Infrared Spectroscopic Characterization of Polymer and Clay Platelet Orientation in Blown Films Based on Polypropylene-Clay Nanocomposite

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Summary: The "tilted film" transmission infrared spectroscopy method was used to characterize the biaxial orientation in a set of blown films containing polypropylene (PP), layered silicate nano-reinforcement, and two different compatibilizing agents based on maleic-anhydride-grafted PP. Both interactive spectral subtraction and peak fitting were used to determine trichroic ratios. The biaxial orientation of the polymer chains could be clearly quantified according to well-established relationships for PP. In addition, the clay platelet orientation could be determined from the trichroism of the Si–O stretching bands around 1100 – 1000 cm^{-1}. The clay orientation was found to be quite high (Hermans orientation function around +0.8) and was not significantly affected by the presence of compatibilizing agent.

Keywords: films; infrared spectroscopy; nanocomposites; orientation; poly(propylene) (PP)

Introduction

In recent years it has been demonstrated that if layered silicates like montmorillonite clays are used as reinforcement in a polymeric matrix and exfoliated into their individual basic silicate layers about 1 nm thick, significant improvements in various properties can be achieved with a relatively low level of reinforcement (less than 5% by weight).[1] However, because the clays are naturally hydrophilic it is not always easy to accomplish exfoliation when the polymer matrix is hydrophobic, like polypropylene (PP). To overcome this problem, the clay is usually treated with an organic intercalant like an onium salt, which replaces the metal cations located between the layers and increases the interlayer spacing. This facilitates further separation and eventual exfoliation when the treated clay is mixed with molten polymer in a melt processing procedure. The process is further aided by incorporating into the hydrophobic polymer matrix a compatibilizing agent (CA) that resembles the matrix but also contains polar groups that lead to better interaction with the clay. For PP, the most commonly used CAs are maleic-anhydride-grafted polypropylenes (MA-g-PP).

It is well known that the shear forces present during melt processing of polymers can lead to significant orientation of the molecular chains. In nanocomposites, because the clay particles (whether exfoliated or not) are highly anisometric, they too can be oriented. This orientation can influence the mechanical properties of the nanocomposite product, as has been demonstrated for polyethylene blown films,[2] syndiotactic polypropylene extruded tape,[3] and uniaxially drawn isotactic polypropylene.[4] In addition, the presence of "nanoclay" in polypropylenes has been shown to decrease the permeability with respect to certain solvents,[5,6] and it is usually considered that this is because the oriented clay platelets block the advancement of the solvent molecules and force them to follow a more tortuous path.

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Given the influence of orientation, it is obviously important to characterize it well so as to correlate it with other properties. In the case of nanocomposites, X-ray techniques seem to be the most widely used method. However, in a recent study of PP blown films, we showed that infrared spectroscopy can provide detailed information on clay orientation as well as polymer orientation. The overall results of this study were briefly summarized in a recent publication.[7] The object of the present paper is to describe the orientation results in particular in greater detail.

Experimental

The PP used was Pro-fax PDC 1274 from Basell Polyolefins. The clay was Cloisite® 15A from Southern Clay Products, Inc.; it consists of montmorillonite treated with dimethyl di(hydrogenated tallow) ammonium salt to give an organic content of about 40% and an interlayer d_{001} spacing of 3.15 nm. The two CAs used were both MA-g-PPs: (i) Epolene 43 from Eastman Chemical Company, with a low molecular weight ($M_w = 9000$) but high MA content (3.8 wt%), henceforth designated ''E43'', and (ii) Polybond 3150 from Crompton Corp., with a high molecular weight ($M_w =$ 330,000) and low MA content (0.5 wt%), henceforth designated ''PB3150''. Masterbatches containing 10 wt% or 15 wt% nanoclay in PP were prepared by processing in a Leistritz 34 mm twin screw extruder at 200 °C. Appropriate combinations of masterbatch, PP, and CA were then processed under the same conditions to give mixtures containing 0 or 4 wt% CA in combination with 0, 2, 5, or 10 wt% clay. Some mixtures with 2% clay and higher levels of CA (20% or 38%) were also prepared. Blown films with a take-up ratio of 24 and a blow-up ratio of 2.6 were prepared on a Killion machine; their thickness was in the range of 25 to 50 μm.

