

Layer expansion of layered silicates in solid polymer matrices by compression

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Ten years ago, a group of scientists at Toyota demonstrated that expansion and dispersion of layered silicates in nylon-6 could improve the performance envelope of the polymer well beyond the domain of known polymer technologies¹⁻⁶. They adapted a traditional in-situ polymerisation approach to insert the polymer precursor, ϵ -caprolactam, between the layers of a montmorillonite and then to further expand and disperse the clay layers into the matrix by polymerisation. This success has stimulated significant research activities in the development of synthetic methods to produce clay/polymer nanocomposites for various polymer systems⁷. Two methods were immediately developed based on solvent assisted solution synthesis for polyimide² and polymer melt intercalation for poly(ethylene oxide)⁸. The solution synthesis is to use a polar solvent to disperse and swell an organoclay and then to add a polymer solution to intercalate the polymer between the clay layers, while the melt synthesis involves heating a polymer with either an organoclay⁸ or a hydrophilic clay⁹ above the melt or glass transition temperature (T_g) depending on the polymer being crystalline⁸⁻⁹ or amorphous¹⁰. The further development was essentially the application of these three approaches to other polymers including poly(ethylene terephthalate)¹¹, poly(methyl methacrylate)^{12,13}, polystyrene¹³⁻¹⁶, polypropylene¹⁷⁻¹⁹, epoxy²⁰ and polyurethane²¹ etc..

This paper reports another approach to synthesise clay/polymer nanocomposites based on intercalation in solid phase. It has been observed that it is possible to expand interlayer distance of either a hydrophilic layered-silicate or an organophilic clay in a polymer simply by blending and compression of their solid mixture. The results to be shown were obtained from a crystalline polymer, poly(ethylene oxide) (PEO) and an amorphous polymer, polystyrene.

Fig. 1 shows the x-ray diffraction (XRD) patterns of the hybrid tablets of a poly(ethylene oxide) with different loadings of a sodium based montmorillonite, G-105. The tablets were produced by blending the powders with the clay and compressing the solid mixture in a mould under 330 MPa pressure at ambient temperature. The sodium montmorillonite, G-105, is a commercial product from the Nanocor. The PEO had Mw 600,000 and was supplied by the BDH Chemicals Ltd.. The X-ray diffractograms were obtained using a Phillip diffractometer with CuK α ($\lambda = 0.154$ nm) as the radiation source. The compressed solid mixtures were directly used. The experiment was carried out using 40kVx25mA covering the scanning range between 3° and 125°.

It can be observed from Fig.1 that the (001) peaks of the clay have been shifted to lower angles for all of the hybrids. This indicates that the interlayer distance of the clay has been expanded in those samples. The extent of the layer expansion is a function of the clay content in the polymer. The interlayer distance of the clay, $d_{(001)}$, increased significantly when the clay content was below 10wt%. At 5% loading, $d_{(001)}$ expanded from the original 1.20 nm to 1.74 nm. The extent is similar to that of the composites produced using melt and solution syntheses⁹.

The layer expansion also occurs when using an organophilic clay. Fig. 2 shows the XRD patterns of the composites produced from the PEO and an ammonium ion exchanged

montmorillonite, I-28, using the same method as mentioned in the previous paragraph. The organoclay, I-28, is also a commercial product from the Nanocor. The (001) peaks of the composites have been shifted from the original 2θ at 3.8 degree to the values below 3 degree which is the limit of the XRD equipment. However, the (002) peaks of the clay in the chart are clear so that the interlayer distance, $d_{(001)}$, can be calculated from the angle of the (002) peaks. The calculated $d_{(001)}$ data are listed in the chart. It appears from these data that the layer expansion of the clay is independent of the clay content in the PEO. The interlayer distance has been increased from the original 2.32 nm to over 3.07 nm. The fluctuation of the $d_{(001)}$ data between the composites may be associated with the fluctuation of the pressure applied during processing.

