SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 10 , N° 11, 2002

A STUDY OF PARAMETERS RELATED TO ANALYSIS OF TRANSITION TEMPERATURES AND ENTHALPIES OF POLYPROPYLENE BY DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Carlos R. Wolf * and Emir Grave

Ipiranga Petroquímica S.A., Pólo Petroquímico do Sul, Triunfo, RS, Brasil, CEP 95453-000
E-mail: crwolf@ipiranga.com.br Tel. 00 55 51 4575598
E-mail: emir@ipiranga.com.br Tel. 00 55 51 4575596

ABSTRACT

Polypropylene is a thermoplastic polymer, widely employed by converter industries to produce different plastic objects. In order to control and optimize the final properties of the polypropylene material, the evaluation of transition temperatures and enthalpies by Differential Scanning Calorimetry (DSC) has a very important role. Therefore, it is fundamental to know how the analytical conditions influence the results. In this study heating and cooling rates, 10°C/min and 20°C/min, and two different rates of nitrogen flow, 20 mL/min and 50 mL/min, were investigated. It was concluded that thermal properties are influenced by rates of heating and rates of nitrogen flow. Best precision was obtained with the low heating rate, 10°C/min, and high flow rate, 50 mL/min. These conditions are being used with the DSC method for polyolefin quality control and material characterization.

KEY WORDS: Polypropylene, Differential Scanning Calorimetry, Thermal Analysis.

RESUMO

O polipropileno é uma resina termoplástica largamente utilizada por transformadores na produção de diferentes artefatos plásticos e a determinação das temperaturas de transição e das entalpias por Calorimetria Exploratória Diferencial (DSC) é extremamente importante no sentido de controlar e otimizar as propriedades finais do polímero. Assim, é fundamental conhecer a influência das condições analíticas nos resultados, sendo que neste trabalho foram avaliados os efeitos das taxas de aquecimento e resfriamento de 10°C/min e 20°C/min, e dos fluxos de nitrogênio de 20 mL/min e 50 mL/min. Foi possível concluir que as propriedades térmicas são influenciadas pelas taxas de aquecimento e resfriamento e pelos fluxos de nitrogênio. A maior precisão nas determinações foi obtida com taxa de aquecimento de 10°C/min e com fluxo de nitrogênio de 50 mL/min. Estas condições foram adotadas no método de DSC para controle de qualidade e de caracterização de poliolefinas.

* Corresponding author

DOI: 10.48141/SBJCHEM.v10.n11.2002.75_2002.pdf

INTRODUCTION

Polypropylene is a thermoplastic polymer widely employed by converter industries for different applications such as fibers (carpets, tape, cordage, nonwoven fabrics,...), injection molded products (rigid packaging, home appliances, ...), films, automotive parts and others.

The growing use of polypropylene (PP) for the plastic compounders and processors can be related to both low cost and thermal and mechanical properties of the material. They allow its use in the production of fibers, films, parts molded by injection, etc[1]. The final properties of the PP product depends on polymerization conditions, stabilization recipies and other variables. In order to design the performance of the compound, the evaluation of melting temperature (Tm), crystallization temperature (Tc), enthalpies of fusion (ΔHf) and crystallization (ΔHc) by Differential Scanning Calorimetry (DSC) are very helpful[2]. Therefore, it is important to improve the analytical conditions and this study represents an effort to understand the effect of variables such as heating and cooling rates and nitrogen flow.

METHODOLOGY

In this work samples of PP random copolymer and PP homopolymer produced by the bulk polymerization according to the Spheripol process were analyzed. The DSC equipment used was the DSC 2920 from T.A. Instruments previously calibrated with In and Sn. Approximately 6 mg of the sample was weighed and placed inside an aluminum pan. In order to get the results, every experimental measurement was evaluated ten times. The analytical conditions follow ASTM standards[3,4] and the variables evaluated are presented in Table 1.

