

# IMPREGNATION OF PET FILMS AND PHB GRANULES WITH CURCUMIN IN SUPERCRITICAL CO<sub>2</sub>

L. C. S. Herek<sup>1</sup>, R. C. Oliveira<sup>1</sup>, A. F. Rubira<sup>2</sup> and N. Pinheiro<sup>1\*</sup>

<sup>1</sup>Universidade Estadual de Maringá, Depto. de Engenharia Química, Bloco D-90,  
Av. Colombo 5790, Zona 07, CEP: 87020-900 Maringá - PR, Brazil  
E-mail: nanci@deq.uem.br

<sup>2</sup>Universidade Estadual de Maringá - Depto. de Química,  
Av. Colombo 5790, Zona 07, CEP: 87020-900 Maringá - PR, Brazil.

(Received: October 20, 2004 ; Accepted: February 8, 2006)

**Abstract** - The process of dyeing poly(ethylene terephthalate) - PET films at 50, 60 and 65°C and poly(hydroxybutyrate) - PHB granules at 60, 70 and 80°C using supercritical carbon dioxide (scCO<sub>2</sub>) as solvent and ethanol as cosolvent was studied by DSC, TGA analysis and measurements of shrinkage to determine the morphological modifications caused by the scCO<sub>2</sub> treatment of these materials. A comparison of the effects of annealing both polymers in scCO<sub>2</sub> provided evidence that PHB had plasticization activity due to its crystallinity and that PET favored the dyeing process at high pressure when its temperature was raised to close to the T<sub>g</sub> value. DSC and TGA measurements were obtained for all the samples. The DSC results showed that there was no significant structural change and the TGA data showed that thermal stability was not affected in the samples analyzed.

**Keywords:** Supercritical CO<sub>2</sub>; PET films.

## INTRODUCTION

Researchers have directed their attention to the process of dyeing polymeric materials with supercritical fluids, popularly known as the green process. The conventional process of dyeing PET fiber produces wastewater contaminated by many kinds of dispersing agents, surfactants and unused dye. The technique of dyeing with supercritical fluids, an alternative that does not contaminate the environment, has been under development since the early 1990s. Poly(ethylene terephthalate) - PET is the most important polyester with a variety of applications, from textile fibers to bottles for carbonated beverages and for photographic film packaging and automobile components. Studies have recently been published on the dyeing of polymers, especially polyesters (Beltrame et al., 1998; De

Giorgi, et al., 2000). According to Stinson and Obendorf (1996), PET absorbs only 0.4% of the water and does not swell in water. This lack of interaction between PET and the aqueous dye bath requires the use of either high-temperature or a high-pressure system in a dyeing with disperse dyes or natural pigments. Santos et al. (2000; 2001) studied the effects of modifying agents and dyeing conditions of dispersed dyes and azo dyes on PET films and fibers. These researchers reported on the process of incorporating dye in unmodified and N,N-dimethylacrylamide - modified PET fibers with scCO<sub>2</sub>. However, the sorption of natural pigments by PET films with scCO<sub>2</sub> at elevated pressures (>10MPa) and temperatures (>50°C) are not very well understood and further research is still necessary.

Poly(hydroxybutyrate) - PHB, which is a bacterially produced thermoplastic polyester with

\*To whom correspondence should be addressed

considerable potential for use in situations where biodegradability or biocompatibility are required – offers an attractive alternative to the disposal of plastics in the environment (Agnelli et al., 1999; Simielle, 1993). PHB is a semicrystalline material with a highly crystalline content and a fairly high melting temperature of around 177°C, at which the polymer degrades quickly (Iriondo et al., 1995). Its chemical resistance is somewhat limited as it is attacked by acids and alkalis and dissolved in chlorinated solvents. Some of the undesirable properties can be modified by copolymerization of hydroxybutyrate (HB) with hydroxyvalerate (HV) units. Increasing the HV content reduces the melting temperature and crystallinity, making the polymer more processable (Avella and Martuscelli, 1988; Kumagai and Doi, 1992; Pearce et al., 1992; Abe et al., 1994; Godbole et al., 2003).