Infrared spectra of the blown films were recorded on a Nicolet Magna 860 FT-IR instrument from Thermo Electron Corp. (DTGS detector, resolution 4 cm^{-1}, accumulation of 128 scans). The beam was polarized by means of a Spectra-Tech zinc selenide wire grid polarizer from Thermo Electron Corp. To characterize the biaxial orientation, the ''tilted film'' method was used.[8,9] For a tubular blown film, three orthogonal directions can be defined as follows: (i) the machine direction MD, corresponding to the longitudinal or ''take-up'' direction; (ii) the transverse direction TD, corresponding to the circumferential or ''blow-up'' direction; and (iii) the normal direction ND, corresponding to the thickness direction. A film sample is first installed in the spectrometer with its plane normal to the beam direction and with the MD vertical. Spectra are then recorded with the beam polarization in the vertical (machine) and horizontal (transverse) directions; they are designated S_M and S_T respectively. The film is then tilted by an angle χ about the MD axis and a spectrum is recorded with polarization in the horizontal direction, i.e. in the TD-ND plane; this spectrum is designated S_{TN}. The spectrum S_N corresponding to polarization purely in the normal direction is obtained by calculation according to the following equation:

$$S_N = \left(\frac{n}{\sin\chi}\right) \times \left(\frac{n^2}{\sin^2\chi} - 1\right)^{\frac{1}{2}} S_{TN} - \left(\frac{n^2}{\sin^2\chi} - 1\right) S_T \quad (1)$$

where n is the effective refractive index of the sample in the direction of the beam propagation. This equation is equivalent to Eq. 4 of Ref. 8. It takes into account the change in optical pathlength resulting from the tilting and beam refraction, so that the S_N spectrum corresponds to the same sample thickness as S_M and S_T. For this work the tilt angle χ was 45° and the index of refraction was taken to be 1.503.[10] Finally, the structural factor (SF) spectrum S_0 is calculated as the average of S_M, S_T, and

S_N:

$$S_0 = \frac{1}{3}(S_M + S_T + S_N) \quad (2)$$

This is the spectrum that the sample would give if no orientation were present.

Only films containing 0 or 2 wt% clay were analyzed, because at higher concentrations the clay peaks were saturated at the film thicknesses involved. Peak fitting of the spectra was performed with the aid of Galactic GRAMS/AI™ software from Thermo Electron Corp.

Results and Discussion

X-ray diffraction[7] and electron microscopy showed that the clay particles were not completely exfoliated but consisted of intercalated stacks. For the film containing no CA, the d_{001} spacing of 2.8 nm was lower than that of the starting clay (3.15 nm), indicating some gallery collapse, but for the films containing CA, the spacing was generally in the range of 3.8 to 4.0 nm.

Figure 1a shows the trichroic spectra obtained for the film containing only PP, i.e. no clay or compatibilizing agent. Only the

