

# Characterization of crystalline and amorphous regions of HMSPP films.

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The introduction of long chain branching and/or some crosslinking into isotactic polypropylene (iPP) backbone changes drastically its melt properties. Rheological properties of the melt are strongly affected by molar mass and distribution of molar mass, and the presence of long-chain branching or crosslinking. This characteristic enhances the density of entanglement, changing the elongational flow of polymer melts which play an important role in many processing operations like film blowing and thermoforming. Therefore, several approaches have been developed to make branching and modified polypropylenes. High melt strength polypropylene (HMSPP) is one of the new materials that exhibit these properties.

It is now established that long-chain molecules can crystallize into a two-phase structure: periodic arrangement of crystalline lamellae and amorphous interlayer. Whether, short and long branching is incorporated into polypropylene chain, how the influence of these changes in the morphology of HMSPP films? The morphology of HMSPP films processed by thermopressing, are being analyzed by sorption measurements and differential scanning calorimetry (DSC). The differences observed at the HMSPP films in the solvent uptake percentage and crystallinity can be attributed to formation of a structure more reticulate.

## Introduction

Isotactic polypropylene (iPP) has been a broad study in the last years due to the desirable and beneficial physical properties such as high stiffness, resistance to corrosive chemicals and low specific gravity. However, commercial polypropylene is a linear polymer, which has relatively low melt strength and exhibits no strain hardening behavior in the melt state [1]. These limits difficult their uses in applications like thermoforming, foaming and blow molding. Therefore, the high melt strength polypropylene (HMSPP) has been developed and put in the market. HMSPP has substantially different rheological characteristics compared to conventional polypropylene resins and opens up new opportunities for PP in the other applicative fields.

Besides the Montell and its predecessor Himont many technologies are being researched and reported to produce HMSPP [2]. In the majority technology the high energy radiation (gamma or electron beam) and different multifunctional monomers have been used to obtain this material [3-8]. Another way is by reaction extrusion in which the peroxides and monomers are added [9].

It's well known to establish the rheological behavior of the HMSPP obtained by these processes, nevertheless

there are so few articles about the morphology of these samples.

The morphology of polymer films can be accessed through several techniques such as x-ray diffraction, differential scanning calorimetry, optical microscopy among others. The properties of transport permit also to obtain some information on the morphology of a sample. The sorption and / or diffusion of a solvent depend on the paths available for solvent to dissolve in the matrix. Crystalline regions tend to be impermeable to solvent, thereby; the percentage of solvent absorbed through polymer is an important result in the assessment of the morphology of the sample [10]. Michelle and Vittoria [11] and Bove et al [12], analyzed samples of PEEK and PET with different stories of processing (physical aged and renewed samples), the results show the changes in the coefficient of diffusion with the equilibrium concentration. Thermodynamic parameters could be found from these data and showed difference in the free volume fraction of the two samples. D'Aniello et al. [10] realized a similar study in blends of Polypropylene atactic and isotactic. The samples were produced with crystallinity varied in the range of 20 to 75%. In this work transport measurements results detected the differences in the crystallinity of the samples mainly for values above 50%, due to the

tortuous path promoted by the presence of impermeable crystals.

The evaluation of the results of sorption can be complex for systems that have a high degree of order two-dimensional with the formation of distinct phase of the crystalline material, but which have sufficient order to serve as impediment to sorption of the solvent at least in low activity.

In order to initiate a study of the HMSPP films morphology, the sorption measurements have been used to evaluate and understand the behavior of these samples. HMSPP is being obtained by irradiation with gamma rays from polypropylene resins in the presence of different kinds of multifunctional monomers such as Ethylene glycol dimethacrylate (EGDMA), Tri-allyl-cyanurate (TAC), Tri-allyl-isocyanurate (TAIC) and Trimethylol-propane trimethacrylate (TMPTMA). In the sorption measurements polymer/solvent system in activity one was analyzed in this work. This condition had been determined through polymer solvent uptake in saturation. These results were correlated with differential scanning calorimetry (DSC) curves. On the other hand crystalline and amorphous regions of these samples were speculated.

