Influence of the CaCO$_3$ Nanoparticles on the Molecular Orientation of the Polypropylene Matrix

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ABSTRACT: The presence of aggregates of CaCO$_3$ nanoparticles in an isotactic polypropylene matrix processed by extrusion promotes the apparition of residual stresses. These stresses are removed with a thermal treatment of the composite, but a higher molecular orientation is then produced. The chain orientation inside the sample is nonhomogeneous due to the presence of the aggregates of nanoparticles. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 947–952, 2003

Key words: nanocomposites; polypropylene; molecular orientation; micro-Raman spectroscopy

INTRODUCTION

The incorporation of inorganic particulate fillers has been proved to be an effective way for the improvement of the mechanical properties of polymeric materials. However, the traditional filler requires much higher loading levels to achieve a similar performance.[1] As a result of this high particle loading, the processability of the compounds is inevitably deteriorated and the weight of the final products becomes much higher than that of the neat polymers. Thus, a composite with improved properties and lower particle concentration is highly desired. With regard to this, the newly developed nanocomposites would be competitive candidates.

Polymer matrix nanocomposites are a relatively new class of materials with typical dimensions in the range of 1–100 nm and percentages 2–10%. In general, because of the ultrafine phase dimensions involved, nanocomposites exhibit new and improved properties when compared to their micro or macro counterparts. Due to the small size of the particles and their high aspect ratio, nanostructured materials are anticipated to exhibit unique behavior compared to conventional materials with micron scale structure.[2,3] This is characterized by the large fraction of filler atoms that reside at the surface of the nanoparticles leading to strong interfacial interactions with the surrounding polymer matrix.

Nanocomposites, which are largely thermoplastics, offer improvements in several of the properties of thermoplastics including tensile strength, modulus, barrier, wearing resistance, and heat distortion temperature.[4,5]

Although the size of the nanoparticle is important, the amenability of the particle to surface modification is also a critical factor. In most cases inorganic nanoparticles are inherently hydrophilic and polymers are hydrophobic. This means that some sort of inorganic surface modification is necessary to render the nanoparticles compatible with the majority of polymers of interest. Although this nonreactive treatment leads to an improvement in dispersion, it decreases the matrix–filler interaction.[6] Consequently, an homogeneous dispersion of nanoparticles in a polymeric matrix is a very difficult task due to the strong tendency of nanoparticles to agglomerate. These nanoparticles can be present in form of the aggregate with a size of about 1–10 μm (Fig. 1), consisting of several primary particles with a size of about 30–100 nm.

The process for preparation of composites can produce molecular orientation that causes changes on the physical properties. The final product processed by extrusion presents differences on the molecular orientation compared with the unfilled material as well as different orientation around the aggregates with consequences on the mechanical properties. In the present investigation we study the influence of the agglomerates of CaCO$_3$ present on the matrix structure of polypropylene on the orientation of the polymer chains, mainly on the interface of matrix–filler.
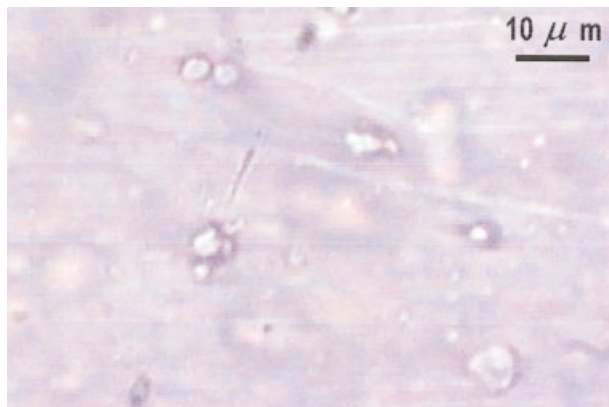
EXPERIMENTAL

Materials

Materials used in this study were an isotactic polypropylene (iPP) (Solvay) and a calcium carbonate supplied by Magnesia. Properties are described in Table I.

Figure 1 Optical photograph of the $CaCO_3$ particles in the iPP composite.