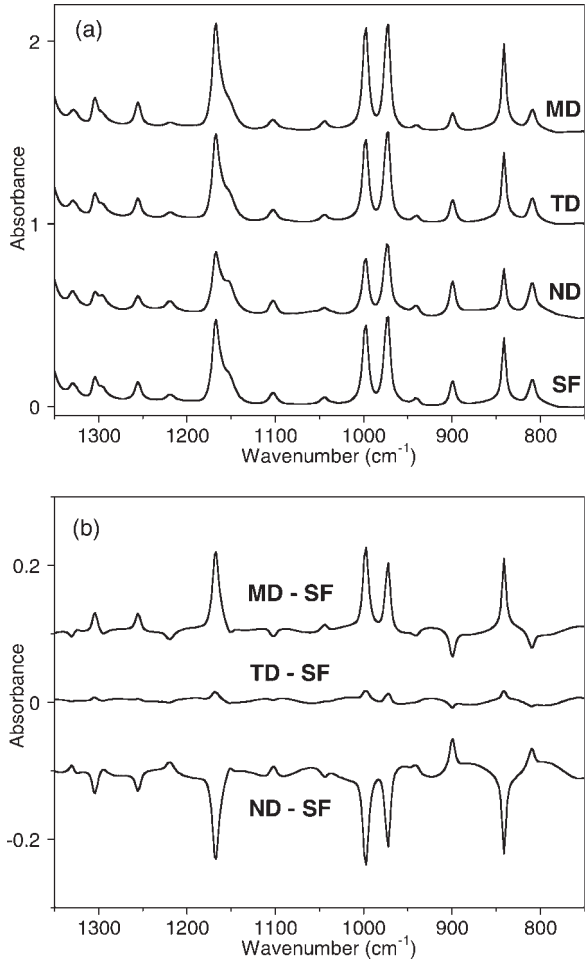

Figure 1.
Trichroic spectra obtained for the film containing only PP: (a) spectra as recorded (MD, TD) or calculated from recorded spectra (ND, SF); (b) difference spectra obtained by subtracting the structural factor spectrum. Spectra are shifted along the y-axis for clarity.

wavenumber range 1350 – 750 cm^{-1} is shown because most peaks at higher wavenumber were saturated. Most of the peaks arise from the helical conformation of PP found in the crystalline phase; the main contributions of the amorphous phase are the shoulder near 1160 cm^{-1} and an underlying peak at 975 cm^{-1}.[11] The effects of the orientation can be more clearly seen by calculating the difference spectra with respect to the structural factor spectrum, as shown in Figure 1b. On the basis of earlier analyses of PP,[12–14] the biaxial orientation expected for a blown film is evident. The following peaks show strong trichroism and are known to have their transition moment along the polymer chain axis: 1305, 1255, 1168, 998, 972, 841 cm^{-1}. Their intensity varies in the order MD > TD > ND, showing that the polymer chains are oriented in the plane of the film and more strongly in the longitudinal (take-up) direction than in the circumferential direction. Consequently, those peaks known to have their transition moment more-or-less perpendicular to the chain axis (1219, 1102, 899, 809 cm^{-1}) show the inverse behaviour with respect to intensity (ND > TD > MD).

It should be noted that the above discussion applies only to the crystalline phase. It is difficult to obtain information about the amorphous phase, but the fact that the shoulder peak at 1160 cm^{-1} does not show up strongly in the difference spectra suggests that the orientation of the amorphous phase is considerably weaker than that of the crystalline phase.

Figure 2 shows the spectra obtained in a similar manner for the film containing 2% nanoclay and 20% of the compatibilizing agent PB3150. (The CA spectrum generally resembles that of PP, except for some weak anhydride and acid carbonyl peaks in the 1800 – 1700 cm^{-1} region.) The PP peaks in these spectra show much the same behaviour as in Figure 1, indicating that the PP orientation is similar. Much more interesting in this case are the strong and broad clay peaks occurring in the 1150–1000 cm^{-1} region. These can be seen more clearly upon subtracting the SF spectrum of the PP film from the SF spectrum of the nanocomposite film, as shown in Figure 3. (The PP peaks do not always cancel completely, probably because of a slight difference in crystallinity.) The infrared spectra of layer silicates have been studied extensively, in particular by Farmer and Russell.[15] They pointed out that montmorillonites show four Si–O stretching bands in this region. Each surface of the basic montmorillonite layer consists of silicon atoms tetrahedrally surrounded by oxygen atoms. Three of these oxygen atoms (the ''basal'' oxygens) lie on the very surface, so that the Si–O bonds are almost (but not perfectly) parallel to the plane of the layer. The fourth oxygen (the ''apical'' oxygen) lies below the silicons and is shared with aluminum atoms at the centre of the layer. This Si–O bond is therefore perpendicular to the plane of the layer. The basal oxygens give rise to three bands at around 1120, 1048, and 1025 cm^{-1} (designated I, III, and IV in Figure 3), whereas the apical oxygen gives rise to a band around 1080 cm^{-1} (designated II in Figure 3). If the clay platelets are oriented within a sample, it is obvious that the trichroic behaviour of Peak II will differ considerably from that of peaks I, III, and IV. This is clearly seen in Figure 2, which confirms that the clay platelets are strongly oriented in the plane of the film. Thus, when the spectrum is measured with polarization in the plane of the film (MD or TD), Peaks III and IV are quite strong while Peak II is very weak. (Unlike the chain-like polymer molecules, the ''round'' clay platelets show no preference with respect to the MD and TD directions, so their peaks have the same intensity in the MD and TD spectra.) When the spectrum corresponds to polarization in the thickness direction (ND), on the other hand, Peak II is very strong and the others are weak. All the nanocomposite films examined showed similar behaviour. It should be stressed that the infrared spectrum corresponds to an average over all clay particles, and does not distinguish between individual layers and platelets consisting of stacked layers.

