11.1. Conclusions

The objective of this work as illustrated in Fig 4.1 was to develop an understanding of the structure-processing-property relationships in polyolefin nanocomposites. Chapters 7-10 describe in detail the work done towards meeting this goal. The structure-property linkages are summarized in Figure 11.1 along with the salient contributions of the work done in this study. The main conclusions have already been summarized in chapter 9. The study reported in this thesis showed that the rheological data, particularly creep data, is sensitive to the microstructure of the PLS nanocomposites. Under quiescent conditions, the microstructure of compatibilized PLS nanocomposites consists of 3D percolating network of clay tactoids, which is responsible for the very high viscosity exhibited by these hybrids. At higher stresses the clay tactoids get oriented in the flow direction, leading to the breakage of this network. Once the network breaks down, the viscosity drops down by orders of magnitude. Thus, these hybrids exhibit the yield–like behaviour. Further, the orientation of clay tactoids, under flow conditions was quantitatively studied by a novel in-situ rheo XRD technique. Both rheological and rheo-XRD studies showed that the yielding corresponded to the orientation of clay in the flow direction. The effect of clay orientation on the solid-state properties was also reported. The tensile modulus was found to increase with the increasing clay orientation. This thesis also reported on the rheological analysis of exfoliated and possibly end tethered PE nanocomposites. The PE nanocomposites were found to be significantly more elastic than the matrix resin, even at very low (1-wt%) clay loading. A percolating network was evidenced at 5-wt% clay loading.

11.2. Future work

The work reported in this thesis suggests that the final product properties of PLS nanocomposites will be dependent on the subtleties of the clay microstructure. For
instance, in the case of PP nanocomposites although the XRD did not reveal significant
differences between the microstructures of the compatibilized and the uncompatibilized
hybrids, large differences were seen for the rheological and the tensile properties of these
two hybrids. Such differences could only result from the presence of the PP-MA
compatibilizer. Thus, the interactions between the PP-MA and the silanol groups (Si-OH)
on the clay are critical to the successful development of a nanocomposite.

There are many reports in the literature about PP nanocomposites synthesized by
using different types of clay and the consequent improvements in properties achieved, but
the understanding of the exact interaction between the polymer matrix, modified or
pristine, and the clay via the PP-MA compatibilizer, remains elusive. For instance, PP
nanocomposites can be prepared by using different types of synthetic clays: such as those
having silanol groups present only the edges and others having silanol groups present
both on the edges and on the surface of platelets. The properties of the hybrids prepared
under similar conditions, but using clays, which are different in terms of the locations of
silanol groups would be a dependent on the nature and extent of interactions of the clay
and the polymer. This kind of study will help to tailor the clay-matrix interactions and to
optimize the hybrid properties.

Further, it was shown in this work that rheological experiments, in particular the
creep measurements are sensitive to the diffusion of the polymer chains into the primary
clay particles. The effect of molecular weight of the resin on the diffusion of polymer
chains into the primary particles and the resultant extent of intercalation was reported in
this thesis. It was suggested that creep measurements could potentially offer a rheological
method to probe the diffusion of polymer chains into the primary clay particles.
However, rheology in itself is an indirect tool to probe the diffusion studies. For example,
as reported in this study, the rheologically probed yield-like behaviour in the polymer
nanocomposites, was attributed to the orientation of clay tactoids. This was then
quantitatively measured and proved by in-situ XRD analysis. Similarly, the diffusion of
polymer chains probed indirectly by the rheological studies can be quantitatively
understood by using coupled techniques like rheo-NMR or in-situ fluorescent
spectroscopic techniques.
It was shown in this work that the tensile modulus increased with increasing clay orientation. The hybrid modulus was predicted only from the clay orientation in a semi quantitative manner even though polymer crystallites were slightly oriented. More accurate predictions of the hybrid modulus may be possible with model polymer systems which orient at very high shear rates and by solving the full tensorial constitutive equation for the composite as suggested by Brune et. al. [1]

Studies reported in this thesis were focused only on the tensile modulus. But other properties like the barrier properties of the nanocomposites are also strongly dependent on the orientation of the clay. Bhardwaj et. al. have proposed a simple model for relating the clay orientation with the barrier properties. [2] It would be interesting to quantify the effects of clay orientation on the barrier properties of polyolefin nanocomposite films.

This thesis also reported preliminary studies on the rheology of PE nanocomposites synthesized by in situ polymerization of ethylene. The purpose of this study was to investigate the difference in the rheological behaviour of the intercalated and exfoliated nanocomposites. The rheological response of nanocomposites is sensitive to both the polydispersity and the clay dispersion in the polymer matrix. The PE nanocomposites studied in this work were highly polydisperse, which made it difficult to separate out the effects of molecular weight distribution and clay dispersion on the rheology of the PE nanocomposites. The rheological response of the clay dispersion would be more clearly seen for a model monodisperse material.

A lot more obviously remains to be done to quantify the structure-property relations in PLS nanocomposites. The study reported in this thesis has provided new insights and has raised new questions in this scientifically interesting and industrially relevant class of materials.

**Reference List:**

Figure 11.1. Schematic of the objectives of this thesis and salient contribution of this work