Composites of these materials were prepared mixing iPP and 5% of calcium carbonate by passing the material twice in a single screw extruder at a temperature of 190°C, obtaining a monofilament of nanocomposite, which was pelletized. Sheets of 0.40–0.45 mm thickness of iPP+5% $CaCO_3$ were produced by extrusion and calendering. The samples presented zones with the presence of aggregates with sizes of around 4 μm.

Four other samples were prepared as a reference, to find out information about the influence of the aggregates on the molecular orientation of the polymer matrix. These samples were (a) iPP melt pressed between heated platens at 200°C in a hydraulic press at 200 bars, (b) highly stretched iPP, (c) iPP processed by extrusion, and (d) iPP with 5% $CaCO_3$ melt pressed in a similar way to the (a) samples.

Samples (a) and (b) allowed the determination of the intensities ratios for the Raman bands, which are sensitive to the chain orientation. Samples (c) and (d) were prepared to separate the contribution of the molecular orientation from the presence of the aggregates and from the extrusion process. Nanocomposites and iPP obtained by extrusion [sample (c)] were later submitted to 160°C for 1 h.

Experimental procedure

Molecular orientation has been analyzed by Raman spectroscopy. By coupling an optical microscope to a
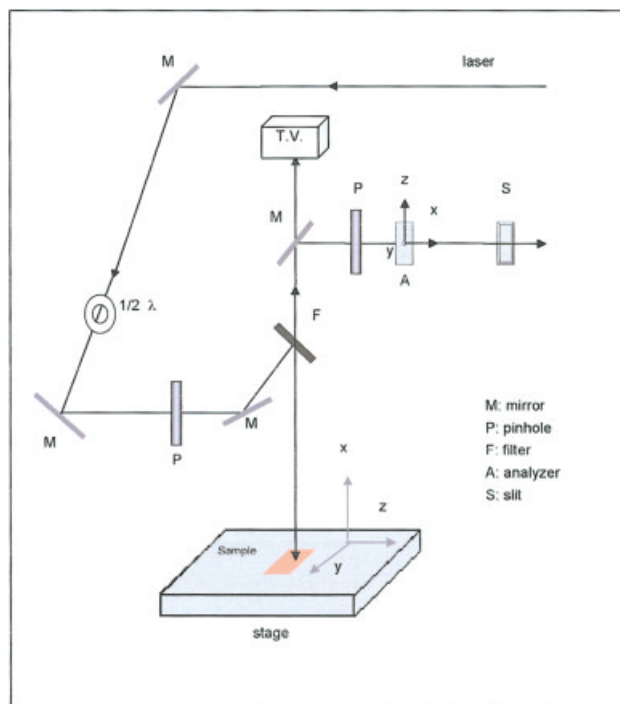

Figure 2 Optical system used for the polarized micro-Raman measurements.

conventional Raman spectrometer, the technique becomes a microprobe with spatial resolution at about 1 μm. Raman microscopy is a nondestructive technique that offers a unique combination of spatial resolution and measurements of molecular orientation.[7] Chain orientation can be detected by the analysis of the polarized Raman and the polarizing optical system used is shown in Figure 2.

Polarized micro-Raman spectra were measured on a DILOR Labram microspectrometer using a He–Ne laser (632.8 nm) of 16 mW. The entrance slit was set to 500 μm corresponding to 4 cm^{-1} spectral resolution. Both the incident light and Raman scattering were collected through an Olympus BH microscope with a 100× objective [numerical aperture (NA) = 0.90]. The confocal system contains a variable diaphragm (pinhole) placed at the image plane of the microscope. This arrangement ensures that only light coming from upper and lower planes were partially attenuated.