Two possible structures could be developed from the layer expansion of clays in the solid polymer, i.e., a simple layer expansion constrained by residual stresses and an intercalated structure similar to those produced by melt and solution syntheses. In the first situation, the layer expansion would be caused by the compression residual stresses applied to the clays in the direction perpendicular to the layers and would not involve the insertion of the polymer between the clay layers. If this were true, the expanded structure should be unstable and should collapse if the polymer is above its melt temperature to release the residual stresses. In addition, the layer expansion should occur by compression of the clays only at the same compression condition. In fact, the experiment showed that the expanded structure did not collapse when heating the tablets up to 90 °C above the PEO melt temperature. The compression of the two clays did not result in any layer expansion.

It appears that the intercalation between the clays and the PEO did occur during the compression. PEO is a crystalline polymer. The flow of the amorphous phase in the crystalline polymer above its glass transition temperature, T_g , may be enhanced significantly by the pressure. This soft amorphous phase could behave similar to a polymer melt in the melt synthesis to flow into the capillary channels between the clay layers. When intercalating with the Na^+ based montmorillonite, the extent of intercalation would depend on the amount of the soft phase in the mixtures. An increase of the clay content in the mixtures tends to decrease the amount of the soft phase in the composites. At higher clay content, the amount of the soft phase in the mixture will be insufficient to wet and flow into the capillary channels. This may result in the decrease of the extent of the layer expansion as shown in Fig. 1. When the organoclay is applied, the interlayer spacing of the clay is already wetted and filled by a hydrocarbon ammonium salt. A small quantity of the soft phase in the composites may be sufficient to flow into the clay galleries. The limit of the layer expansion is determined by the thermodynamic balance between the viscosity of the soft amorphous phase, pressure applied and the original interlayer spacing of the capillary channels. In addition to this, both PEO and the clays are hydrophilic, compatibility between the clays and the polymer also playing an important role.

Corresponding to this observation, a brittle amorphous polymer, polystyrene, has been investigated. The polystyrene had M_w 230,000, M_n 140,000 and was supplied by the Aldrich. Figs. 3 & 4 show the XRD patterns of the composites produced from polystyrene and the Na^+ montmorillonite and the organoclay respectively using the same processing condition as used in the PEO. For the composites produced from the hydrophilic sodium clay, only a minor expansion of the clay layers occurred. The extent of the expansion is independent on the clay content in the polystyrene. The interlayer spacing changed from the original 1.20 nm to 1.29 nm for all the composites with different loadings. This is expected. Polystyrene is an amorphous polymer whose glass transition temperature is much higher than the processing temperature. The polymer at the processing condition is much more brittle than the soft amorphous phase in the PEO and hence exhibits very limited flowing behaviour. However, such a situation changed when the organoclay was applied. The extent of the layer expansion

shown in Fig. 4 is significant and similar to the extent achieved by the PEO. The interlayer spacing has been increased from the original 2.32 nm to approximate 3.5 nm. Such a significant intercalation could be associated with either the improvement of the compatibility between the clay and the polymer or the interactions between the polymer and the hydrocarbon ammonium ions pre-inserted between the clay layers. Apparently, the organoclay is more compatible to polystyrene since polystyrene is more hydrophobic and less compatible to the hydrophilic sodium clay. However, the compatibility could not play an important role if the flow of the polymer is insufficient. It appears that the interactions between the pre-inserted phase and the polystyrene may occur. The brittle polystyrene may be “dissolved” and integrated into a soft phase which is capable of flowing into the capillary channels of the clay galleries.

The observations described here have initiated a new approach to produce clay/polymer nanocomposites. Compared to other synthetic methods, solid intercalation has advantages of avoiding the use of solvents and heat during processing and is capable of producing a well intercalated structure with a high clay content. This would be useful to produce nano-structured pellets with a high clay concentration. The pellets can be used similar to colour pigments for injection moulding and extrusion. Further studies in this approach based on “difficult polymer systems” such as PVC and polyolefins and the development of solid intercalation technology for commercial applications are in progress in our centre.