Supercritical carbon dioxide (scCO<sub>2</sub>) has been shown to have very high solubility in many polymers, similar to those of organic solvents show a swelling action. Moreover, it is able to induce a decrease in the glass transition temperature (T<sub>g</sub>) of polymers such as poly(methyl methacrylate) and its blends with poly(vinylidene fluoride) (Chiou et al., 1985). These properties of scCO<sub>2</sub> support its use as a temporary plasticizer in order to facilitate the uptake of additives (Berens et al., 1992), flavoring agents and dyes in several polymers. Distribution or partitioning of a solute between scCO<sub>2</sub> and the polymer as a stationary phase occurs in cosolvent–modified supercritical chromatography. The addition of small quantities of cosolvent to the scCO<sub>2</sub> mobile phase in SCF usually improves the applicability of SFC in more polar analytes. However, adsorption of cosolvent in the polymeric stationary phase will significantly affect the retention of a solute and thus the thermodynamic properties measured by SFC (Kazarian et al., 1998).

In this paper, the impregnation of PET films and PHB granules with curcumin under different conditions of temperature, pressure and time was studied by using supercritical carbon dioxide with ethanol as cosolvent. Factorial designs were used to assess the effects of these variables on the impregnation of PET and PHB and DSC and TGA techniques were used to analyze occasional changes in the structure and properties of the PET and PHB.

Curcumin obtained from rhizomes of *Curcuma longa* is one of the main pigments produced in Brazil (Manzan et al., 2003). Besides the yellow pigment for food, this plant is widely used as a seasoning. Mature rhizomes are ground to give an aromatic yellow powder, employed as the coloring ingredient

in curry powder. With the growing demand for natural colors, the use of turmeric is likely to increase.

## MATERIAL AND METHODS

### Raw Materials

The PHB granules used were obtained from PHB Industrial S/A (Brazil). The average molecular weights, as determined by gel permeation chromatography in chloroform at room temperature, were M<sub>w</sub> ≅ 200,000. The particle size distribution of the PHB granules was determined using sieves of the Tyler series (35 and 48 mesh) or their corresponding metric units (0.417 and 0.297mm) and an agitator (Belter, Piracicaba, Brazil). The physical characteristics were the following: (i) appearance: yellow/white solid; (ii) odor: mild; (iii) melting point: ≅ 170°C and (iv) solubility in water: negligible.

The commercial samples of PET films (thickness of 100µm) were kindly supplied by COCAMAR, Maringá, Brazil and the PET samples were cleaned prior to use with analysis grade ethyl alcohol (Nuclear)<sup>®</sup>.

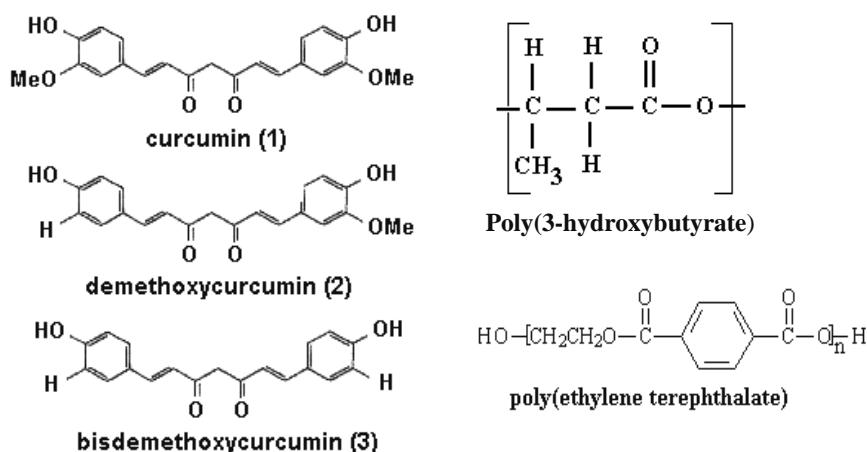
Pure standard curcumin, indexed under no. 75300, E-100 (Takahashi & Nazário, 1987), was acquired from Sigma-Aldrich Chemical Representações Ltda (São Paulo, Brazil). Demethoxycurcumin and bisdemethoxycurcumin, homologues of curcumin, are sold together and have the same coloring capacity (Sanagi and Ahmad, 1993).

CO<sub>2</sub> liquefied at a high pressure (White Martins)<sup>®</sup> served with solvent. Analysis grade N,N-dimethylformamide (Induslab, Araçongas, Brazil) was also used to extract the pigment from the film after dyeing. The solvent (modifier) was analysis grade ethanol (Induslab, Araçongas, Brazil).

