Chapter 7: Conclusions and Further Work

Single screw extrusion has been used to prepare PE-MMT blends from an o-MMT-containing masterbatch and a 90 : 10 BPE : LPE blend, each masterbatch formulation giving rise to a different clay size distribution. The Nanocor-based materials contained agglomerates as large as 100 μm, giving rise to low angle X-ray scatter that was comparable with a composite that was deliberately poorly dispersed via a solution route. Nonetheless, TEM revealed that a significant fraction of clusters are distributed with characteristic dimensions of less than 200 nm. Conversely, agglomerates larger than 1 μm were rarely seen in the Nanoblend systems. Neither, however, was the clay seen to be dispersed in clusters smaller than 1 μm, implying a much narrower size distribution than in the Nanocor systems.

On the basis of that, according to WAXS, the clay in these systems is in an intercalated state, can these materials be justifiably described as nanocomposites? Both the Nanoblend- and Nanocor-based materials contain significant amounts of >1 μm filler particles, and it is certainly possible that the dielectric and electrical breakdown behaviour is principally determined by these. On the other hand, the constrained chain behaviour demonstrated in both sets of systems by SEM and thermal analysis is at the very least due to the intercalated nature of the clay clusters. It may also result from a dilute exfoliated phase which was not seen in the TEM images due to sample thickness and section bias issues. Even in the former case, the materials may still be termed nanocomposites as their morphologies are dependent on the nanostructures that are the intercalated particles.

7.1 Discussion of original aims and objectives

The outcomes of this project are now considered in terms of the original aims and objectives laid down in Chapter 1:

"To gain an understanding of the nature of the PE-MMT interactions via their effect on the crystallisation kinetics and morphological evolution."

This study has made a significant contribution to the polymer science community by using the permanganic etching process to demonstrate the wide range of ways in which the macromolecular lamellar organisation can be altered by MMT dispersed on the sub-micron level. The Nanoblend-based systems show mobility constraints at the intralamellar organisation level, leading to straight, holey lamellae and, possibly, banding suppression. Conversely, the Nanocor-based systems are strongly dependent on crystallisation temperature, with high nucleation densities and morphological disorder present above critical clay concentrations and below critical temperatures. This work has demonstrated that to define a nanocomposite in terms of a dominant fraction of some interfacial region, helpful though it may be in glassy system, is generally useless for semicrystalline materials: where nucleation and growth are substantially altered, the interface is coextensive with the material.

A question which arises out of this work concerns the lamellar long period, which was demonstrated by SAXS to be essentially invariant in all of the materials. In these systems, it is clear that this property is determined by polymer-polymer interactions, raising the possibility that this parameter might be controlled independently of the clay by using metallocene catalysis to control the molecular architecture of the host polymer. On the other hand, increasing the amount of clay uniformly dispersed on this length scale would eventually lead to polymer-clay interactions dominating. It would be valuable therefore to gain an understanding of the nature of the competition of the polymer-polymer and polymer-clay interactions in this regard, and to study any transitional effects which may arise.

“To investigate the usefulness of PE-MMT nanocomposites as dielectric insulation materials, with particular consideration of their dielectric breakdown behaviour.”

AC ramp breakdown testing has been successfully employed to demonstrate that, in terms of electrical breakdown performance, the Nanoblend-based materials are the most promising. Both the breakdown strength and shape parameters were consistently and monotonically improved with loading level. The breakdown strength of the unfilled behaviour was low due to the presence of extruder-degraded material, and this effect was counteracted by the presence of the Nanoblend. It is likely that, at least at higher fields, a surface erosion resistance mechanism was responsible for the enhanced strength. This is evidenced by SEM images of a clay-rich layer in laser ablated samples. These materials are therefore worthy of more research, if only for their potential in outdoor insulation applications. However, the need for controlling the particle size distribution (PSD) is witnessed in the poor electrical breakdown behaviour of the Nanocor-filled materials. Furthermore, in performing the electrical breakdown testing in parallel with dielectric and mechanical testing, this work demonstrates that none of the systems studied are suitable for commercial application without a considerable amount of further work. The high dielectric losses and low frequency permittivities indicate that improvements need to be made with regard to masterbatch manufacture.

The tensile mechanical behaviour of these materials warrants special concern. The Nanocor-based materials have a very long memory of their shear history, leading to very non-uniform residual stress fields. Any advantage the material may have against partial discharge may be completely undone if it is energetically favourable for internal surfaces to form in the material. Further experiments on NB20, not reported in Chapter 5, indicate that the brittleness is in fact a consequence of boundaries between pellets of extrudate. Dog bone samples were pressed out of single lengths of extrudate oriented in the load direction. It was found that, rather than having the anomalously low break strength previously detected, they exhibited behaviour which was indistinguishable from NC20. The implication is that there exists a shear memory even in the Nanoblend-based systems which would create significant difficulties in a commercial manufacturing process. Furthermore, it is believed that the isothermally crystallised morphologies in NC10 and NC20 are in large part determined by this shear memory. It would therefore be a valuable experiment to study the morphologies of the materials as a function of shear rate and residence time during processing.

