Chapter 6  Microstructure of as-prepared nanocomposites

This chapter describes the structural investigations related to the microstructure of as-prepared sPP, iPP and PE nanocomposites using techniques like x-ray diffraction, transmission electron microscopy and optical microscopy. X-ray diffraction is used as the main technique to elucidate the microstructure of intercalated and exfoliated polymer nanocomposites in this study.

6.1. Isotactic polypropylene (iPP) nanocomposites

6.1.1. X-ray diffraction analysis

Figure 6.1 shows the x-ray diffraction patterns for the as-extruded the compatibilized (iPP3/9/9) and the uncompatibilized (iPP3/9/0) hybrids, at room temperature.

![X-ray diffraction pattern](image)

*Figure 6.1. X-ray diffraction pattern of compatibilized (iPP3/9/9) and uncompatibilized (iPP3/9/0) hybrids*
The inset shows the first clay peak in more detail. As it can be seen, the clay peak for the compatibilized hybrid (iPP3/9/9) is shifted to lower d spacing compared to the uncompatibilized hybrid (iPP3/9/0) hybrid. This indicates better intercalation in the presence of the compatibilizer.

High temperature x-ray analysis of clay and extruded iPP nanocomposites was performed. Figure 6.2 shows WAXD patterns for DMDHTMC clay (Closite6A) as a function of annealing time. The clay showed three distinct peaks at $2\theta = 2.2^\circ$, 4.5$^\circ$ and 7.0$^\circ$ corresponding to the d spacing of 3.3 nm, 2.0 nm and 1.0 nm respectively. On annealing the clay at 200$^\circ$C for 30 minutes, a distinct shift in the peaks towards the higher $2\theta$ region and a decrease in peak intensities were observed. The peak shift towards higher $2\theta$ values indicate a decrease in d spacing, which could be due to slow degradation of the organic modifier at the high annealing temperature resulting in gradual collapse of the gallery heights.

![Figure 6.2. X-ray diffraction data for the clay during in-situ annealing at T = 200°C](image)

An important point to be noted from the WAXD pattern of DMDHTMC is that the d spacing of 3.3 nm is already significantly higher than that of the unmodified Na$^+$ clay, which has a d spacing of about 1 nm. The large gallery heights in DMDHTMC are
conducive to intercalation of the polymer chains in between the silicate layers provided the interactions between the polymer and the clay are favourable.

The WAXD data for the compatibilized hybrid (iPP3/9/9) and the uncompatibilized hybrid (iPP3/9/0) are shown in Figure 6.3 and 6.4, respectively, as a function of annealing time. Semicrystalline isotactic polypropylene homopolymer does not show any peak in the 2θ region between 1° and 10°. Hence the peaks in the diffraction patterns in Figure 6.3 and Fig.6.4 are those arising from the clay alone. As seen in the figures, the clay peaks did not shift to lower 2θ region for either of the hybrids indicating no further increase in d spacing even if intercalation might have occurred. The shift towards higher 2θ values might be an indication of the degradation of the organic modifier. A decrease in the peak intensity accompanied by a broadening of the peaks can be clearly seen in the Figure 6.3. The WAXD data indicates that stacks of silicate layers (i.e., clay tactoids) are present in both the uncompatibilized (iPP3/9/0) and the compatibilized (iPP3/9/9) hybrids. Calculation based on Scherrer's formula (see e. q. 2.5) suggests a slight decrease in the clay tactoid size with annealing. Roughly 4-5 platelets in the clay tactoid at time (t= 0 min) decreased to about 3 platelets, after 3 hrs annealing. This decrease in the crystallite thickness in the compatibilized hybrid (iPP3/9/9) could be due to possible exfoliation of a few layers from the end of the stacks into the melt.
Figure 6.3. X-ray diffraction data for the compatibilized hybrid (iPP3/9/9) during in-situ annealing at $T = 200^\circ$C

Figure 6.4. X-ray diffraction data for the uncompatibilized hybrid (iPP3/9/0) during in-situ annealing at $T = 200^\circ$C

The uncompatibilized hybrid (iPP3/9/0) also showed a similar decrease in peak intensity with annealing time. There is no distinct qualitative difference in the XRD patterns of the uncompatibilized (iPP3/9/0) and the compatibilized (iPP3/9/9) hybrids.
Thus it can be said that the WAXD data is rather inconclusive of subtle differences, if any, between the morphology of the compatibilized (iPP3/9/9) and that of the uncompatibilized (iPP3/9/0) hybrids.

6.1.2. Optical microscopy

Optical micrographs of the iPP nanocomposites for both the compatibilized (iPP3/9/9) and the uncompatibilized (iPP3/9/0) hybrids are shown in Figure 6.5. The optical micrographs of both the uncompatibilized and the compatibilized hybrids show primary particles of clay dispersed in the polymer matrix. The clay particles are \( \sim 50-70 \) \( \mu \)m in size.

