USE OF MELT FLOW INDEX MEASUREMENTS TO EVALUATE THE RHEOLOGICAL PROPERTIES OF POLYBUTYLENE SUCCINATE (PBS) WHEN SUBMITTED TO DRYING

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Abstract: Polybutylene succinate (PBS) is a biodegradable polymer that has the potential to replace conventional plastic, however it has limitations such as processing viscosity and high cost. In this work, melt flow index index (MFR) measurements were used to evaluate the influence of the way PBS was packaged before processing and whether this condition could influence the rheological characteristics of the polymer. For this purpose, samples of PBS packaged by the manufacturer (humid PBS) and after drying for 5 hours at 70°C (dry PBS) were evaluated. The results confirmed the degradation condition of the PBS, before being submitted to drying, since the MFR of the sample presented a reduction of 75% of the value indicated by the manufacturer. The melt flow index, obtained from the variation in weight, was used to evaluate the rheological curve of the PBS and a pseudoplastic behavior was verified that did not vary with the form of packaging.

Keywords: Polybutylene succinate, Melt Flow Index, Drying.

UTILIZAÇÃO DE MEDIDAS DE ÍNDICE DE FLUIDEZ PARA AVALIAÇÃO DAS PROPRIEDADES REOLÓGICAS DO POLYBUTYLENE SUCCINATE (PBS) QUANDO SUBMETIDO À SECAGEM.

Resumo: O polibutileno succinato (PBS) é um polímero biodegradável que apresenta potencial de substituição do plástico convencional, no entanto possui limitação como viscosidade de processamento e seu custo alto. Neste trabalho, medidas de índice de fluidez (MFR) foram utilizadas para avaliar a influência da forma de acondicionamento do PBS antes do processamento e se esta condição pode influenciar nas características reológicas do polímero. Para tanto, foram avaliadas amostras de PBS acondicionadas pelo fabricante (PBS úmido) e após secagem por 5 horas à 70°C (PBS Seco). Os resultados confirmaram a condição de degradação do PBS, antes de ser submetido a secagem já que o MFR da amostra apresentou uma redução de 75% do valor indicado pelo fabricante. O índice de fluidez, obtido a partir da variação de peso, foi utilizado para avaliar a curva reológica do PBS e verificou-se um comportamento pseudoplástico que não variou com a forma de acondicionamento.

Palavras-chave: Polibutileno succinato (PBS), Índice de Fluidez, Secagem.

1. INTRODUCTION

The current awareness of the importance of preserving the environment, as well as more restrictive environmental legislation, have encouraged society and industry to encourage, research and use less impactful materials, such as biomaterials and biodegradable materials, in the most varied applications. Polymeric materials that have these characteristics have been an alternative to possible problems of disposal of conventional plastic waste [1].

Biodegradable polymers are materials whose physical and chemical properties deteriorate when discarded, with a concomitant reduction in their molecular weight. The reduction of properties occurs due to the presence of microorganisms in aerobic and anaerobic environments, aided by chemical reactions such as photochemical oxidation and hydrolysis to form CO_2, H_2O, CH_4 and other low molar mass products [2].

Currently, several plastics with biodegradation characteristics are already available on the market, however, in some applications, there are limitations regarding the use of biodegradable polymers, especially when there is a need for better thermal and mechanical properties.

Among the biodegradable polymers with industrial prominence, Polybutylene succinate (PBS) can be mentioned. Biodegradation of PBS chains is initiated by the hydrolysis of ester bonds, leading to the formation of water-soluble fragments with low molar mass. Small segments of PBS chains can be consumed by microorganisms and finally transformed into environmentally friendly products, ie carbon dioxide, water and biomass [3-4]. However, this polymer has thermal and mechanical properties so good that they can be compared with those of polymers traditionally used in industry such as polyethylene (PE) and polypropylene (PP). It also presents good processability allowing it to be used in conventional equipment with injection and extrusion [5]. Therefore, some properties of PBS, such as processing viscosity and its relatively high cost, have limited the increase in applications using this polymer.

In this context, the study of rheological properties, as a preliminary step to processing, can be important to optimize parameters such as time, temperature and shear. Knowledge of the behavior of polymers under flow is crucial for selecting them for an application and/or process.

Among the rheological properties, the melt flow index is a characteristic of polymers widely used as a raw material quality control, it is a parameter inversely proportional to the viscosity and characterizes the flow properties during processing. It consists of the mass flow of the molten polymer through the cylindrical capillary present in the plastometer, equipment used to determine the melt flow index.

