# Beta Phase Formation of Polypropylene with Bentonite Filler

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**Abstract**

In this paper, a study on Polypropylene (PP)/bentonite composites is presented. PP/bentonite composites were prepared using 5%, 10% and 25% of concentration in weight of unmodified and modified bentonite filler. The relative level of the beta phase of the samples was calculated using Wide Angle X-ray Diffraction (WAXD). Differential scanning calorimeter (DSC) was used to observe the melting and crystallization behaviour of the samples. The dispersion state of the composites was observed using optical microscopy. The obtained results show the possibility of inducing the beta phase in PP material using bentonite as filler. However, only the composites of polypropylene with modified bentonite showed the beta signal and higher content was at 10% of filler. Although at 10% of modified bentonite the dispersion is worse than in 5%, at 10% there are more nucleating sites for beta phase formation and consequently more beta content. However, as concentration of the filler increases to 25%, the nucleating sites also increase but its dispersion into the compound becomes worse which strongly decreases the beta phase formation.

**Keywords:** Composites, polypropylene, beta phase, bentonite, treated filler, dispersion state

## 1. Introduction

Fillers with size in the micron scale are still used in polymers for a variety of reasons such as cost reduction, improved processing conditions, density control, improve the electrical properties, flame retardants and for the improvement of mechanical properties (Svab et al. 2008; Meng and Dou 2008).
The most used fillers in thermoplastics are chalk, talcum, kaolin, mica and wollastonite. The choice of filler is based on the properties which are required for the intermediate or final product. Different properties of the final product are influenced by the composition, size, shape and structure of the chosen filler. The wollastonite has acicular structure (needle-like), chalk comprises irregular shaped particles, whereas the mica and talcum have platy or layered structures (Jarvela and Jarvela; 1996). Bentonite filler could be interesting filler by its large amounts in Mexico, and by its price lower than chalk, kaolin, mica and wollastonite respectively.

The polypropylene (PP) is the choice polymer for home appliances, packaging and automotive industry due to their mechanical properties, simplicity of processing, the ability to incorporate varied types of fillers, and its relative low cost (Tjong et al., 1997). It is well known that the PP exhibits several crystalline forms, namely the monoclinic alpha-phase, the hexagonal beta-phase and the orthorhombic gamma-phase (Keith et al., 1959; Meille et al., 1990; Bruckner and Meille, 1989). Among all crystal structures, the alpha-phase, obtained under ordinary industrial processing conditions, is the most stable. The presence of beta-phase improves properties of PP, such as increasing the impact strength and the elongation at break (McGenity et al., 1992; Tjong et al., 1996; Tjong et al., 1997).

It has been shown that the beta phase of polypropylene could be formed under specific conditions, e.g., by shear forces in the melt (Dragaun et al., 1977), by temperature gradient (Crissman, 1969), and in presence of a special nucleator (Jacoby et al., 1986), and by using fillers Liu et al. (1990).

Some filler have been reported to induce beta phase of polypropylene, i.e.: Liu et al. (1990) have studied compounds of a copolymer of ethylene-propylene with wollastonite. These authors detected beta phase of polypropylene in the copolymer induced by the incorporation of wollastonite. Smit et al. (2004) have studied ternary PP/EPDM/wollastonite composites, and binary PP/wollastonite composites with a content of filler from 2 to 6 vol. % and reported the beta phase content of PP in these compounds.

McGenity et al. (1992), Labour et al. (2001) and Lozano et al. (2004) have studied some properties of polypropylene/calcium carbonate compounds and beta phase formation of polypropylene was found.

However, to our knowledge, no study has been made concerning the formation of beta phase of polypropylene using bentonite filler. Therefore, in this paper, a study the on PP/bentonite composite is presented.

## 2. Experimental

### 2.1 Materials and sample preparations

The materials used in this study were a polypropylene (PP) isotactic (Valtec trademark, HG009) supplied by Indelpro, Mexico and Bentonite mineral provided by BARMEX Mexico which was used as a filler. The mean diameter of the filler was 5 $\mu$m and the specific surface area was $12m^2/g$.
Modified filler was prepared using the following stearic acid procedures proposed by Tabtiang and Venables (1999). The dried bentonite was loaded into the chamber of the Henschel blender with the stearic acid. The mixing was initiated at low speed of 1400rpm during 5 min and then increased to the high speed of 2800rpm for 15 min and in this speed the temperature of the blending was kept at 75 °C. Finally, the chamber was cooled up to 40 °C at low speed. Coated filler was stored at room temperature in desiccators until their used.