In Figure 1 the PET, PHB and three curcuminoid structures are shown.

### Factorial Design

The factorial design was developed and the parameters of the supercritical CO<sub>2</sub>-aided dye sorption on (i) the PHB granules were pressure (P) at five levels (14, 18, 22, 26 and 30MPa) and temperature (T) at three levels (60, 70 and 80°C) and on (ii) the PET films were pressure (P) at three levels (16, 21 and 26MPa), time (t) at two levels (2 and 8 hours) and temperature (T) at three levels (50, 60 and 65°C).



**Figure 1:** Structures of the Poly(3-hydroxybutyrate), Poly(ethylene terephthalate) and of the three curcuminoids (1. curcumin; 2. demethoxycurcumin; 3. bisdemethoxycurcumin).

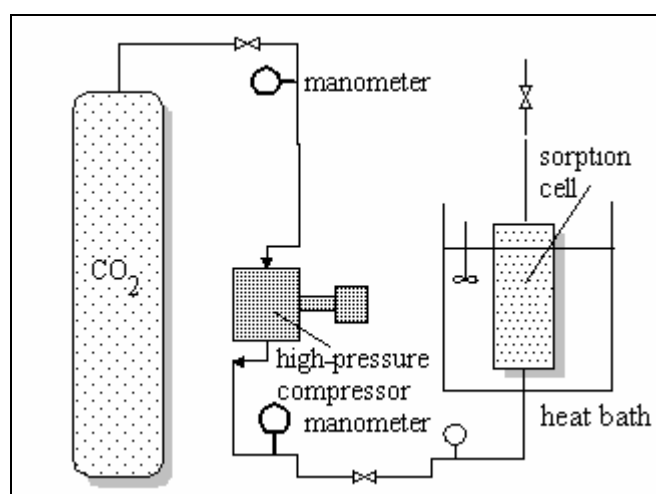
### Procedures

The experiments were performed in a module of supercritical sorption in a static process using commercial CO<sub>2</sub>, which was compressed until the required pressure was obtained with a high-pressure compressor. The infusion cell was immersed in a heat bath, maintained at the required temperature. The PET film-dye and PHB granule-dye-cosolvent systems were placed inside the sorption cell with scCO<sub>2</sub>, as shown in Figure 2.

A factorial design was used for the purpose of analyzing the effect of each variable under study on the process of the dye incorporation as well as the effects of interaction between them (i) 18 samples of

PET films were precisely weighed, washed with ethanol and water and then dried; (ii) 15 samples of PHB granules of 35 and 48 mesh sizes and 1 mL of ethanol as cosolvent were used.

In each experiment, the sample placed inside the sorption cell had an amount of dye that was 2% of the weight in relation to the mass of the PET film or PHB granules. The amount of dye greatly exceeded the average pigment solubility in supercritical CO<sub>2</sub>. The system was heated to the desired temperature and then it was pressurized, maintaining the static system. After being submitted to the procedures of dyeing in scCO<sub>2</sub>, the concentrations of pigment absorbed by PHB and PET were measured spectrophotometrically.



**Figure 2:** Scheme of supercritical impregnation equipment scheme

## Measurements

The amount of curcumin absorbed on (i) the PHB granules with ethanol was measured at 60°C in two steps of 45 min each, using 5 mL in each step, under constant stirring and on (ii) PET films the dye was extracted in 5mL of N,N dimethylformamide at 85°C, under stirring for about 1 hour. The samples were read by spectroscopy UV-VIS (spectrophotometer Shimadzu UV1203) at 425 nm.

Differential scanning calorimetry (DSC) measurements were obtained to determine melting temperature of PHB before and after impregnation. The thermogravimetric (TGA) analyses were performed to verify the thermal stability of the polymer. The DSC and TGA measurements were obtained using Shimadzu equipment, model 50.

