains stable for relatively longer times in the molten state. Typical time resolved SAXS study shows that for the end tethered nylon nanocomposites the relaxation period is around 12 min (at T = 240°C, \( \dot{\gamma} = 60 \text{ s}^{-1} \)). The slow relaxation of clay is ascribed to the tethered polymer chains, which are expected to have extended relaxation time. [142] Schmidt et.
al. studied shear orientation in aqueous solutions of PEO nanocomposites using flow birefringence and SANS. [143-148] It was found that the clay platelets were oriented in the flow direction with their surface normal perpendicular to the flow direction. They also reported that the randomization of the oriented silicate layers upon cessation of flow was much faster than that described by Brownian motion.

Recently Somwangthanaroj et. al. studied early stage quiescent and flow-induced crystallization kinetics of intercalated polypropylene nanocomposites by in situ rheo-optics. [152] They observed that crystallization kinetics of intercalated polypropylene nanocomposites, prepared with PP-g-MA as a compatibilizer, differs significantly from that of pure polypropylene. The use of PP-g-MA as a compatibilizer contributed to the retardation of the quiescent isothermal crystallization kinetics of the intercalated nanocomposites compared to the pristine polypropylene. However, the application of shear-flow accelerated the crystallization kinetics of the intercalated PLS nanocomposites under conditions at which the polypropylene showed no flow-induced effects.

Several references on the rheology and flow-induced orientation of PLS nanocomposites cited in this chapter are contemporary to the work reported in this thesis in chapter 7-9 and will be discussed in that context in more detail later in the thesis.

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