PP/bentonite compounds were prepared using 5%, 10% and 25 % concentration of unmodified and modified bentonite filler, based on a total sample weight of 230g. Each sample was mixed during a time period of 12 minutes using a Brabender internal mixer (DDRV-502 type) with a rotation speed of 50 RPM and a chamber temperature of 200ºC. A 0.2% concentration of antioxidant Irganox B225 from Ciba-Geigy was added to all samples in order to prevent thermal degradation of the polymer during the mixing process.

### 2.2 Thermal analysis

A Perkin Elmer Diamond differential scanning calorimeter was used to observe the crystallization temperatures of the samples. The samples obtained directly from the mixing chamber were heated from 50 to 200ºC and then cooled to the initial temperature. Both heating and cooling processes were conducted at a scanning rate of 10ºC/min. The endothermic and the exothermic peaks were taken as the melting and crystallization temperature respectively.

### 2.3 Wide angle X-ray diffraction (WAXD)

The X-ray diffraction technique was used to quantify the relative level of the beta phase of polypropylene with the modified and unmodified bentonite. A Philips X-pert diffractometer with CuK$_\alpha$ radiation at room temperature was used to collect the corresponding X-ray diffraction patterns. Radial scans of intensity vs. diffraction angle (2$\theta$) were recorded ranging from 5° to 35°. The analysis was carried out directly on the flat part and smooth of the samples obtained directly from the mixing chamber.

### 2.4 Dispersion state

In order to characterize the dispersion state of the samples, thin films of approximately 50 $\mu$m thicknesses of the PP/bentonite composites were prepared using compression molding at 200ºC. The dispersion state of the composites was observed on the thin films using a JENCO optical microscope.

## 3. Results and Discussion

The melting behavior for the polypropylene samples and composites samples of polypropylene with unmodified and modified bentonite, are presented in Figures 1 and 2 respectively. In these behaviours, the transition between 144 and 152°C corresponds to the melting of the beta phase and transition between 158 and 166°C to the melting of alpha phase crystallites of PP (Liu et al., 1990; Jacoby et al., 1986; Tjong et al., 1996b). It can be seen that the compounds with unmodified bentonite shows a slightly beta phase signal only for samples with 10% of bentonite (see Figure 1), whereas the compounds with modified bentonite all the samples exhibits beta phase signal (see Figure 2). These behaviours clearly confirm that the used modified bentonite as filler in PP compounds increases the amount of beta phase.
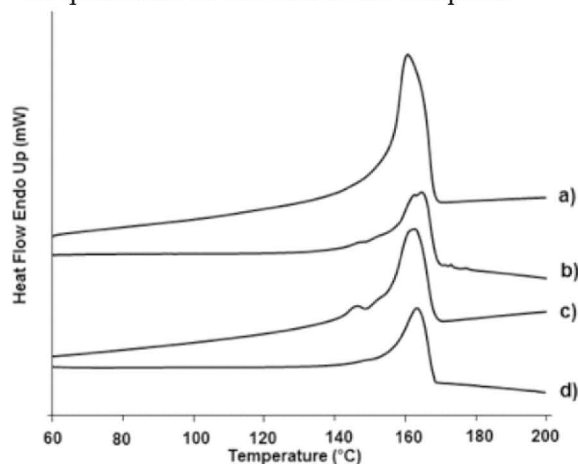


**Figure 1.** The melting behavior for the polypropylene samples and composites samples of polypropylene/unmodified bentonite: a) PP, b) PP/bentonite 95/5, c) PP/bentonite 90/10 and d) 75/25 PP/bentonite 75/25.
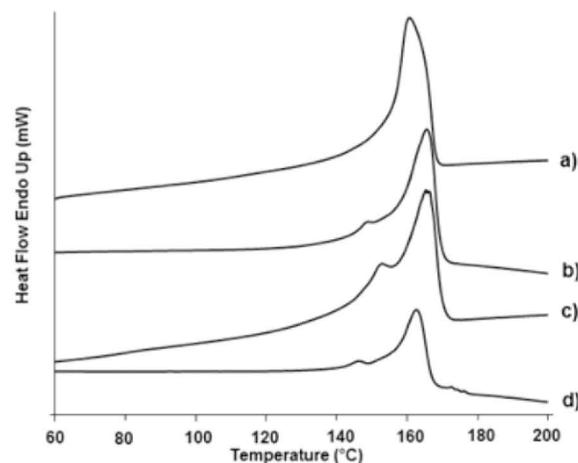