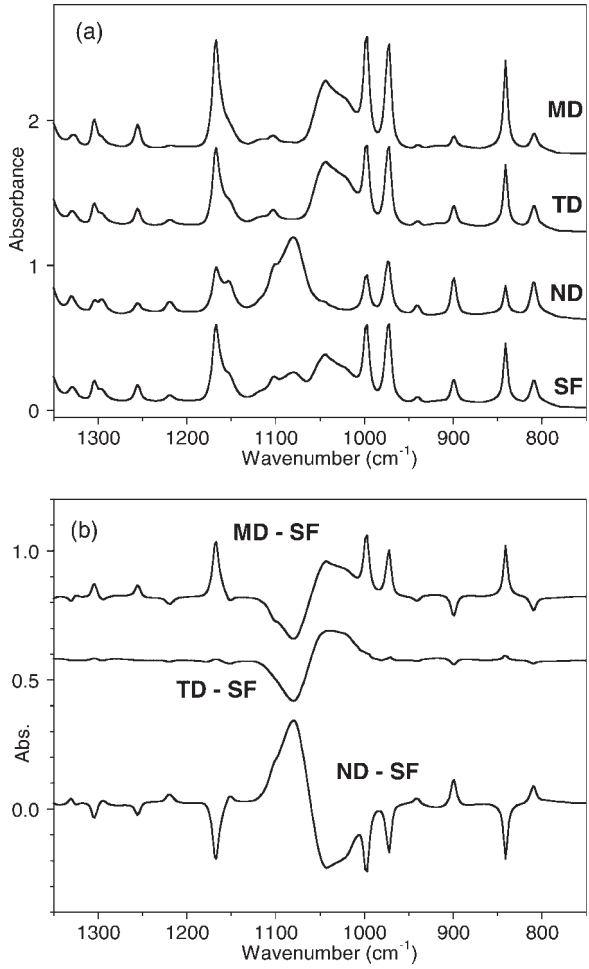

Figure 2.
Trichroic spectra obtained for the film containing 2% clay and 20% PB3150: (a) spectra as recorded (MD, TD) or calculated from recorded spectra (ND, SF); (b) difference spectra obtained by subtracting the structural factor spectrum. Spectra are shifted along the y-axis for clarity.