## RESULTS AND DISCUSSION

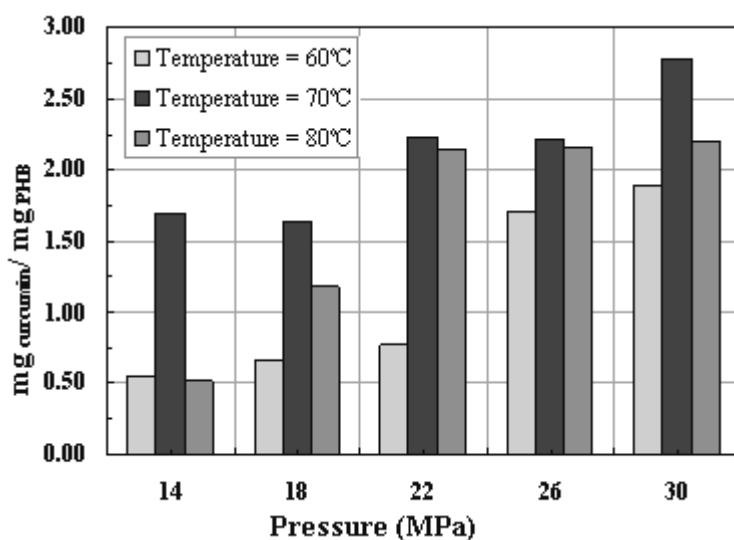
The amount of curcumin incorporated into PHB at three different temperatures as a function of pressure is shown in Figure 3. As can be observed, the increase in pressure at all temperatures, resulted in an increase in the impregnation of PHB with curcumin as well as the mass transfer rate, except at 70°C and 14 and 26MPa. The decrease in impregnation and absorption at these pressures can probably be attributed to changes in the isolated ordered chain to short-range changes in PHB crystallinity. These results are in accordance with the data on other systems in which a semicrystalline

polymer is annealed by plasticization with CO<sub>2</sub>, thereby allowing polymer chains to reorient to more thermodynamically favorable positions, forming crystallites (Lambert & Paulaitis, 1991; Santos et al., 2000). At 80°C equilibrium was obtained at 22MPa, while at 60°C and 70°C, equilibrium was not reached. Comparing the experimental data in Figure 3, a retrograde condensation can be observed because there was a considerable increase in impregnation at 70°C. On the other hand, the impregnation of PHB with curcumin was increased by use of a cosolvent (ethanol) at 60, 70 and 80°C.

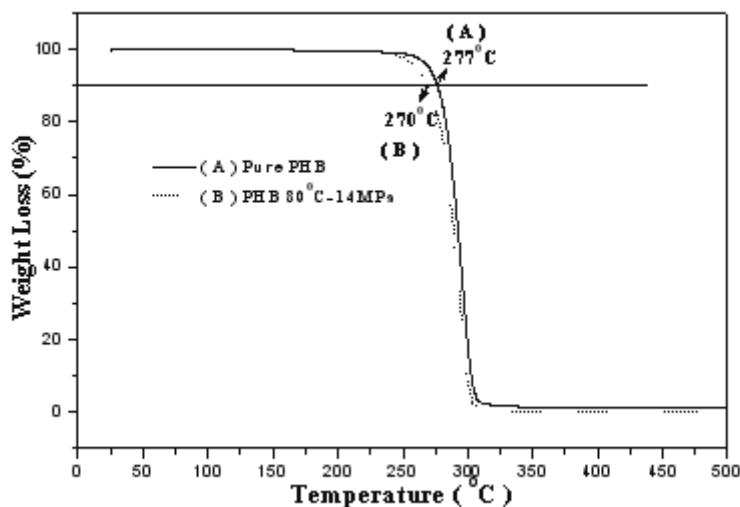
A statistical analysis was conducted using impregnation of PHB as the response variable. The results showed that pressure (P) and temperature (T) exerted significant effects on impregnation ( $p=0.0031$ ,  $p=0.0025$ , respectively). Impregnation was not affected by the interaction between P and T.

The decomposition temperature at a 10% level determined by thermogravimetric (TGA) analysis for pure PHB and PHB dyed in scCO<sub>2</sub> at 70°C and 22MPa are 277 and 270°C, respectively (Figure 4). This is evidence that the dyeing process does not alter the thermal stability of the polymer.