**Figure 2.** The melting behavior for the polypropylene samples and composites samples of polypropylene/modified bentonite: a) PP, b) PP/treated bentonite 95/5, c) PP/ treated bentonite 90/10 and d) 75/25 PP/ treated bentonite 75/25.

To quantify the relative level of beta phase in PP/bentonite samples, the X-ray technique was used. Figures 3 and 4 show the WAXD patterns for the composites samples of polypropylene with unmodified and modified bentonite, respectively. The ordinary PP shows the diffraction peaks at the 2θ angles of 14.1°, 16.9° and 18.5° corresponding to the crystal planes (110), (040) and (130) respectively. The beta crystalline form is known to exhibit a strong peak at a 2θ angle of 16° corresponding to the crystal plane (300) (Turner-Jones et al., 1964; Samuels and Yee, 1972).
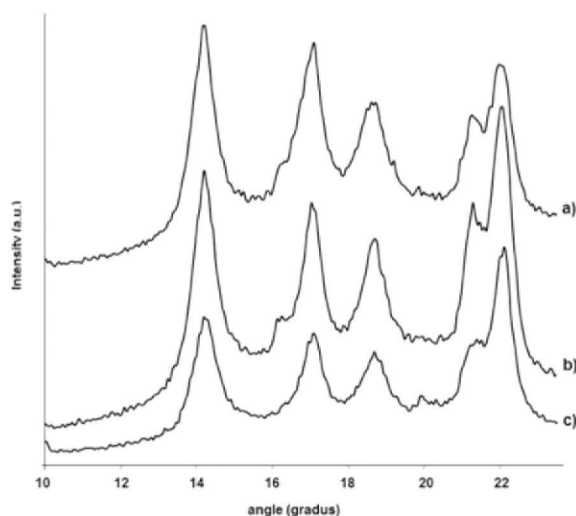


**Figure 3.** The WAXD patterns for the composites samples of polypropylene with unmodified bentonite: a) PP/bentonite 95/5, b) PP/bentonite 90/10 and c) 75/25 PP/bentonite 75/25.
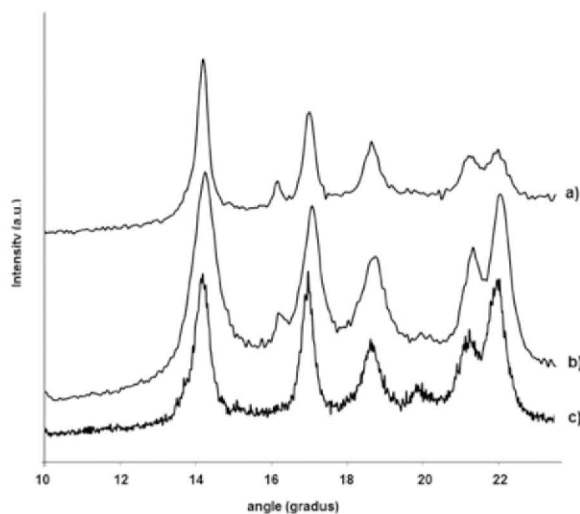


**Figure 4.** The WAXD patterns for the composites samples of polypropylene with modified bentonite: a) PP/treated bentonite 95/5, b) PP/ treated bentonite 90/10 and c) 75/25 PP/ treated bentonite 75/25

The relative amount of the beta phase is usually described in terms of the K value, which is defined by the following relation (Turner Jones et al., 1964):

$$K = H_\beta / [H_\beta + (H_{\alpha1} + H_{\alpha2} + H_{\alpha3})]$$

where $H_\beta$ is the height of the strong single β-form peak (300), and $H\alpha_1$, $H\alpha_2$, and $H\alpha_3$ are the heights of the three strong equatorial α-form peaks (110), (040) and (130), respectively. The obtained K values are present in Table 1.