7.2 Other issues arising

How may the early stages of material processing be improved so as to obtain better control over the PSD? It is known that alkylammonium compounds are thermally unstable and tend to degrade during melt processing. If a solvent is instead used to expand the galleries prior to in-situ polymerisation, the polymer chains must have a polar graft in order to prevent reagglomeration of the clay during subsequent melt processing. However, polar grafts may pose their own problems. For example, it was found that the MA-grafted materials used in this study were difficult to process because of their tendency to bond with metal surfaces. It may be possible to prevent reagglomeration by crosslinking a layer of polyethylene around each clay particle once the desired level of dispersion has been reached. A crosslinking reagent would be required that could bind with the clay and be activated via microwave heating of the bound water associated with the clay.

It is possible that more control over the PSD may be found through developments in the in-situ polymerisation process. Supercritical CO_2 may prove useful to this end. This high temperature, high pressure phase behaves as a liquid in regard to its ability to diffuse into clay galleries and as a gas in its drive to expand and fill the available space. Alternatively, layered double hydroxides (LDH), which are a synthetic alternative to MMT, are likely to become economically viable. The fact that their chemical composition can be precisely controlled is an obvious bonus in terms of controlling charge transport and trapping behaviour. It may be that precise control of their PSD can be obtained through development of the stepwise deposition process.

This work concurs with the literature that there is much hope for nanocomposite materials which are electrically stronger in a terminal sense.

We might reasonably extend this hope to longer term processes such as partial discharge and electrical treeing resistance. Certainly, the highly disordered morphologies seen in the Nanocor-based materials might be expected to hinder the development of electrical trees through crack blunting and deflection. However, to what degree can we have faith that the long-term ageing behaviour of these materials would not be disastrous? From a chemical point of view, we do not know the extent to which the diffusion of impurities into the materials may take place over a period of years. Much research is currently taking place into the effects of water shells in nanocomposites, and it would be valuable to perform accelerated ageing tests in salt solutions to evaluate the influence of impurity ions on the low frequency dielectric behaviour in particular.

Even if the behaviour of these materials were fully characterised in terms of accelerated ageing tests, we must remember that the precise nature of long-term electrical ageing is a mystery even in simple polymers. The complex coupling of internal space charge fields and mechanical stress distributions, together with the manner and statistical processes by which energy is absorbed from the field and converted into damage, is still a matter of debate. One can only expect that the complex electrical and thermodynamic interactions found in these materials would add to the mystery.

The nanocomposites research community is still desperately in need of a reliable means for complete PSD characterisation. The invention of the helium ion microscope may provide the answer to this problem. This machine functions in the same way as an SEM except that it uses He^+ ions rather than electrons. As the He^+ ions penetrate to much shallower depths than electrons, the backscattered ions are capable of producing images with resolutions comparable to TEM. The advantage over TEM is that the samples neither need to be small nor ultra-thin. In theory at least, the PSD can be mapped using suitable image processing software, assuming of course that it is possible to generate representative surface topographies by etching. Of course, more research would be required to develop a suitable etching procedure. It is likely that a multistage process would be required, consisting of aggressive stages to reveal the larger material, followed by a slow stages to reveal the sub-100 nm clusters. Thinner samples, also prepared via etching, could be analysed by TEM to check for any remaining bias. It would not be possible to remove orientational bias, although this is much less important. If the PSD can be mapped accurately, known model systems can then be prepared for analysis under a variety of techniques such as WAXS, rheology and dielectric spectroscopy. These can be evaluated and developed as robust tools for rapid PSD determination during the production process.

7.3 Conclusions

- The Nanocor- and Nanoblend-based materials have different states of clay dispersion and particle size distribution, despite being processed under identical experimental conditions.

- Whereas the crystallisation kinetics of the Nanoblend-based materials are only subtly modified by the filler, in the Nanocor-based systems they are massively enhanced below 120 °C. In these latter systems, significant immobilisation of the polymer occurs leading to low crystallinity and deviation from Avrami behaviour.

- Extensive morphological disorder is present in NC10 and NC20 below 120 °C, whereas more subtle, local effects are observed in all Nanoblend-based materials.

- All filled materials show evidence of long-term shear memories which would render them unsuitable for commercialisation in their present form.

- Both masterbatches increase the dielectric loss and low frequency permittivity, though the relative contribution of impurities and compatibilisation by-products to these interfacial effects is not known.

7.4 Future work

- Investigate better ways of controlling and characterising the clay PSD.
- Investigate the use of metallocene polymers to study the competition between polymer-polymer and polymer-clay interactions insofar as they determine the lamellar long period.
- Study the PE-MMT interactions in the melt phase
- Study the relationship between shear history and morphological evolution. Do this under isothermal and stepwise isothermal conditions in order to examine the effect of molecular weight on chain mobilities.
- Investigate the viability of designed engineering materials with morphological control achieved through a combination of polymer chain architecture and molecular weight distribution, clay PSD, melt phase rheological and crystallisation thermal history.
- Determine the sensitivity of useful electrical and mechanical parameters to each of the above parameters, particularly the PSD and the shear history as these are the most problematic from a processing perspective.
- Investigate the effect of cleaner organoclay preparation on the dielectric response, space charge and breakdown behaviour. In particular, determine the sensitivity of these parameters to impurities, and in turn to ageing processes, in order to establish the robustness of these materials for electrical insulation applications.

There is increasing agreement among international standards organisations that nanocomposites research would progress much faster if there were more collaboration between institutions. For example, it would be better for materials which are studied at different institutions to be processed centrally so that results obtained by different analytical techniques can be compared. Otherwise, it becomes impossible to determine whether differences in results are due to differences in chemical composition, impurity levels, PSD or morphology.