Table 1. Variables Studied

Variable Description*	Heating and Cooling Rate (°C/min)	Nitrogen Flow (mL/min)
R10F20	10	20
R20F20	20	20
R20F50	20	50

*** R means rate, 10°C/min or 20°C/min, and F means flow, 20 mL/min or 50 mL/min;**

RESULTS AND DISCUSSION

Figure 1 illustrates typical results obtained for the melting temperature (Tm) and Figure 2 shows a representative result measured for the crystallization temperature (Tc).

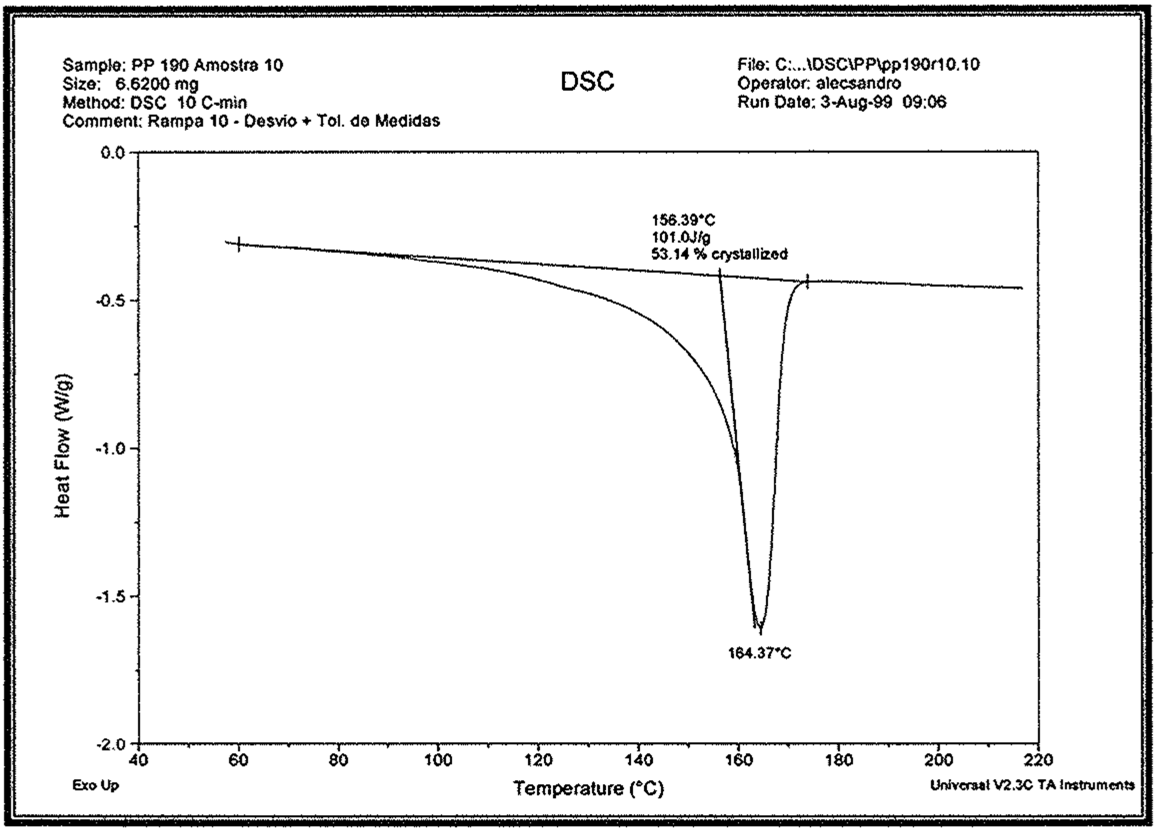

Figure 1. Determination of Melting Temperature of a Polypropylene (PP) Sample by DSC

Table 2 presents the results for the analysis keeping the nitrogen flow at 20 mL/min and changing the heating/cooling rates. In the calculation of the crystallinity, it was considered that PP (100% crystalline) releases 190 J/g. The statistical values are related to 95% confidence level and the Dixon test was done to exclude outliers.