**Table 1.** The obtained K values in percent.

| (% PP / % bentonite) | K value | |
| --- | --- | --- |
| | Unmodified bentonite | Modified bentonite |
| 95/5 | – – – | 13.64 % |
| 90/10 | – – – | 14.47 % |
| 75/25 | – – – | – – – |

The beta signal in WAXD patterns for the composites samples of polypropylene with unmodified bentonite it is not well defined therefore is impossible to calculate their content. Nevertheless, the composites samples of polypropylene with modified bentonite the beta signal it is clearly defined for the samples with 5% and 10% of bentonite and is absent for the compounds with 25% of bentonite. However, the beta content obtained for the sample with 10% of modified bentonite was higher than for the sample with 5% of modified bentonite (see table 1). At 10% there are more nucleating sites (more amount of filler particles) for beta phase formation and consequently more beta content.

Figure 5, 6 and 7 show micrographs of the composites samples with 5%, 10% and 25% of bentonite respectively. From these figures can be observed that as the concentration of the filler increases, its dispersion into the compound becomes worse. However, the samples with modified bentonite showed smaller agglomerations for all concentrations of the filler.

Rybnikar (1989) has studied crystallization of polypropylene filled with talc particles at various concentrations of the filler. He found that only a small fraction of the filler act as nucleator and there is a certain limit of concentration of the filler to reduce the spherulite size. On the other hand, Labour (2002) and Lozano et al. (2004) have reported that beta phase of PP is favored with a good dispersion state of the filler.

Therefore, from our results we can enface that at 10 % of filler there are more nucleating sites for PP than at 5% and consequently more beta level. However at

25% would have more sites but their dispersion into the compound becomes worse which decreases the beta phase formation.
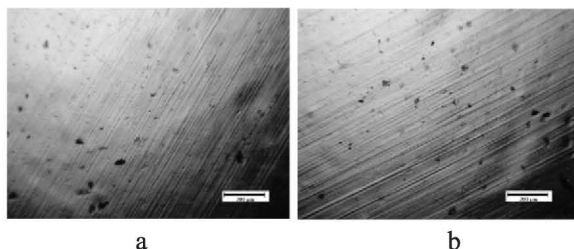


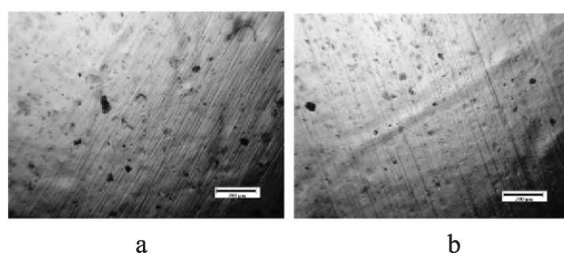**Figure 5.** Micrographs of the composites samples with 5 % of a-unmodified and b-modified bentonite.



**Figure 6.** Micrographs of the composites samples with 10 % of a-unmodified and b-modified bentonite.
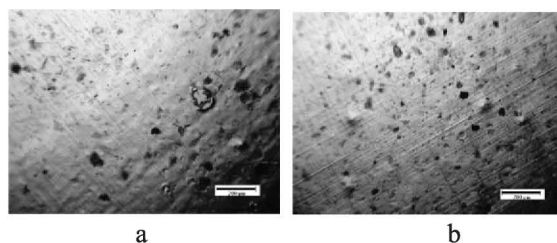


**Figure 7.** Micrographs of the composites samples with 25 % of a-unmodified and b-modified bentonite.

## 4. CONCLUSIONS

In the present work the beta phase induction in PP was achieved using bentonite as filler. However, only the composites samples of polypropylene with modified bentonite showed the beta signal. The beta content obtained for the sample with 10% of modified bentonite was higher than for the sample with 5% of modified bentonite. This behaviour was related with concentration of the filler and it can be shown that as the concentration of the filler increases, its dispersion into the compound becomes worse However, our results we can enface that at 10 % of filler there are more nucleating sites for PP than at 5% and consequently more beta level. Although at 25% would have more sites, their dispersion into the compound becomes worse which decreases the beta phase formation.

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