Viscosity is the most important rheological property in polymer processing because flow rates, pressure drops and temperature increases depend on this property [6-7]. In molten polymers, the viscosity depends a lot on the orientation of the macromolecules in the flow direction, which reduces the impediments arising from the interactions between them, changing their behavior and thus classifying the molten polymers in non-Newtonian fluids [8-9].

2. METHODOLOGY

2.1 Materials

To carry out this study, a PBS with the trade name BioPBSTM FZ71 supplied by MCC Biochem was used. BioPBS™ is a soft and flexible semicrystalline polyester with excellent properties suitable for the injection process [10].

Table 1. PBS properties indicated in the polymer data sheet [10].

Properties	Values
Density	1.26 g/cm³
MFR (190°C, 2.16 kg)	22 dg/min
Melting Point	115°C

2.2 Methods

One of the main forms of degradation of PBS is hydrolytic, this condition is due to the sensitivity of polyesters to water, which in turn is strongly influenced by temperature [11]. Therefore, the rheological properties of this polymer were evaluated in two possible storage conditions before being processed. The conditions of the samples analyzed were: Humid PBS, polymer packaged in the manufacturer's packaging, Dry PBS, polymer subjected to drying at 70°C for 5 hours. For drying the PBS, a digital sterilization and drying oven with air circulation and renewal with a capacity of 150L model EESCRA-150D by Vulcan was used.

Initially, the melt flow index of the samples was determined using a standardized plastometer at the ICTI Materials Development Laboratory, based on the ISO–1133 standard with a temperature of 190°C and a weight of 2.16 kg.

Melt flow index measurements were used to define the shear rate and melt viscosity. These properties were estimated due to the balance of momentum in the fluid flowing in the capillary of the plastometer generated from a weight, which in this study varied between 1.2; 2,385; 3,260 and 4,025 Kg [12]. The driving force required for this movement is the pressure difference between the inlet and outlet of the capillary. At steady state, disregarding viscous friction in the barrel and capillary inlet effects, the capillary inlet pressure can be estimated from the mass of the weight loaded in the plastometer and the cross-sectional area of the piston. Therefore, the shear rate (γ_a) in the capillary wall and the melt viscosity (η_a) can be estimated from the melt index, weight mass and the density of the polymer melt according to Equations 1 and 2 [13].

$$\gamma_a = 1.845\ \frac{MFR}{\rho} \tag{1}$$

$$\eta_a = 4.860 \frac{M}{MFR} \quad (2)$$

Where:

M is the mass of the plastometer, which in this study varied by: 1.2; 2,385; 3.26 and 4.025kg.

ρ is the density of the polymer, 1.26g/cm³, considering the density provided in the technical sheet.

MFR is the melt index found at 190°C in 10 g/min or dg/min.

Eqs.(1)-(2) were obtained taking into account the dimensions of the standardized plastometer and assuming that the melt behaves like a Newtonian fluid. For this reason they are called apparent shear rate and viscosity.

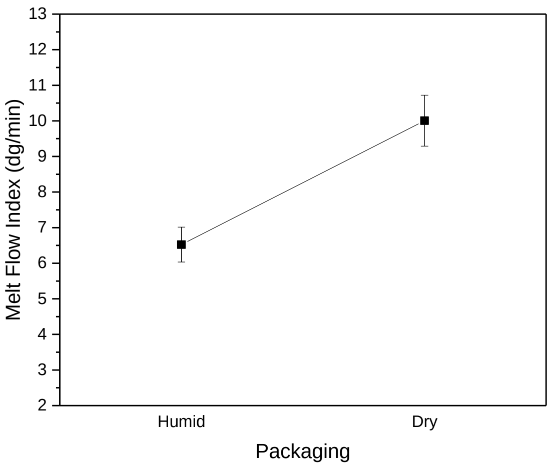
The use of different weights with the same sample allowed a shear rate scan between 5 and 50 s-1. The samples' rheograms were presented graphically in the form of double-logarithmic plots of η_a aversus γ_a .

3. RESULTS AND DISCUSSION

With the aim of verifying the influence of PBS packaging conditions, before processing, and predicting how this polymer behaves in the presence of humidity, determinations of the PBS melt flow index were carried out in different packaging ways.

Figure 1 shows the results of the melt index obtained for wet and dry PBS.