## Experimental

### Material and sample preparation

The isotactic polypropylene (iPP) homopolymer used in this study was a reactor grade from Braskem in the sphere form, with a melt flow index (MFI) of 1.5 g min<sup>-1</sup> at 230°C.

EGDMA, TAC, TAIC and TMPTMA, at a concentration of 1.5 mmol/100g of iPP were mixed at room temperature to produce each samples of HMSPP. After mixed the samples were extruded in a twin-screw extruder Haake with a die diameter of 2mm. The extruder polymer strand was cooled at room temperature and was being cut. After that, all samples were irradiated with gamma radiation (<sup>60</sup>Co) at a dose of 20kGy under nitrogen gas atmosphere, using the source from Embrarad with a dose rate of 10kGy h<sup>-1</sup> and the dosimetry was performed with Harwell Red Perspex 4034.

HMSPP films were been obtained by thermopressing at processing temperature of 190°C, cooling into water bath at room temperature and finally prepared to sorption measurement.

### Sorption Experiments

Dried disc-shaped HMSPP were weight before sorption measurements. The samples were placed in screw-tight test bottles containing about 15 to 20ml of dichromethane. Samples were removed periodically; the surface adhered at the liquid is being dried by carefully pressing the samples between filter paper wraps and weighed it up on a digital Shimadzu to an accuracy of ± 0.01mg. The samples attained

equilibrium saturation generally within 1 h and these did not change over a further immersion period of 1 or 2 days. The percent weight gain (%wt) during solvent sorption was calculated as:

$$\% \text{ wt gain}(t) = [(wt - w_0)/w_0] \times 100 \quad (1)$$

where wt is weight of polymer sample after time t and w<sub>0</sub> is initial weight of the sample.

### DSC measurements

Differential scanning calorimetry (DSC) was carried out over the temperature range 30 to 250°C, using a Rheometric Scientific DSC SP. The samples were sealed in aluminum pans with lids and purged with ultra-pure dry nitrogen at a flow rate of 20 mL/min. Runs were conducted at a heating rate of 20°C/min.

## Results and Discussion

Sample of iPP/Taic exhibited result of melt strength around the 50% higher than pure iPP. In the cases of iPP/Tac and iPP/Tmptma all around of 18% and for iPP/Egdma 5% lower in comparison of pure iPP. Nevertheless, all samples are being showed by other results like as complex viscosity at the low frequency and gel fraction rheological and structural changes.

From the above results it can be supposed a change in the chemical structure of main chain polypropylene through the reaction occurs during the radiation process. Therefore, probably the morphology will be affected in relation of the amorphous and crystalline regions.

Sorption curves are obtained by fitting the weight gain results in the following empirical relationship:

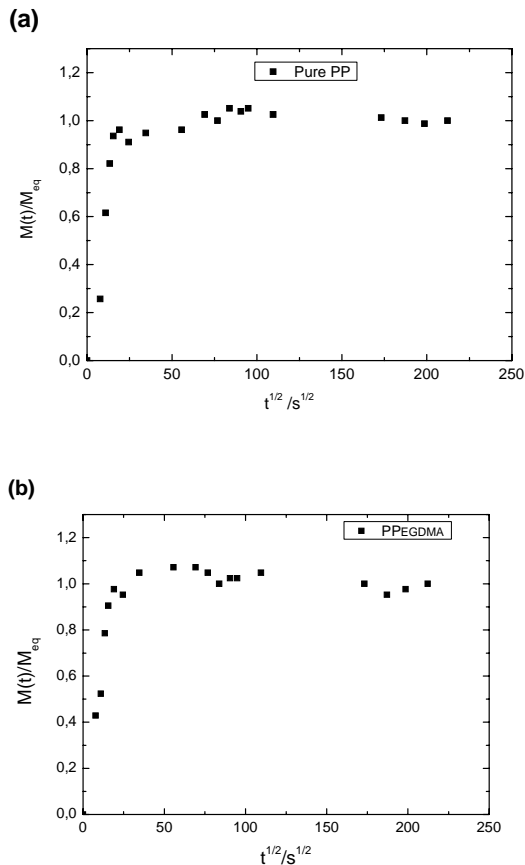
$$M(t)/M_{eq} = Kt^{1/2} \quad (2)$$

where M(t) and M<sub>eq</sub> refer to weights of solvent uptake at time t and in an equilibrium region; K is an empirical parameter depending on the structural characteristics of polymer and getting onto liquid-polymer interactions. The curves for pure iPP and iPP/Egdma mixture are shown in Figure 1.

The curves showed an increase of the weight uptake linear with the square root of time and a curvature to reach a value of solvent saturation. The small variation observed of M(t)/M<sub>eq</sub> values above one in figure 1(b) can be interpreted as a possible release of monomers that did not react with polypropylene to promoted crosslink or possible morphological changes at the polymer in the presence of solvent in activity one. However the later seems more unlikely since the kinetics sorption curve for PP original does not present this type of phenomenon. Moreover the sorption has been started latter than pure iPP (0.4 to 0.27 of the

$M(t)/M_{eq}$ . This means likely the existence of impermeable structure.

It's an interesting result since it is possible to evaluate the result of solvent uptake in equilibrium as information about the original morphology of the polymers after processing without consideration about structural changes due solvent sorption in high activity.



**Figure 1** - Sorption curves at 25°C for pure iPP (a) and iPP/Egdma (b).

The sorption curves for iPP/Taic, iPP/Tac and iPP/Tmptma showed the same behavior in the case of iPP/Egdma.

**Table 1** – Equilibrium sorption values (wt%) for several HMSPP films obtained with different kinds of monomers in dichloromethane at 25°C.

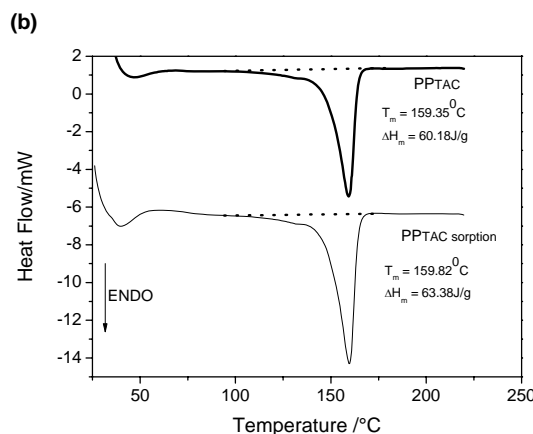
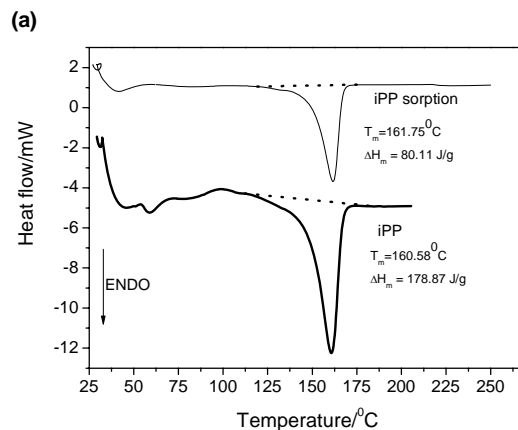
Samples	wt%
Pure PP	12.5
iPP/Egdma	8.3
iPP/Tac	11.4
iPP/Taic	9.1
iPP/Tmptma	9.3