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Captions for Figures

- Figure 1. X-ray diffractive patterns of the composites produced from the PEO and the Na⁺ montmorillonite, G-105, by the compression of the solid mixtures under 330 MPa pressure.
- Figure 2. X-ray diffractive patterns of the composites produced from the PEO and the organoclay, I-28, by the compression of the solid mixtures under 330 MPa pressure.
- Figure 3. X-ray diffractive patterns of the composites produced from the polystyrene and the Na⁺ montmorillonite, G-105, by the compression of the solid mixtures under 330 MPa pressure.
- Figure 4. X-ray diffractive patterns of the composites produced from the polystyrene and the organoclay, I-28, by the compression of the solid mixtures under 330 MPa pressure.

Figure 1.

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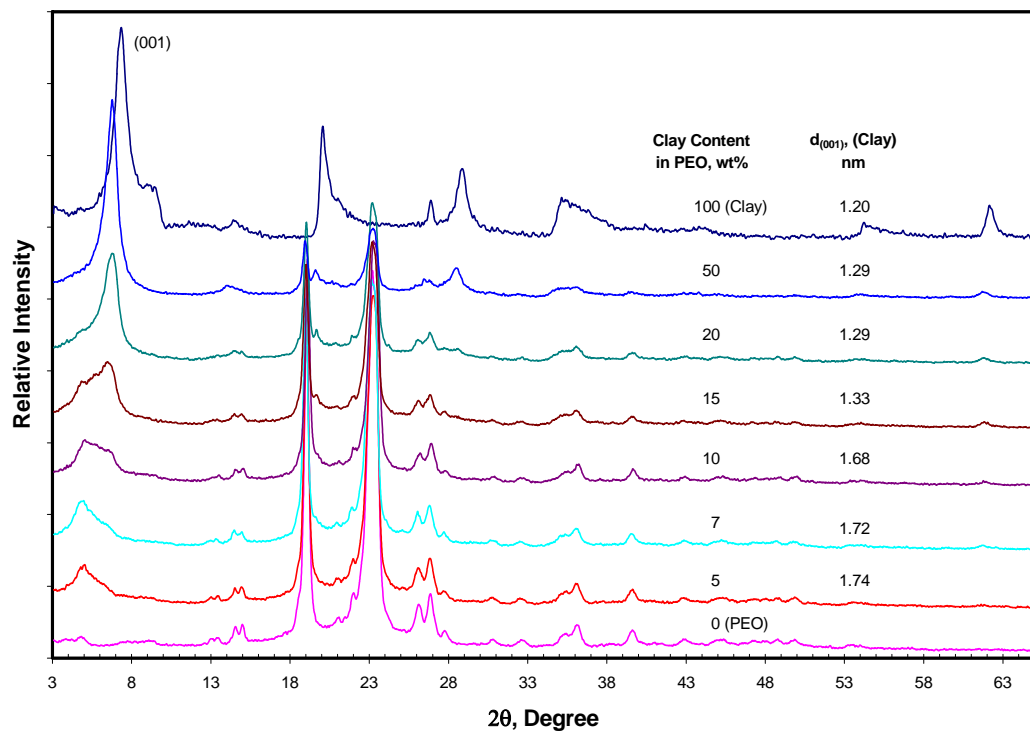


Figure 2.