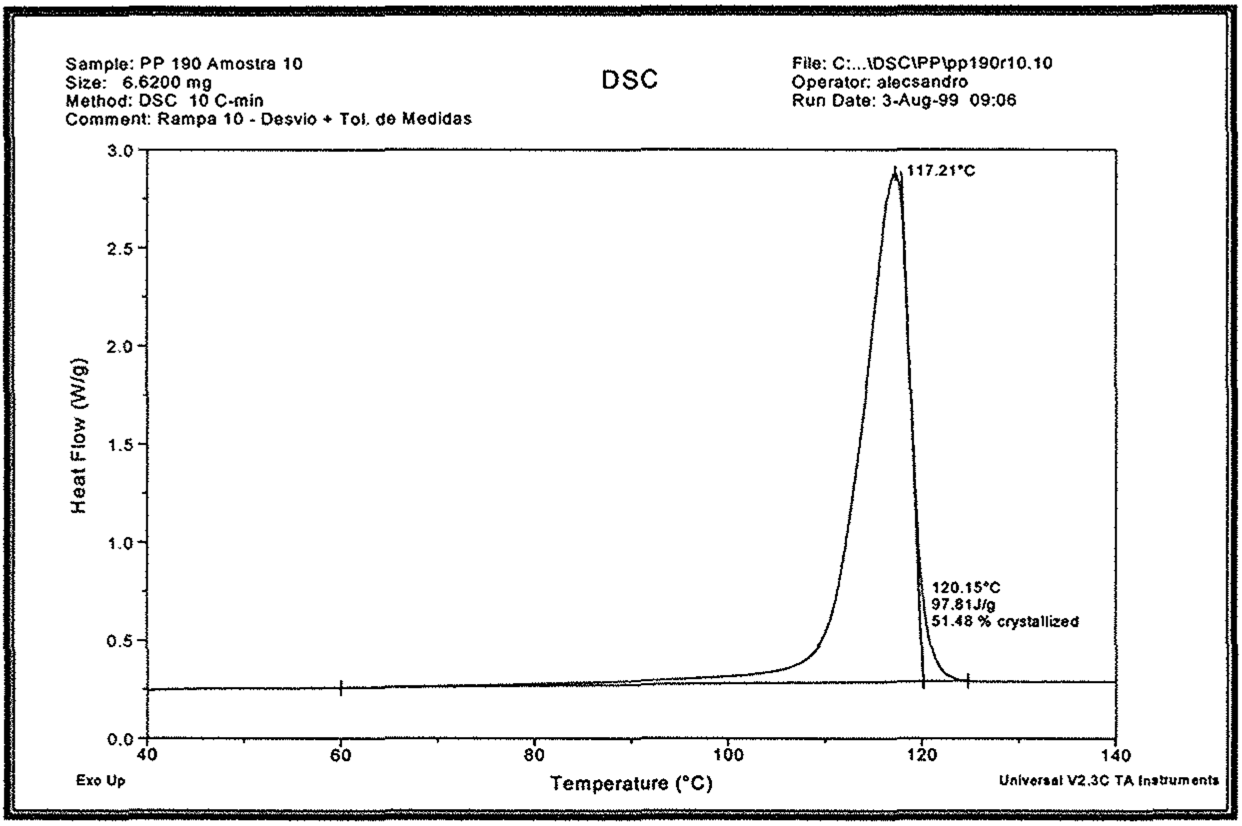

Figure 2. Evaluation of the Crystallization Temperature Tc for a Polypropylene (PP) Sample by DSC

Table 2. Results of Properties of PP Obtained Changing Heating Rates and Constant Flow