Since the orientation of both PP and clay has been clearly established, it remains to quantify it. This is done by comparing peak intensities in the MD, TD, and ND spectra to those in the SF spectrum. The Hermans orientation function $f_{iJ} = \frac{1}{2}\langle 3\cos^2\theta_{iJ} - 1\rangle$ describes the degree of orientation of a given molecular axis i with respect to the sample direction J, where $J = \mathrm{M}, \mathrm{T}, \text{or } \mathrm{N}$, θ_{iJ} is the angle between the i-axis and the J-direction, and the angle brackets indicate averaging over all molecules. For a vibrational mode whose transition moment lies along the i-axis direction, f_{iJ} is given by:[16]

$$f_{iJ} = \frac{1}{2}\left[\frac{A_J}{A_0} - 1\right] \tag{3}$$

where A_J and A_0 are respectively the intensities in the J-direction spectrum and the structural factor spectrum for the peak(s) whose vibrational transition moment lies along the i-axis. This equation is derived from Eq. 23a of Ref. 16 by setting $\theta_m = 0^\circ$ and $\mathrm{J} \equiv 3$. The ratio A_J/A_0 can be determined in different ways. If the peak is well separated from other peaks it is

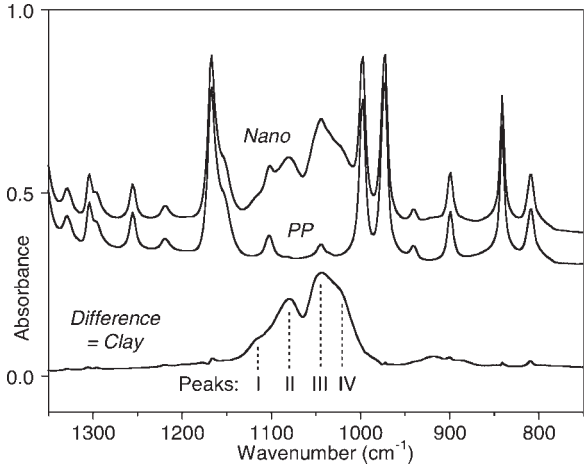

Figure 3.
SF spectrum of the nanocomposite film containing 2% clay and 20% PB3150, SF spectrum of the pure PP film, and the nanoclay spectrum obtained by subtraction.

sufficient to use its height or its area. When this is not so, or even when it is, one can also use interactive spectral subtraction or peak fitting, both of which we have applied in the present case.

The subtraction approach is illustrated in Figure 4 for the PP film. When the SF spectrum (Fig. 4b) is interactively subtracted from the MD spectrum (Fig. 4a), a subtraction factor of 1.29 (Fig. 4c) cancels all the crystalline bands that are considered to have their transition moment (t.m.) at an angle of 0° with respect to the chain axis (1325, 1305, 1255, 1168, 1044, 998, 972, and 841 cm^{-1}). The residual negative features that remain in certain cases are different bands. (For instance, those at 1330 and 1296 cm^{-1} are perpendicular bands, while those at 1154 and 975 are known to arise from the amorphous phase.[11] The weak band at 1000 cm^{-1} may also arise from the amorphous phase.) A subtraction factor of

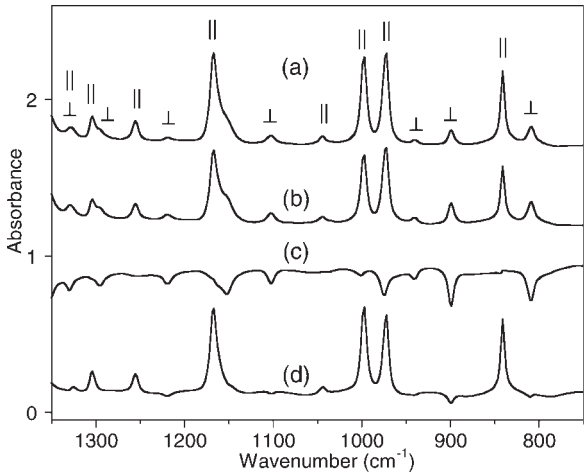

Figure 4.
Illustration of the subtraction procedure for the PP film: (a) the MD spectrum; (b) the SF spectrum; (c) the difference spectrum MD – (1.29 × SF), multiplied by 3 to enhance the visibility; (d) the difference spectrum MD – (0.855 × SF), multiplied by 3.