![Optical micrographs](image)

(a) compatibilized hybrid (iPP3/9/9)  
(b) uncompatibilized hybrid (iPP3/9/0)

Figure 6.5. Optical micrographs of (a) compatibilized hybrid (iPP3/9/9)  
(b) uncompatibilized hybrid (iPP3/9/0)

6.1.3. Transmission electron microscopy

Figure 6.6 shows the TEM of as–extruded compatibilized (iPP3/9/9) hybrid at a magnification of 46000 x. It is clear that the silicate layers forming the clay tactoids are dispersed within the polymer matrix. Also, the edges of the clay tactoids appeared to be better dispersed into the surrounding matrix.
Thus, the as-extruded iPP nanocomposites show a hierarchy of morphologies. Primary particles of 50–70 μm size are dispersed in the sample. At the same time the sample also contains dispersed clay tactoids, which are made up of stacks of 3-5 silicate layers on an average. The d spacing of the silicate layers is about 3.3 nm, which is the same as that for the clay itself. Annealing of the samples causes degradation of the organic modifier and consequent collapse of the galleries. There is also some edge exfoliation from the tactoids. However, there appears to be no distinct difference between the microstructure of the compatibilized and uncompatibilized hybrids.

6.2. Syndiotactic polypropylene (sPP) nanocomposites

6.2.1. X-ray diffraction analysis

Figure 6.7 shows the diffraction patterns at 190°C for the organically modified clay, the uncompatibilized hybrid (sPP20/9/0) and the compatibilized hybrid (sPP20/9/9). The presence of a dominant peak indicates that the nanocomposites contain intercalated clay tactoids. The d spacing (gallery height) of the clay platelets in the tactoids was about 30 Å in the pure clay, about 32 Å in the uncompatibilized hybrid and about 34 Å in the
compatibilized hybrid. The inset shows more clearly that clay peak for the compatibilized hybrid is at a lower $2\theta$ value.

Similar to the iPP nanocomposites, the slight increase in the gallery height for the compatibilized hybrid (sPP20/9/9) compared to the uncompatibilized (sPP20/9/0) hybrid shows better intercalation possibly due to the presence of the compatibilizer.

![Figure 6.7. X-ray diffraction data for the clay (C20A), uncompatibilized hybrid (sPP20/9/0) and compatibilized hybrid (sPP20/9/9) at T = 190°C](image)

Figure 6.7. X-ray diffraction data for the clay (C20A), uncompatibilized hybrid (sPP20/9/0) and compatibilized hybrid (sPP20/9/9) at T = 190°C

The Cambridge MultiPass Rheometer (MPR) was used for in-situ rheo-XRD measurements on sPP nanocomposite melts during shearing. The rheo x-ray experiments reported in this study have been used to study the microstructural changes occurring in the hybrid during flow. As described in the chapter 5.2, the MPR uses Be capillary aligned in front of a collimated beam of x-rays. The scattered x-rays transmitted from the sample were collected on the area detector. The data collected by the area detector of the MPR-XRD equipment was processed and analyzed to correct for warping, background scattering, smoothing and peak searching. The peak $2\theta$ positions for pristine C20A clay
obtained from the Rigaku Dmax 2500 diffractometer was used as a one-point calibration for converting the diffraction ring data into intensity-2θ data.

Figure 6.8 shows the scattered x-ray intensity from the clay, the uncompatibilized hybrid (sPP20/9/0) and the compatibilized hybrid (sPP20/9/9) under quiescent conditions at 190°C. The inset in the figure shows, as an example, the two-dimensional diffraction pattern of the compatibilized hybrid. The clay tactoids in the compatibilized nanocomposite have a slightly larger gallery height of 34 Å than that in the uncompatibilized sample or the clay (~30 Å). These peak positions are similar to those obtained from the Rigaku Dmax 2500 diffractometer shown in Fig. 6.5. The inset shows the 2D x-ray diffraction pattern of the compatibilized hybrid (sPP20/9/9). The diffraction rings corresponding to the peaks at 2θ ~ 6° were not easily visible on the area detector. This is because of the lower intensity source of the x-rays in the MPR-XRD equipment compared to the Rigaku machine. Thus, the peak 2θ positions obtained from the Rigaku diffractometer are expected to be more accurate. The MPR-XRD apparatus, on the other hand, was used specifically to obtain data on flow-induced orientation.

### 6.2.2 Optical microscopy

Cross polarized optical micrographs of the sPP nanocomposites for the compatibilized (sPP20/9/9) and the uncompatibilized (sPP20/9/0) hybrids are shown in Figure 6.9. The micrographs show that both the uncompatibilized and the compatibilized hybrids have primary particles of clay ~ 40–50 μm in size.
Figure 6.8. X-ray diffraction data for the clay (C20A), uncompatibilized (sPP20/9/0) and compatibilized (sPP20/9/9) hybrid at T = 190°C, in MPR rheo-XRD equipment under quiescent conditions.