TABLE I
Polymer and Nanoparticles Characteristics

	Company	Trade Name	MFI 230/2,16 g/10 min ISO 1133	Flexion module 23°C, N/mm^2 ASTM D 790
iPP	Solvay	ELTEX P HS 200	6	1200

	Company	Trade Name	Particle size (nm)	Coated
$CaCO_3$	Magnesia	Socal 322V	30–50	Estearic acid
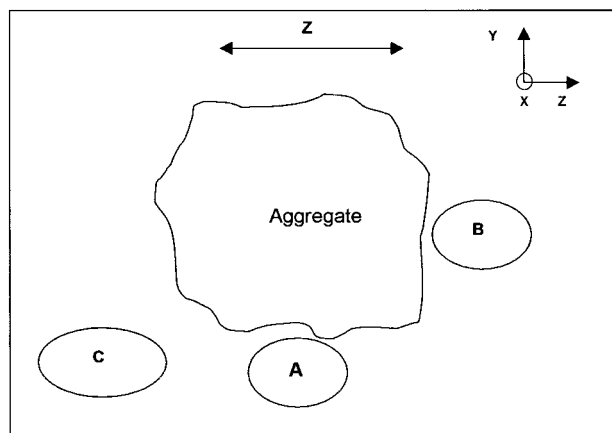
Figure 3 Experimental scheme. **X**: incident direction of the laser beam. **Y,Z**: polarized directions of the laser. **z**: melt flow extrusion direction.

Hence, the depth resolution of the microscope is also increased. The confocal microscope also offers improved lateral resolution compared with conventional microscopes. The combination of a $100\times$ objective with a pinhole of 100 μm diameter gives rise to a lateral resolution of approximately 1 μm and a depth resolution of about 2 μm. The scanning time was 60 s and ten spectra were accumulated.

In order to analyze the molecular orientation in the samples, an incident linearly polarized laser beam in conjunction with a polarization analyzer for the collected Raman scattering was used. In the polarizing optical system shown in Figure 2, the laser radiation is directed along the X axis with its electric vector oriented along the Y or Z axes. Rotation of the plane of polarization of the incident laser beam was made by using a half wave plate. The analyzer was placed just in front of the spectrograph slit. Two different polarization geometries of the Raman experiment, represented according to Porto notation,[8] have been used: X(YY)X and X(ZZ)X (parallel/parallel condition).

RESULTS AND DISCUSSION

The Raman bands of uniaxially oriented iPP can be classified into three groups: those polarized in a parallel direction with respect to the molecular chain (type A∥), perpendicular (A⊥), and unpolarized bands (E). The Raman bands detected at 809, 973, and 1167 cm⁻¹ have been proposed for the study of molecular orientation in uniaxially oriented iPP.[9] Bands situated at 841, 997, and 1151 cm⁻¹ were found not sensitive to the polarization conditions. In the present study the information on the orientation of the polypropylene chains has been obtained by collecting Raman spectra under the parallel/parallel polarization condition and subsequent calculation of the ratio of the area under the Raman bands at 973 cm⁻¹ (corresponding to the

CH₃ rocking and C—C stretching: type A∥) and 997 cm⁻¹. The average values were obtained through the evaluation of the Raman bands in five different points of the samples.