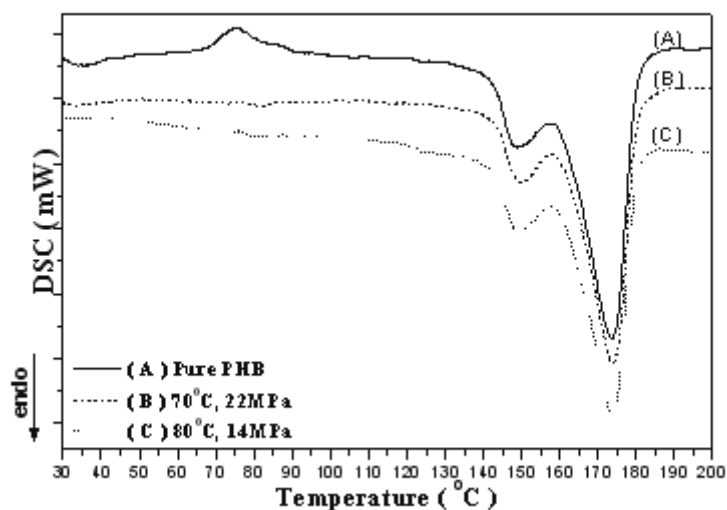
Analysis of the DSC data on pure PHB (Figure 5-A) and on PHB dyed in scCO<sub>2</sub> at 70°C and 22MPa (Figure 5-B) and at 80°C and 14MPa (Figure 5-C) showed the main melting temperature peak of the samples was at around 174°C with a second melting peak due to the thinner lamellae at around 150°C. As was shown, the melting temperature of PHB does not depend on dyeing conditions.



**Figure 3:** Amount of curcumin incorporated into PHB at three different temperatures as a function of pressure.



**Figure 4:** TGA curves of pure (A) and dyed (B) PHB.



**Figure 5:** DSC curves of pure PHB (A) and PHB dyed in  $scCO_2$  at 70°C and 22MPa (B) and at 80°C and 14MPa (C).

The data on impregnation of PET films with curcumin are shown in Figure 6. These data are in the form of histograms in order to give an idea of the behavior of the process in relation to the modifications under experimental conditions. The results obtained by use of the SAS<sup>®</sup> software show that pressure is a significant parameter for the impregnation of PET films ( $p=0.0285$ ) and that temperature is not significant ( $p=0.2025$ ).

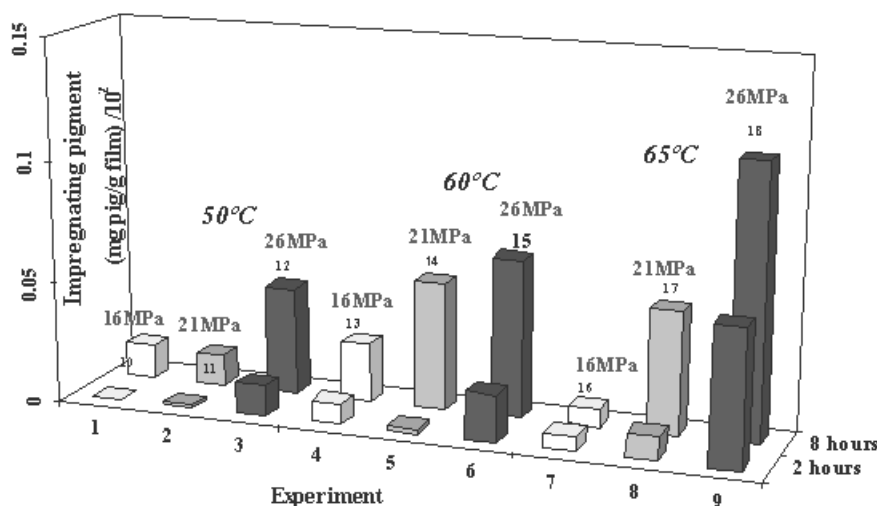
The results indicate an increase in impregnation with time, justifying the large quantity of impregnated dye at equilibrium (8 hours). An increase in

impregnation as temperature increased was also verified at pressures of 16 and 21MPa and at a temperature of 65°C. The solubility of the curcumin in  $CO_2$  was higher at a temperature of 50°C than at temperatures of 60 and 65°C when the pressure was around 20MPa. It was observed that by increasing the pressure to over 20MPa, impregnation increased with temperature. Sicardi et al. (2000) and Santos et al. (2001) found that by increasing the pressure, there was a small increase in the diffusion coefficient, and these results were explained by the  $CO_2$  plasticizing effect. On the other hand, at a temperature of 65°C the