Figure 6.9. Optical micrographs of (a) compatibilized hybrid (sPP20/9/9) (b) uncompatibilized hybrid (sPP20/9/0)
6.3. Polyethylene (PE) nanocomposites

6.3.1. X-ray diffraction analysis

PE nanocomposite were synthesized by in-situ polymerization of ethylene in the presence of a suitably modified clay (see chapter 5.3). The XRD data shown in figures 6.10 and 6.11 was kindly provided by Mr. Saptarshi Ray (see relevant references in chapter 5). Figure 6.10 shows the XRD patterns of the PE nanocomposites (PENC-1) series having ~1-wt% clay and made with catalyst heterogenized on the clay surface. The nanocomposites in this series were made using different catalyst: co-catalyst ratio (see Table 5.6). XRD data was acquired for 10 min to get sufficient signal from clay, since the clay concentration was low. As it can be seen from Figure 6.10, the PE nanocomposites appear almost completely exfoliated, at least to an extent determinable by WAXD. Figure 6.11 shows the XRD pattern of the PE nanocomposites (PENC-3) series, having ~5-6-wt% clay and made with catalyst heterogenized on the clay surface. Again, the nanocomposites in this series were made using different co-catalyst: catalyst ratio (see Table 5.6). The (PENC-3) nanocomposites were not as exfoliated as the (PENC-1) series, with the clay peaks evident in the XRD. However, the major clay peak is still not visible in the PENC-3 hybrids.

Thus under similar conditions of polymerization the extent of exfoliation was dependent on the clay concentration.
Figure 6.10. X-ray diffraction patterns of the (PENC-1) series and pristine clay

Figure 6.11. X-ray diffraction patterns of the (PENC-3) series and pristine clay

Interestingly, it also can also be seen from Figure 6.11 that the peak intensity decreases and the peak width increases with the increase in co-catalyst: catalyst ratio for
the same clay concentration. This implies an increase in the extent of intercalation with increase in the co-catalyst: catalyst ratio. It may be noted that increasing this ratio decreases the average molecular weight of the polymer as mentioned earlier in chapter 5.

PE nanocomposites were also synthesized by in situ polymerization, wherein the catalyst was not heterogenized on the clay surface. Figure 6.12 shows a comparison of the XRD patterns for the PE nanocomposites synthesized with heterogenization and without heterogenization of the catalyst keeping other polymerization conditions identical.

![X-ray diffraction patterns of the PENC-1 (1600) and PENC-2 (1600)](image)

**Figure 6.12. X-ray diffraction patterns of the PENC-1 (1600) and PENC-2 (1600)**

As seen from the Figure 6.12, under similar conditions of polymerization, the nanocomposite prepared using the catalyst heterogenized on the clay surface [PENC-1 (1600)] were nearly exfoliated, while the nanocomposite synthesized without the heterogenization of the catalyst [PENC-2 (1600)] had remnants of intercalated microstructure.
Thus, the heterogenization of the catalyst on the clay surface played a very crucial role in determining the microstructure of the hybrid. As mentioned earlier in chapter 5, there is a strong possibility that the heterogenization of the catalyst would result in hybrids with polymer chains tethered to the clay surface, although no direct evidence for this has been presented here.

6.4. Summary

XRD, optical microscopy, and TEM suggest that the polypropylene hybrids investigated in this study were mainly intercalated hybrids, with clay tactoids having typically 3-4 clay platelets. The compatibilized hybrid showed slightly better intercalation compared to the uncompatibilized hybrids. The d spacing in the compatibilized and the uncompatibilized hybrids as indicated by WAXS are not significantly different. Even with the annealing times as high as 3 hrs the x-ray diffraction pattern of the compatibilized and the uncompatibilized hybrids did not show any significant difference. However, as we will see in the chapters 7 and 8, the rheological response of the compatibilized and the uncompatibilized hybrids are qualitative different.

The microstructure of the PE nanocomposites can be classified as being of nearly exfoliated type. However, subtle differences in the extent of exfoliation were observed as a function of clay loading and catalyst: co-catalyst ratio specifically, the PENC's containing higher clay loading and lower co-catalyst: catalyst ration had more intercalated microstructure. At the same time molecular weight of the matrix resin was also determined by these parameters. It is not yet clear whether there is a definitive relation between the extent of exfoliation and resin molecular weight. These parameters affect the rheological response of PENC's as will be shown in chapter 10.

WAXD was found to be a sensitive technique to study the microstructure of the nanocomposites synthesized with and without heterogenization of the catalyst on the clay surface. It might be possible that some polymer chain will be tethered to the clay surface. The rheological response of these hybrids also is vastly different, as will be discussed in chapter 10.