Figure 1. PBS Melt Flow Index 190°C/2.16 kg



Melt flow index measurements, carried out under the conditions established by the ISO–1133 standard, using 190°C and 2.16 kg weight, indicate an increase of approximately 35% in this property when the PBS is subjected to drying. During the drying time it is expected that the moisture is removed from the sample and thus it is possible to avoid the hydrolytic degradation of the PBS. Hydrolytic degradation is one of the main forms of degradation of PBS due to the sensitivity of polyesters to water. This type of degradation generates a decrease in the molar mass of PBS through chain scission and is influenced by temperature [11]. It is known that the increase in the melt flow index under standard conditions is an indirect indication of the decrease in molar mass [14]. Therefore, it is possible to associate the increase in this property with degradation by PBS chain scission [11].

The drying conditions established in this study, 70°C for 5 hours, are recommended by the manufacturer. It presents, in the technical data sheet of the polymer, a melt flow index of 22 dg/min [10]. However, after drying, the melt flow index found was 55% lower than that indicated by the manufacturer. Studies indicate that the occurrence of crystallization is induced by the low molecular weight chains present in the degraded PBS. The amorphous regions of these semicrystalline polymers degrade preferentially, in relation to the crystalline ones, leading to chain scission and a reduction in the number of molecular tanglings in this region, in such a way, small chains are generated with the potential to rearrange themselves in crystalline form, increasing crystallinity of the polymer and thus reducing the melt flow index [5,15]. Therefore, it is believed that the PBS sample used in this study may be degraded, which allowed the molecular arrangement of the smaller chains and the reduction of the melt flow index after drying.

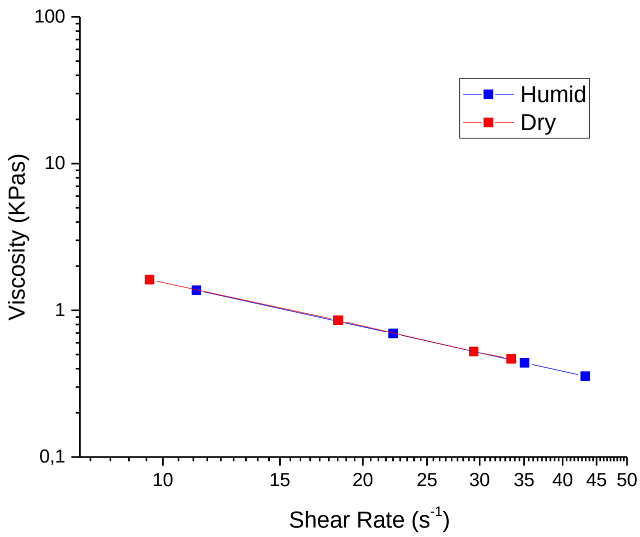
Table 2 shows the mean and uncertainty of the melt index measured in five 60 second "cuts", as well as the shear rate and apparent viscosity calculated for wet and dry PBS.

Table 2. Melt flow index (MFR), shear rate (γ_a) and apparent viscosity (η_a) calculated for all samples tested with different weights.

PBS	M (kg)	MFR (dg/min)	γ_a (s^{-1})	η_a (kPas)
Humid	1.20	7.671 ± 0.255	11.233 ± 0.374	1.370 ± 0.048
	2.38	15.180 ± 1.168	22.228 ± 1.710	0.695 ± 0.055
	3.26	23.940 ± 0.341	35.055 ± 0.499	0.439 ± 0.06
	4.02	29.550 ± 1.232	43.270 ± 1.804	0.356 ± 0.015
Dry	1.20	6.520 ± 0.295	9.547 ± 0.433	1.617 ± 0.078
	2.38	12.540 ± 1.928	18.362 ± 2.823	0.856 ± 0.137
	3.26	20.067 ± 0.608	29.383 ± 0.891	0.524 ± 0.017
	4.02	22.855 ± 2.716	33.466 ± 3.977	0.466 ± 0.065

Based on the viscosity and shear rate data, the rheogram in Figure 2 shows that the curves are the same under different storage conditions. It is possible to verify viscosity variation as a function of shear rate. This behavior is expected for a polymer classified as pseudoplastic, that is, there is a reduction in viscosity with increasing shear rate [16].

Figure 2 . Rheogram of commercial polyethylenes



4. CONCLUSION

The packaging of PBS influenced the melt flow index of this polymer. When compared to the value reported by the manufacturer, there was a 70% reduction in this property, which indicates a degradation of this material. If subjected to drying, this reduction is 55%. The effect of temperature on the polymer during drying causes a rearrangement of the chains and consequently an alignment that facilitates fluidity.

The weight variation during the melt flow index measurement allowed an estimation of the rheological behavior of the PBS in the different packaging ways. The PBS presented characteristics of a non-Newtonian fluid of the pseudoplastic type and this condition did not change after drying.

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