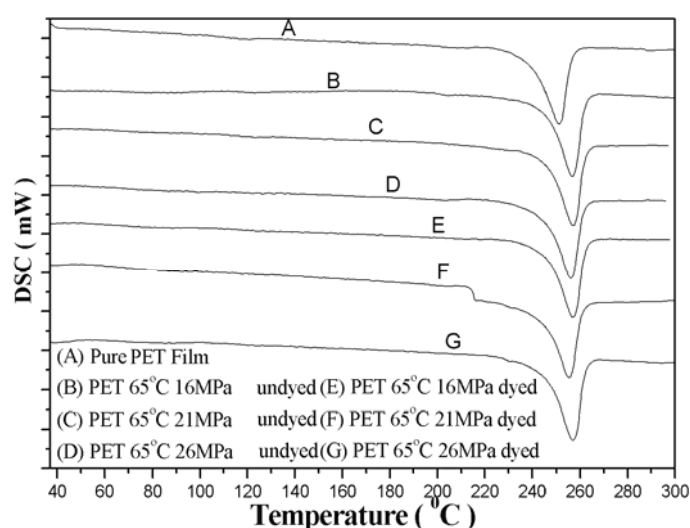
system approximated the transition glass temperature of PET, at which the molecules are more mobile, improving the effect of diffusion and slightly increasing the quantity of impregnated pigment as the system reached equilibrium. Thus, it should be emphasized that the amount of pigment that can be incorporated into a PET film is limited by high pressure and by transition glass temperature.

In Figure 7 it can be seen that there were no

significant modifications of the structure of the material. The fusion heat of PET for the samples (16MPa, 65°C without dye) and (26MPa, 65°C with dye) was calculated and the values obtained were 43.8 J/g and 44.3J/g, respectively; the insignificant difference between the values shows that the presence of dye in the system does not modify it. The same behavior was found by Santos et al. (2000) when working with PET films.



**Figure 6:** Amount of curcumin impregnating PET films as a function of temperature and pressure, using scCO<sub>2</sub>.



**Figure 7:** DSC curves of PET samples: (A) pure PET film and undyed (C-D) and dyed (E-F) PET films submitted to CO<sub>2</sub> at a temperature of 65°C and pressures of 16, 21 and 26MPa.

## CONCLUSIONS

The melting temperature of PHB did not depend on dyeing conditions and the thermal stability of the polymer was not affected during the dyeing process. The dyeing process did not produce waste effluents and the CO<sub>2</sub> could be reused after being compressed. Thus, the process with supercritical CO<sub>2</sub> is an interesting alternative to the process of dyeing polymeric because neither pre nor posttreatment is necessary. Carbon dioxide acted as a low-molecular-weight plasticizing agent, which enhanced the mobility of the monomer inside the swollen substrate but did not change the compatibility of the polymers with the dye. Thus, it should be emphasized that the amount of pigment that could be incorporated into a polymer was limited by high pressure and transition glass temperature.

## ACKNOWLEDGEMENT

The authors are grateful to PHB-Industrial S/A (Brazil) and COCAMAR (Brazil), which supplied the PHB granules and PET films.