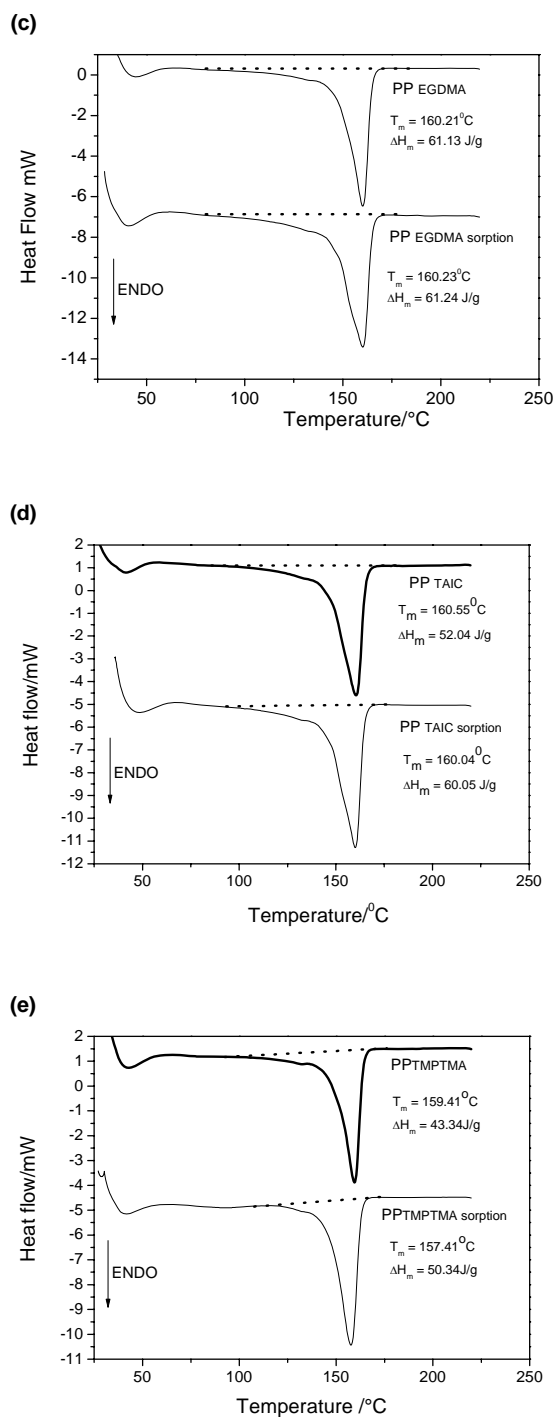
Table 1 presents the data for solvent uptake percentage for evaluated HMSPP films. It is possible to observe that the iPP unmodified (original) show higher solvent

uptake than iPP modified by monomers except in the case of iPP/Tac. This fact can be associated to differences in the samples related to crystallinity and/or crosslink including little branching degree achieved with the addition of monomers in the processing of the polymers. For iPP/Tac the high value of solvent weight is probably due to micro-holes or cracks.

The way of solvent go beyond the polymers films detect differences related to crystallinity which is impermeable to solvent and due the value observe in Table 1, the sorption result seems sensible to morphological modifications related to crosslink promoted by irradiated of samples with the monomers. The sorption results should be evaluated in correlation with DSC results.

The DSC curves can be observed in figures 2 for iPP unmodified (a) and iPP modified figures 2(b), 2(c), 2(d) and 2(e).

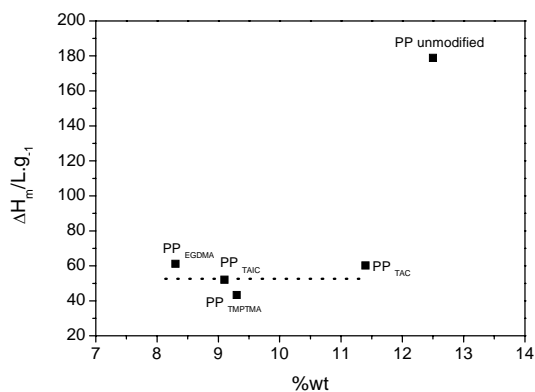




**Figure 2** – DSC curves for iPP samples: iPP unmodified (a), iPP/Tac (b), iPP/Egdma (c), iPP/Taic (d) and iPP/Tmptma (e).