Bands intensities were obtained using the curve-fitting tool of Grams 32 (Galactic Industries Corp.). The analytical Raman band used to fit spectroscopic data was the conventional product of Lorentzian and Gaussian profiles. Prior to the deconvolution procedure, a baseline correction was performed.
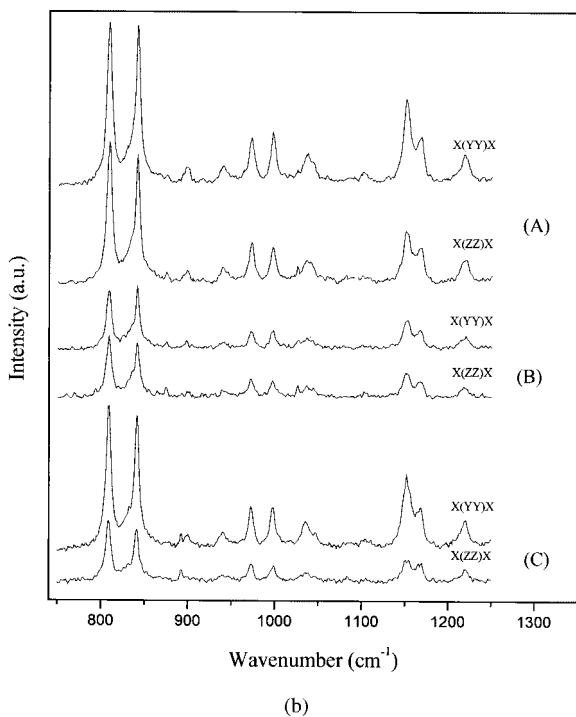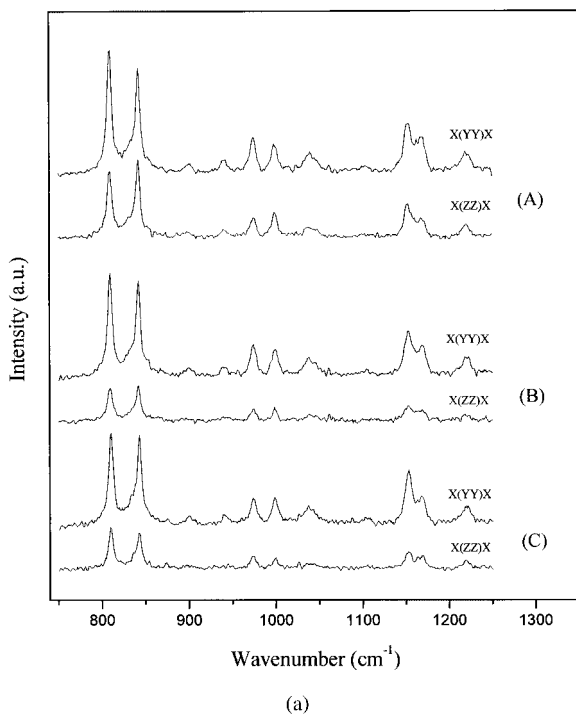
In order to detect the influence of the agglomerates on the chain orientation of the iPP around the particles, polarized Raman analysis in different points of the sample were obtained. In Figure 3 are noted the points of the nanocomposite where the spectra were obtained. Two different points of the matrix at 1 μm from the agglomerate are analyzed to detect the influence of the extrusion process (A and B). Results on the matrix far away from the aggregate (point C) are also presented.

The samples were illuminated with a laser polarization direction parallel and perpendicular to the extrusion direction and the scattered radiation was collected with the same polarization conditions. The sample was put in the stage of the Raman spectrometer with the extrusion direction parallel to the z direction of laser polarization.

Raman spectra for the iPP samples analyzed (a–c) are presented in Figure 4. The analyzed Raman bands present a different behavior for the samples obtained by the different processes. Figures 5 and 6 show the
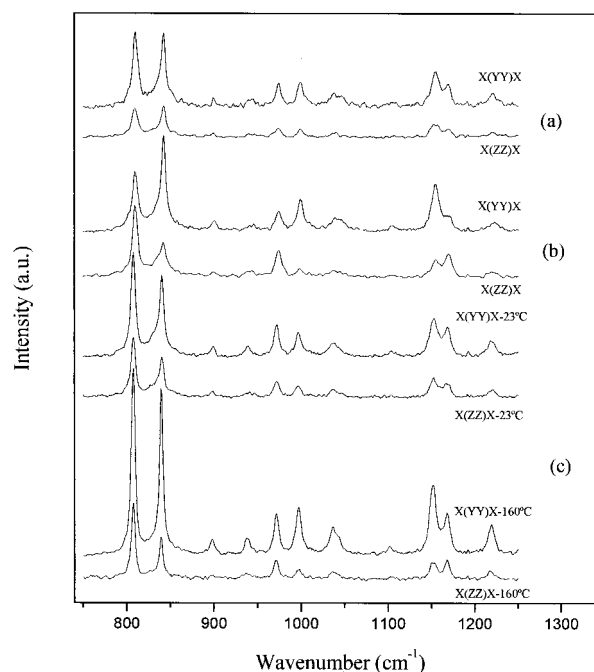
Figure 4 X(YY)X and X(ZZ)X Raman spectra of the iPP obtained by melt compression (a) and stretched (b); extrusion and extrusion with annealing (c).

around five aggregates with different sizes and shapes are similar, and Table III presents the average values of the intensity ratio.