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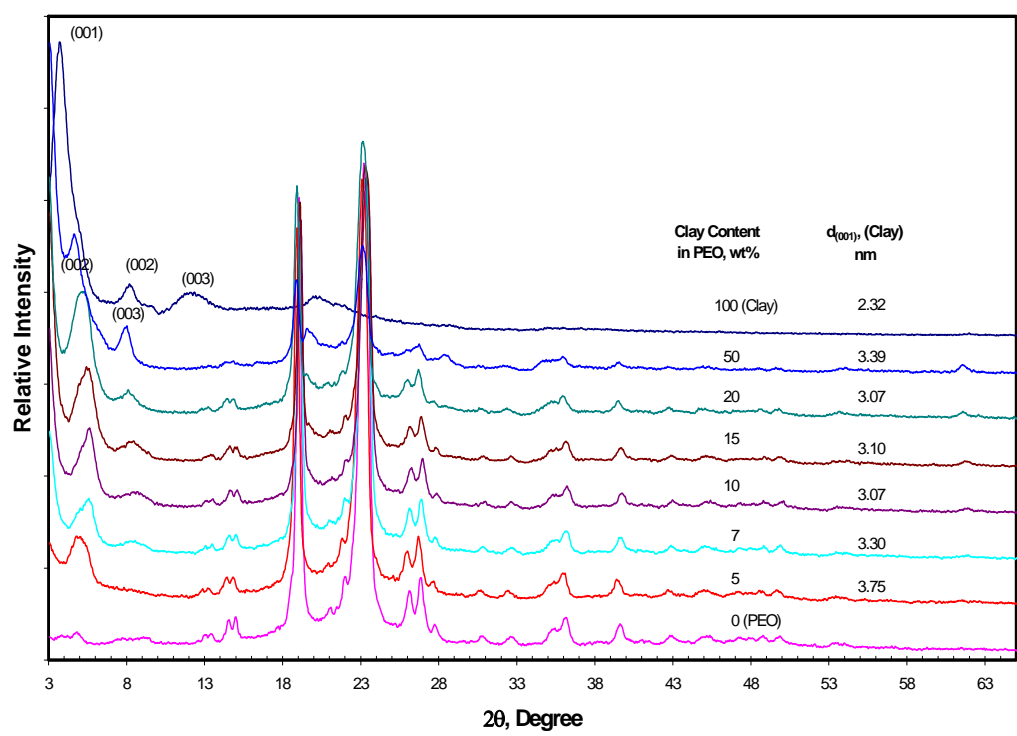


Figure 3

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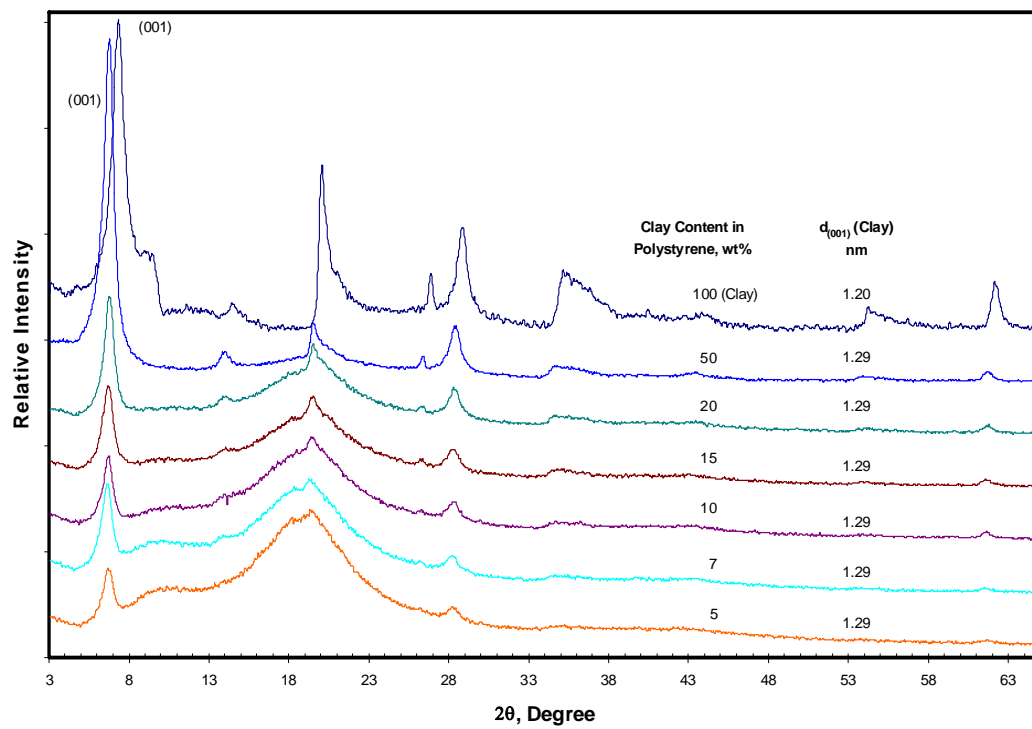


Figure 4

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