Property	Tm (°C)		Tc (°C)		ΔHf (J/g)		ΔHc (J/g)	
Condition*	R10F20	R20F20	R10F20	R20F20	R10F20	R20F20	R10F20	R20F20
Results	164,44	163,56	117,16	113,41	107,93	101,87	99,15	97,76
Crystallinity (%)	-	-	-	-	57 ± 1	54 ± 1	52 ± 1	51 ± 1
CL (±)	0,16	0,36	0,29	0,35	1,73	2,07	1,30	1,66
CV (%)	0,14	0,30	0,34	0,41	2,25	2,41	1,83	2,64
R	0,72	1,55	1,28	1,53	7,75	8,02	5,80	7,42

* R means rate, 10°C/min or 20°C/min, and F means flow, 20 mL/min or 50 mL/min;

Significance tests were used to decide if there were differences between the conditions. The results are shown on Table 3.

Table 3. Significance Test Results

Test	Method Precision (Variance)		Average Comparison
Item	F Snedecor Test	Cochran Test	t Test
Tm	Rate 10°C/min and flow 20 mL/min has better precision	Rate 10°C/min and flow 20 mL/min has better precision	Averages are different
Tc	No differences	-	Averages are different
ΔHf	No differences	No differences	Averages are different
ΔHc	No differences	No differences	Averages are different

The following equations were applied:

$$CL = \frac{ts}{\sqrt{n}}$$

$$CV = \frac{s.100}{X}$$

$$R = ts\sqrt{2}$$

where,

CL = confidence limits,
t = coefficient from t Student distribution,
s = standard deviation of a sample,
n = sample size,
CV = coefficient of variation or relative standard deviation,
X = arithmetic mean of a sample,
R = repeatability.

It is possible to conclude that the analytical procedure with the low heating rate has better precision in the Tm determination than the condition using 20°C/min. No precision differences were noticed in the other evaluations but the methods are really different.

Tests were carried out keeping the heating/cooling rate at 20°C/min and changing the nitrogen flow from 20 mL/min to 50 mL/min. The results and the statistical interpretation of the analysis are presented on Tables 4 and 5.

Table 4. Property Results Changing Flow Rate and Keeping the Heating Rate Constant

Temperature	Tm (°C)		Tc (°C)	
Condition*	R20F50	R20F20	R20F50	R20F20
Average Value	163,92	163,56	112,91	113,41
Nitrogen Flow (mL/min)	50	20	50	20
CL (±)	0,22	0,35	0,22	0,36
CV (%)	0,19	0,30	0,28	0,41
R	0,97	1,55	1,00	1,53

* R means rate, **10°C/min or 20°C/min, and F means flow, 20 mL/min or 50 mL/min;**

Table 5. Significance Test Results

Test	Method Precision (Variance)		Average Comparison
Item	**F Snedecor Test**	**Cochran Test**	**t Test**
Tm	No differences	No differences	No differences
Tc	No differences	-	Averages different

No significative differences between the precision and methods averages were noticed but there is a tendency that the better precision is obtained using the high flow.

CONCLUSIONS

The heating/cooling rate alter the results and the best precision is obtained using 10°C/min rate. Anyway, the differences are not big. Changing the nitrogen flow from 20 mL/min to 50 mL/min seems optimize the precision a little bit.

REFERENCES

1. Moore, Edward P. Jr.; *Polypropylene Handbook*; Carl Hanser Verlag, Munich, Germany, Vienna, Áustria, New York, USA, 1996.
2. Turi, Edith; *Thermal Characterization of Polymeric Materials*; Vols.1, 2; Academic Press, San Diego, California, USA, 1997.
3. ASTM D 3417-97 - *Standard Test Method for Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry (DSC)*, American Society for Testing and Materials, p. 325-328, Pennsylvania, USA, 1999.
4. ASTM D 3418-97 - *Standard Test Method for Transition Temperatures by Thermal Analysis*,), American Society for Testing and Materials, p. 329-332, Pennsylvania, USA, 1999.