From the DSC curves can be observed that fusion enthalpy of polypropylene decreases in a meaningful way with the addition of monomers. This result was already expected since the crosslink should occur and increase the disorganization of the polymer. Another important point observed is the decrease in fusion enthalpy of iPP unmodified after the process of

sorption. This fact can be attributed to the effect of plasticization promoted by the presence of the solvent. It is important to highlight that change does not occur significantly to the samples modified with monomers. This indicates that the solvent does not change the morphology of these samples significantly during sorption. It's important because the result obtained by this technique can be related to original morphology. The correlation between DSC measurements and sorption solvent uptake can be observed in figure 3. It can be observed that the sample which presents higher solvent uptake in equilibrium is also that presents the greatest melting endotherm showing the most crystalline sample. This result seems contradictory since should reflect the difficulty in the process of diffusion due to the hindrance caused by crystalline structures. However, the measure of sorption can also detect other types of morphological structures of the system. So it is not strange that the samples with lower degree of crystallinity (samples modified with monomers) present wt% results lower than the sample iPP unmodified, mainly the samples where monomers TAIC, TMPTMA and EGDMA were used.



**Figure 3** - Correlation between fusion enthalpy obtained by DSC techniques and wt(%) obtained by sorption.

The differences observed can be seen related to crystallinity of the samples but mainly due to formation of a structure more reticulate. Thus the decrease in percentage solvent sorption particularly for iPP/EGDMA sample can be attributed to growing presence of crosslinking leading to a two-dimensional spatial structure that can be detected by the results of sorption. This fact could be seen in the results and will be better investigated using measures of sorption held in low activity of the solvent.

## Conclusions

HMSPP films obtained by irradiation process with different multifunctional monomers are being investigated by sorption measurement presented

distinct amorphous and crystalline regions. All modified samples of iPP showed lower solvent uptake percentage in comparison with pure iPP.

EgDMA was more effective in reacting with iPP showing lower wt% followed by Taic and Tmptma. These results were corroborated through crystalline results. Nonetheless these samples should be better investigated in low activity.

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### References

1. J. Tian, W. Yu, C. Zhou. *Polymer*. 2006, 47, 7962.
2. P. Galli, G. Vecellio. *Prog. Polym. Sci.* 2001, 26, 1287.
3. M. Rätzsch, M. Arnold, E. Borsig, H. Bucka, N. Reichelt *Prog. Polym. Sci.* 2002, 27, 1195.
4. T. M. Ojeda, S. Tokumoto, A. L. D. Bracana, L. F. Cassinelli, A. B. Lugão, B. W. H. Artel. USP 20.040.171.712, 2004.
5. A.B. Lugão, H. Otaguro, D.F. Parra, A. Yoshiga, L.F.C.P. Lima, B.W.H. Artel and S. Liberman. *Rad. Phys. Chem.* 2007, 76, 1688.
6. A.B. Lugão, B.W.H. Artel, A. Yoshiga, L.F.C.P. Lima, D.F. Parra, J.R. Bueno, S. Liberman, M. Farrah, W.R. Terçariol, H. Otaguro. *Rad. Phys. Chem.* 2007, 76, 1691.
7. H. Otaguro, S. O. Rogero, A. Yoshiga, L. F.C.P.Lima, D. F. Parra, B. W. H. Artel, A. B. Lugão. *Nuclear Instruments Methods Phys. Research B.* 2007, 265, 232.
8. J. Vega, M. Aguilar, J. Peón, D. Pastor, J. Martinez-Salazar. 2002, 46, 1.
9. G. Moad. *Progress in Polymer Science.* 1999, 24, 81.
10. C. D'aniello, G. Gorrasi, L. Guadagno, V. Vittoria. *Polymer*, 2000, 41, 2515.
11. A. Michele, V. Vittoria. *Polymer*, 1993, 34, 1898.
12. L. Bove, C. D'aniello, G. Gorrasi, L. Guadagno, V. Vittoria, *Polymer*. 1996, 37, 5309.