1.29 means that $A_M/A_0 = 1.29$ for these bands, so that the orientation function of the chain axis c with respect to the machine direction is $f_{cM} = \frac{1}{2}(1.29 - 1) = +0.145$. Because the sum of the orientation functions for any three orthogonal molecular axes a, b, c must add up to zero, this means that the orientation function for the two axes perpendicular to the chain should be $f_{aM} = f_{bM} = -0.0725$ (assuming cylindrical symmetry about the chain axis). This in turn means that the trichroic ratio A_M/A_0 for a perfectly perpendicular band (t.m. at 90° with respect to the chain axis) should be 0.855, based on Eq. 3. Figure 4d shows that a subtraction factor equal to this value does indeed cancel very well the perpendicular peaks at 1330, 1296, 940, and 809 cm^{-1}, so the t.m. of these bands probably lies close to 90° with respect to the chain. However, the residual negative peaks seen for the perpendicular peaks at 1219, 1102, and 899 cm^{-1} (especially the latter) suggest that their t.m. angles may be somewhat less than 90°. Because the situation is more clear for the parallel peaks, they were used to determine the orientation functions f_{cM}, f_{cT}, and f_{cN} for the crystalline phase of the PP.

The same interactive subtraction approach was used to determine the trichroic ratios for the clay peaks, as illustrated in Figure 5 for the film containing 2% clay and 4% E43. In this case it would have been difficult to use simple peak heights or areas because of the overlap of the broad clay peaks with each other and with the PP peaks. For the clay platelets we define the unique c-axis as the normal to the plane of the platelet, which coincides with the t.m. of the peak near 1080 cm^{-1} (Peak II). Because of the broadness of the clay peaks, it is more difficult than for PP to decide when exactly a peak has been cancelled. We chose the point at which the peak is reduced to the baseline level. Thus, in the example given, for the out-of-plane Peak II the best subtraction factor was found to be 2.56 (Fig. 5d). This leads to an orientation function $f_{cN} = +0.78$. For the in-plane peaks III and IV, the best factor was 0.45 (Fig. 5c), which leads to orientation functions $f_{aN} = f_{bN} = -0.275$. The sum $f_{aN} + f_{bN} + f_{cN}$ is therefore +0.23, when it should be zero. The most likely reason for this is that the transition moments of Peaks III and IV do not lie exactly in the plane of the platelet, so consequently the values calculated for f_{aN} and f_{bN} are in error. Because of this, to characterize the clay orientation we use the f_{cN} value determined from the out-of-plane Si–O band. It is interesting to note that the

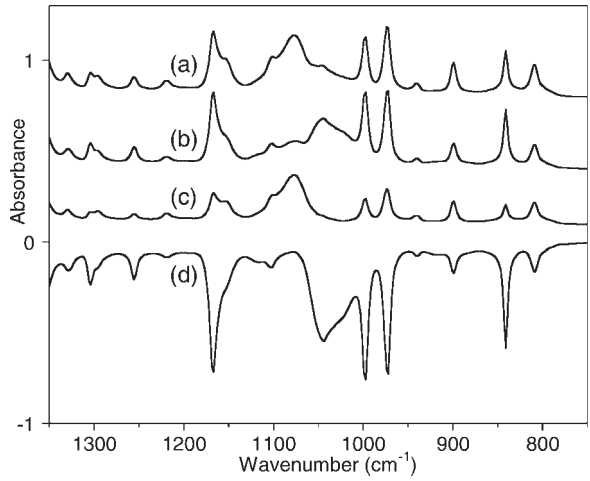

Figure 5.
Illustration of the subtraction procedure for the film containing 2% clay and 4% E43: (a) the ND spectrum; (b) the SF spectrum; (c) the difference spectrum ND – (0.45 × SF); (d) the difference spectrum ND – (2.56 × SF).

inconsistency between the in-plane and out-of-plane peaks can be explained if the transition moment of the ''in-plane'' bands deviates from the plane by about 18°.