The intensity ratios for the polarized Raman band analyzed in the melt compressed iPP are approximately 1. This corresponds to a nonoriented material
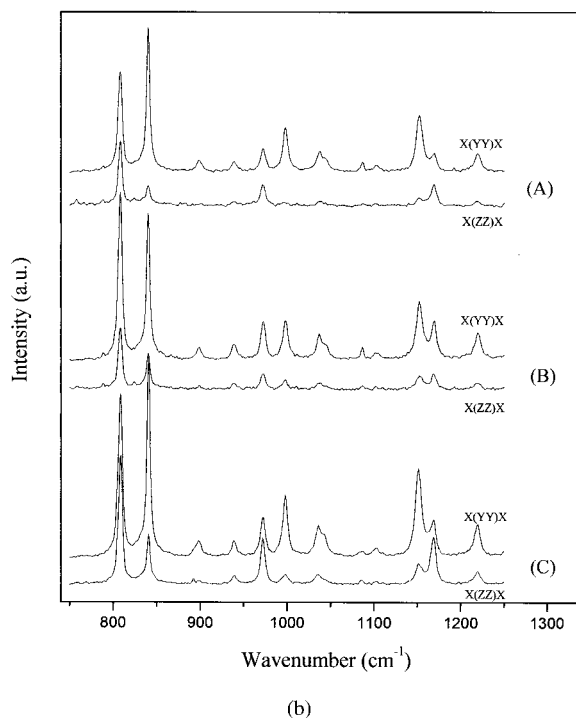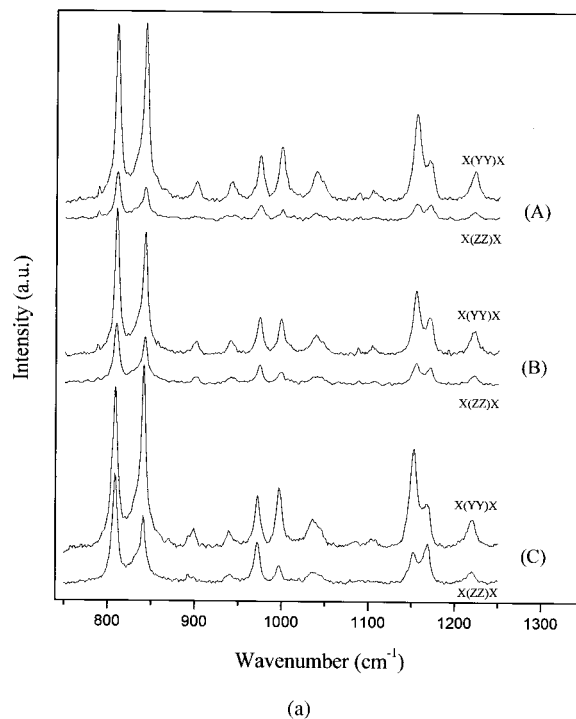

Figure 5　X(YY)X and X(ZZ)X Raman spectra at the A, B, and C points of Figure 3 of the nanocomposite obtained by melt compression (a). (b) Spectra of the compound after annealing.

Figure 6　X(YY)X and X(ZZ)X Raman spectra at the A, B, and C points of Figure 3 of the nanocomposite obtained by extrusion (a). (b) Spectra of the compound after annealing.

polarized Raman spectra for the nanocomposites obtained by extrusion. The intensity ratios calculated for both polarizations of 973 and 997 cm^{-1} bands and for all the samples are presented in Tables II and III. The Raman spectra on the reinforced iPP samples obtained

TABLE II
Intensity Ratio I_{973}/I_{997} from the Polarized Spectra of iPP Melt Compressed, Stretched and Extruded

	Polarization	I_{973}/I_{997}	
PP compressed	X(ZZ)X	1.1	
	X(YY)X	1.0	
	Polarization	I_{973}/I_{997}	
PP stretched	X(ZZ)X	6.7	
	X(YY)X	0.5	
		23°C	160°C
	Polarization	I_{973}/I_{997}	I_{973}/I_{997}
PP extruded	X(ZZ)X	1.7	1.9
	X(YY)X	0.8	0.6

(isotropic) and consequently no preferential chain orientation must be observed. However, for an oriented sample (b), the value for the intensity ratio for the X(ZZ)X polarization is higher than 1 because the polarization laser and the analyzer are parallel to the direction of deformation, and most of the polymer chains have been oriented into this direction. On the contrary, the X(YY)X polarization value is diminished. In Table II it can also be observed that the values of the intensity ratios for the extruded iPP show a slight chain orientation along the stretching direction. The orientation is barely increased after the thermal treatment.