## REFERENCES

- Abe, H., Doi, Y., Satkowski, M. M. and Noda, I., Miscibility and Morphology of Blends of Isotactic and Atactic Poly(3-hydroxybutyrate), *Macromolecules*, vol. 27, p. 50 (1994).
- Agnelli, J.A.M., Santos, A.F.S. and Manrich, S., Estudo da Influência de Resíduos Catalíticos na Degradação de Plásticos Reciclados (Blenda HDPE/PP e PET) Provenientes de Lixo Urbano, *Polímeros: Ciência e Tecnologia*, vol. 9, no. 4, p. 189 (1999).
- Avella, M. and Martuscelli, E., Poly-D(-)(3 hydroxy butyrate)-poly(ethylene oxide) blends. Phase Diagram, Thermal and Crystallization Behavior, *Polymer*, vol. 29, p. 1731 (1988).
- Beltrame, P L., Castelli, A., Selli, E., Mossa, A., Testa, G., Bonfatti, A M. and Seves A., Dyeing of Cotton in Supercritical Carbon Dioxide, *Dyes and Pigments*, vol. 39, no. 4, p. 335 (1998).
- Berens, A.R., Huvad, G.S., Korsmeyer, R.W. and Kunig, F.W., Application of Compressed Carbon Dioxide in the Incorporation of Additives into Polymers, *J. Appl. Polym. Sci.*, vol. 46, p. 231 (1992).
- Chiou, J.S., Barlow, J.W. and Paul, D.R., Plasticization of Glassy Polymers by CO<sub>2</sub>, *J. Appl. Polym. Sci.*, vol. 30, p. 2633 (1985).
- Giorgi, M.R. de., Cadoni, E., Maricca, D. and Piras, A., Dyeing Polyester Fibers with Disperse Dyes in Supercritical CO<sub>2</sub>, *Dyes and Pigments*, vol. 45, p. 75 (2000).
- Godbole, S., Gote, S., Latkar, M. and Chkrabarti, T., Preparation and Characterization of Biodegradable Poly-3-hydroxybutyrate-starch Blend Films, *Bioresource Techn.*, vol. 86, p. 33 (2003).
- Iriondo, P., Iruin, J.J. and Fernandez-Berridi, M.J., Thermal and Infrared Spectroscopic Investigations of a Miscible Blend Composed of Poly(vinyl phenol) and Poly(hydroxybutyrate), *Polymer*, vol. 36, no. 16, p. 3235 (1995).
- Kazarian, S.G., Vincent, M.F., West, B.L. and Eckert, C.A., Partitioning of Solutes and Co-solvents between Supercritical CO<sub>2</sub> and Polymer Phases, *J. Superc. Fluids*, vol. 13, p. 107 (1998).
- Kumagai, Y. and Doi, Y., Enzymatic Degradation of Poly(3-hydroxybutyrate) Blend. *Poly Degrad. Stab.*, vol. 35, p. 87 (1992).
- Lambert, S.M. and Paulaitis, M.E., Crystallization of Poly(ethylene terephthalate) Induced by Carbon Dioxide Sorption at Elevated Pressures. *J. Superc. Fluids*, vol. 4, p. 15 (1991).
- Manzan, A.C.M., Toniolo, F.S., Bredow, E. and Pinheiro Povh, N., Extraction of Essential Oil and Pigments from *Curcuma longa* [L.] by Steam Distillation and Extraction with Volatile Solvents, *J. Agr. Food Chem.*, vol. 51, no. 23 p. 6802 (2003).
- Pearce, R., Jesudasan J., Ortis, W., Marchessault, R.H. and Bloembergen, S., Blends of Bacterial and Synthetic Poly(B-hydroxybutyrate) - Effect of Tacticity on Melting Behavior, *Polymer*, vol. 33, p. 4647 (1992).
- Sanagi, M.M. and Ahmad, E.K., Application of Supercritical Fluid Extraction and Chromatography to the Analysis of Turmeric, *J. Chromatogr. Sci.*, vol. 31, p. 20 (1993).
- Santos, W.L.F., Porto, M.F., Muniz, E.C., Olenka, M.L., Baesso, A.C. Bento and Rubira, A. F., Poly(ethylene terephthalate) Films Modified with N,N-Dimethylacrylamide: Incorporation of Disperse Dye, *J. Appl. Polym. Sci.*, vol. 77, p. 269 (2000).
- Santos, W.L.F., Porto, M.F., Muniz, E.C., Pinheiro Povh, N. and Rubira, A.F., Incorporation of Disperse Dye in N, N dymethylacrilamida Modified PET Fibers with Supercritical, J.

- Superc. Fluids, vol. 19, p.177 (2001).
- Sicardi, S., Manna, L. and Banchemo, M., Diffusion of Dispersed Dyes in PET Films during Impregnation with a Supercritical Fluid, J. Superc. Fluids, vol. 17, p. 187 (2000).
- Simiello, C., Polímeros: Ciência e Tecnologia, vol. 45, Jan/Mar. (1993).
- Stinson, R.M. and Obendorf, S.K., Simultaneous Diffusion of a Disperse Dye and a Solvent in PET Film Analyzed by Rutherford Back Scattering Spectrometry, J. App. Poly. Sci., vol. 62, p. 2121 (1996).
- Takahashi, M. and Nazário, G., Monografias de Corantes Naturais para Fins Alimentícios. 2nd ed.; São Paulo, Brasil, Editora do Instituto Adolfo Lutz, (1987).