Because of the uncertainty associated with the subtraction of the clay peaks, we also tried a peak fitting approach. This requires care in the choice of lineshape, number of peaks, etc. Although the theoretical lineshape for infrared bands is Lorentzian, the bands in polymer spectra often show some Gaussian character, because the less-than-perfect order results in a distribution of structures. To account for this, we used a Pearson VII lineshape function,[17,18] which includes a parameter m that allows the lineshape to vary from purely Lorentzian ($m = 1$) to purely Gaussian ($m = \infty$). After trials with a number of spectra, we chose an m-value of 1.25 (roughly 20% Gaussian character) for the crystalline PP peaks and a value of 4 (75% Gaussian character) for the other PP and clay peaks. Typical fits for PP and a clay-containing nanocomposite are shown in Figures 6 and 7. Karacan et al.[14] fitted the 1080 – 750 cm^{-1} region for PP and obtained similar results, including the minor peaks. The complexity of the peak near 1160 cm^{-1} is worth noting – it seems to require four peaks. The clay Si–O bands are also more complex than expected; to obtain a good fit, it was necessary to use two components for both Peak II and Peak III. This does not necessarily imply distinct vibrational bands. It may simply reflect an asymmetric distribution of structures, since transmission electron microscopy shows that the clay layers are far from perfectly flat and ordered.

To calculate the orientation of crystalline PP from the peak fitting data, trichroic ratios A_J/A_0 were calculated from the areas of the peaks at 998 and 841 cm^{-1}. Both gave very similar results, so the average value for the two peaks was taken. For the clay platelets, f_{cN} was calculated from the combined area of peaks IIa and IIb (both components showed similar trichroism). The resulting orientation functions obtained by both methods (subtraction and peak fitting) for the different films analyzed are summarized in Table 1.

First of all, it is interesting to compare the results obtained by the two approaches – subtraction and peak fitting. While they are generally in good agreement, there are large discrepancies for the clay orientation function in two of the films (4% PB3150 and 38% PB3150). This is attributed to the presence of noticeable interference fringes in the spectra of these particular films. Because the width of the fringes is similar to that of the clay peaks, they introduce a

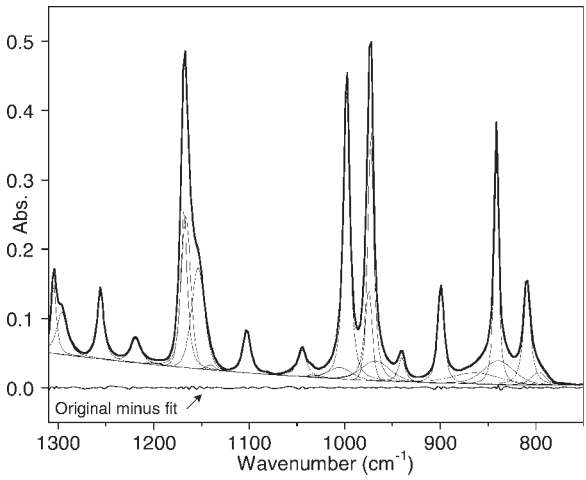

Figure 6.
Peak fitting for the SF spectrum of the PP film.

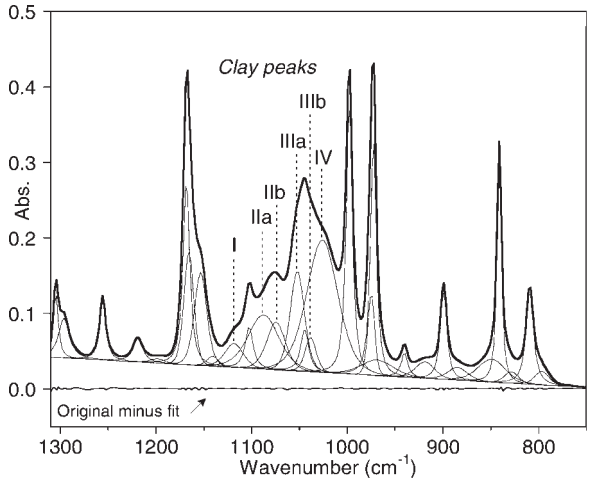

Figure 7.
Peak fitting for the SF spectrum of the nanocomposite film containing 2% clay and 4% E43.

significant error into the peak fitting results. The PP results are also affected to some extent, as can be seen by calculating the sum $f_{cM}+f_{cT}+f_{cN}$, which should be equal to zero. For the subtraction results, this sum is less than ± 0.01, but for the peak fitting results it is as large as ± 0.04. Thus, the subtraction results are considered to be more reliable and are used as the basis for the following discussion.