Table III shows the values for the intensity ratios from the nanocomposites obtained by compression and extrusion. The Raman experiments from the melt compressed nanocomposite have been carried out to determine the possible influence of the aggregates on the chain orientation. The values of the intensity ratios in different points around the particle and far from it are approximately 1, and consequently no chain orientation in this sample has been detected.

Values of the intensities ratios measured from the Raman spectra of the extruded nanocomposite (Table III) point out a chain orientation along the extrusion direction in any part of the sample, but more important in the point A of Figure 3. The rest of the matrix has a similar orientation to the extruded iPP (Table II). After the thermal treatment at 160°C, a very important chain orientation at the point A is detected and also far away from the aggregate (point C). The behavior of the crystallinity obtained by differential scanning calorimetry is similar to the extruded iPP (40–50% after annealing for the iPP and 41–52% after annealing for the composite); thus, no influence of the nanoparticles on the crystallinity is produced.

From these values we can conclude that the extrusion process for the nanocomposites produces an orientation of the polymer chains similar to the one produced in iPP. However, a more important chain orientation is observed near the aggregate at the point A of Figure 3. The thermal treatment of this nanocomposite produces a slight increase of the polymer orientation at the point B (ahead and behind the particle in the extruded direction). The most relevant result from Table III is the high chain orientation produced at the point A. Also, an important increase of this orientation is produced far away from the particle.

This behavior suggests the presence of residual stresses produced during the extrusion process, which increase with the presence of the aggregates. Residual stresses and molecular orientation are two separate but highly interactive characteristics of extruded and molded polymers. Both are sensitive to processing conditions, and it is almost impossible to control one of them in a systematic fashion without changing the other. These stresses are partially concentrated in the matrix–aggregate interface in an asymmetric distribution and higher than in the iPP matrix. The thermal treatment increases the crystallinity and the residual

TABLE III
Intensity Ratio I_{973}/I_{997} from the Polarized Spectra at the A, B, and C Points of Figure 3 of the Nanocomposite Obtained by Melt Compression, Extrusion, and Both after Annealing

		23°C			160°C		
		A	B	C	A	B	C
	Polarization	I_{973}/I_{997}	I_{973}/I_{997}	I_{973}/I_{997}	I_{973}/I_{997}	I_{973}/I_{997}	I_{973}/I_{997}
PP+5% CaCO₃ melt compression	X(ZZ)X	1.0	1.1	1.0	1.1	1.1	1.0
	X(YY)X	1.1	1.1	1.1	1.0	1.1	0.9
		23°C			160°C		
		A	B	C	A	B	C
	Polarization	I_{973}/I_{997}	I_{973}/I_{997}	I_{973}/I_{997}	I_{973}/I_{997}	I_{973}/I_{997}	I_{973}/I_{997}
PP+5% CaCO₃ extrusion	X(ZZ)X	2.6	1.5	1.5	7.0	1.8	4.9
	X(YY)X	0.7	0.8	0.7	0.5	0.8	0.5

stresses orient the crystalline part in the extrusion direction.

CONCLUSIONS

Both nanocomposites of iPP with the presence of aggregates of $CaCO_3$ nanoparticles and iPP obtained by melt flow extrusion present a similar molecular orientation The presence of aggregates in a composite has as a consequence the apparition of residual stresses. A thermal treatment at 160°C for one hour to the nanocomposite produces a relaxation of the residual stresses, obtaining an important orientation of the polymer chain in the melt flow extrusion direction. Therefore, the production of nanocomposites in which the processing produces aggregates of nanoparticles will generate stress concentration on the interface and molecular orientation with anisotropic characteristics.

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