For the crystalline PP, the data in Table 1 confirm a moderate degree of biaxial orientation in the plane of the film, with the polymer chains more highly oriented in the longitudinal direction than in the circumferential direction. (For perfect in-plane orientation, the sum $f_{cM}+f_{cT}$ would be $+0.5$ and f_{cN} would be -0.5.) The variations among the different film samples, although real, are small and are not considered to be highly significant; they are probably no greater than those that would be observed from point to point in a single blown film as a result of process variations. Thus, neither clay nor compatibilizing agent appears to have a large effect on the PP orientation in these blown films. This is in contrast with the results reported for extruded PP-nanoclay samples, where the PP orientation was measured by the X-ray method and found to increase significantly and monotonically with clay content.[4] On the other hand, the opposite effect has been reported for PP nanocomposite samples prepared by dynamic packing injection moulding.[19]

For the clay platelets, the orientation is rather high in all cases, and again does not vary significantly with respect to the presence of compatibilizing agent. The orientation function values of $+0.74$ to $+0.80$ are

Table 1.
Summary of Hermans orientation functions obtained by interactive spectral subtraction (left-hand value) or by peak fitting (right-hand value).

Film	Polypropylene			Clay
	f_{cM}	f_{cT}	f_{cN}	f_{cN}
No clay, no CA	+0.15 | +0.15	+0.02 | +0.04	−0.17 | −0.16	—
2% clay, no CA	+0.20 | +0.20	−0.02 | 0.00	−0.18 | −0.21	+0.78 | +0.80
2% clay, 4% E43	+0.17 | +0.15	−0.04 | −0.04	−0.12 | −0.12	+0.78 | +0.75
2% clay, 4% PB3150	+0.22 | +0.20	0.00 | −0.01	−0.21 | −0.23	+0.80 | +0.95
2% clay, 20% PB3150	+0.24 | +0.22	+0.02 | +0.03	−0.25 | −0.26	+0.74 | +0.79
2% clay, 38% PB3150	+0.20 | +0.22	+0.02 | +0.04	−0.21 | −0.24	+0.75 | +0.58

considerably higher than those measured by X-ray for extruded syndiotactic PP nanocomposites (maximum value +0.32)[3] or for poly(ethylene oxide) nanocomposites prepared by layer-by-layer deposition from solution (maximum value 0.51).[20] However, values as high as +0.85 have been reported for *in situ* X-ray measurements on a flowing melt of syndiotactic PP and layered silicate.[21]

The mechanical, optical, and permeability properties of the films discussed here were briefly summarized in a recent publication[7] and will subsequently be reported in more detail.[22] Some improvements were observed, particularly when the compatibilizing agent used was PB3150 rather than E43. Since the results reported here show little variation in orientation, it is clear that these improvements do not result from increased orientation and must be attributed to other factors.

Conclusions

It has been demonstrated that the ''tilted film'' transmission infrared spectroscopy method can be used to quantify not only the PP orientation but also the clay platelet orientation in blown films made from PP nanocomposites based on layered silicate reinforcement. In a set of films made without clay or with 2% clay and varying types and amounts of maleic-anhydride-grafted-PP compatibilizing agents, a moderate degree of biaxial PP orientation was confirmed and it did not vary significantly with composition. The clay orientation was found to be rather high (Hermans orientation function +0.74 to +0.80) and also was not significantly altered by the presence of compatibilizing agent.

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