HIGH PERFORMANCE POLYAMIDES FOR INJECTION MOLDING: THERMO-MECHANICAL CHARACTERIZATION AND QUALITY ASSESSMENT

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Abstract

A study of thermal and thermomechanical characterization and evaluation of moisture content of high-performance polyamide composites, namely, polyamide-4,6 (PA-4,6) with a short glass fiber reinforcement of 50 % by weight and polyamide-6,6 / 6 (PA-666) reinforced with short glass fibers of 30% (by weight), both used in high temperature injection molding (about 300 ° C).

Polyamides have a high affinity for water. Even with relatively low moisture content, the processability of these materials is compromised at the high temperatures normally used in injection molding, causing defects that contribute to the rejection of the produced parts Three tests were realized for the performance evaluation of these materials::

a) Differential scanning calorimetry (DSC) tests with high sensitivity to the degree of crystallinity and the processes involved in crystallization.

b) Thermomechanical tests of dynamic-mechanical thermal analysis (DMA or DMTA), with high sensitivity to the processes associated with the vitreous relaxation and the sub-vitreous relaxations, as well as the orientation of the glass fibers.

c) Determination of moisture contents in the granulates and injected parts, and preliminary evaluation of the correlations with the presence of injection defects.

The results obtained show that the composites of PA-4,6 present a greater sensitivity to the ambient humidity, when compared with the composites of PA666. In both materials, the temporal variation of moisture content in both the humidification process and the drying process shows the existence of long tails in the saturation zone or at the end of drying, which indicates the presence of water vapor diffusion cooperative processes..

Key Words

Polyamide-6,6 / 6 with fiberglass; Polyamide-4,6 with fiberglass; Differential Scanning Calorimetry (DSC); Dynamic-mechanical thermal analysis (DMA / DMTA); Drying of polyamides

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I. Introduction

The main objective is the characterization and evaluation of the relevant units to the quality of polyamide composites. These items were made available by JDeus®. The material in question

consists of a polyamide 66 and polyamide 6 (PA666) reinforced with 30% glass fiber (GF) and a PA46 polyamide reinforced with 50% GF.

As the name implies a polymer results from the chemical polymerization reaction. Polymers are substances with high molecular mass, characterized by the repetition of a certain group of atoms. [1][2]

The first commercialization of this polyamide was carried out by DSM Polymers in 1988. This polyamide is produced by condensation of adipic acid and tetramethylenediamine (1,4-di-aminobutane), as shown in Figure 1.

reaction between diamines and carboxylic acids. Its nomenclature is based on the repeating sequence and the number of carbon atoms present in each monomer.

It is important to note that an "AB" type polyamide is designated by an amine group, "A", and an acid group, "B". Thus, a PA 6 is a polyamide 6 (poly (ε-caprolactam)), since it has six carbon atoms between the nitrogen atoms of the amine group. This polyamide is obtained by the hydrolytic polymerization of α-caprolactam, Figure 2.[4][5][6]

The mechanical properties of the polyamides are between an intermediate behavior of an
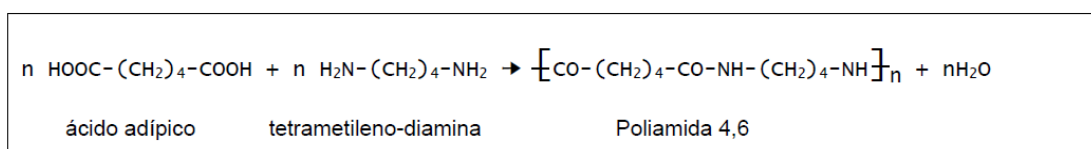

Figure 1 - Condensation reaction of PA46

Due to the four methyl groups, its macromolecule, is distinguished from other polyamides by having many amide groups for a given chain length, in addition to being configured as a highly symmetrical molecular structure. Accordingly, this structure gives the material more crystallinity and crystallization rate than other polyamides, resulting in significantly higher properties such as its high melt temperature, 295

elastic solid and a viscous liquid. For this reason, the application of a hard core over an extended period causes a viscous flow (a permanent deformation in the polymers), since the application of a voltage in a short period of time causes an elastic response.

Inevitably, there are changes in modulus of elasticity, E, and in the viscosity coefficient, η, as such is referred to as viscoelastic behavior.
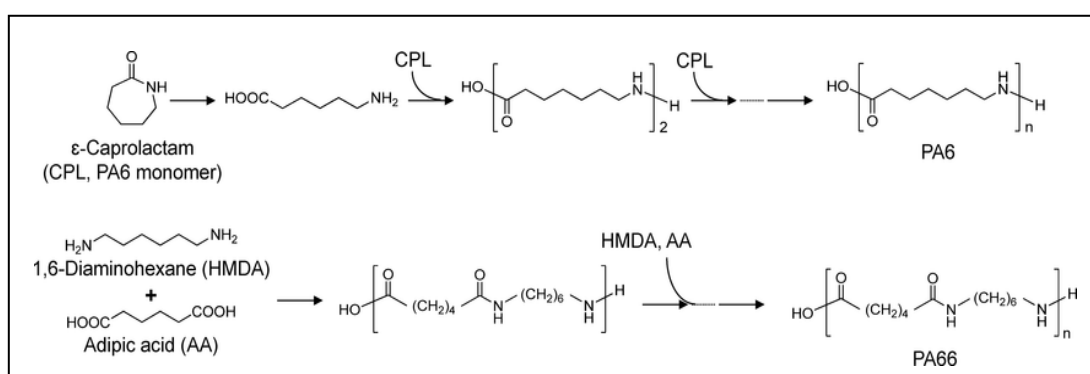

Figure 2 -Polycondensation reaction of PA66

II.   Experimental Techniques

PA666, is characterized as an aliphatic, non-aromatic polyamide, wherein the chemical chain is linear, consisting of carbon and hydrogen atoms produced from the polycondensation

A.   DSC

With the use of this technique it is possible to

obtain information about structural changes in the different compounds following the evolution of the temperature, through its characteristic peaks of phase changes, such as the glass transition and crystalline fusion, recording the necessary energy, that is, the heat flow as a function of time or temperature when the samples are heated gradually.[7]

B. DMA

With this technique it is possible to determine the thermomechanical properties of the materials quickly and efficiently using a small amount of sample. This technique measures properties such as elastic modulus and viscous modulus as a function of temperature, frequency or time. This measurement is made by the variation of temperature, where it is possible to observe the thermal transitions of the material, such as the glass transition (T_g) and the melt temperature (T_f) and relate the structure of each part with its viscoelastic properties.[8][9][10]

C. Drying test

A study was carried out on the drying time required for the optimization of the injection process, since the presence of moisture causes anomalies in the parts. The polyamide was initially saturated in water to have a comparison / control factor. Heating was then carried out in an oven (at 80 ° C), to which samples were drawn along the heating.

III. Results and Discussion

A. DSC

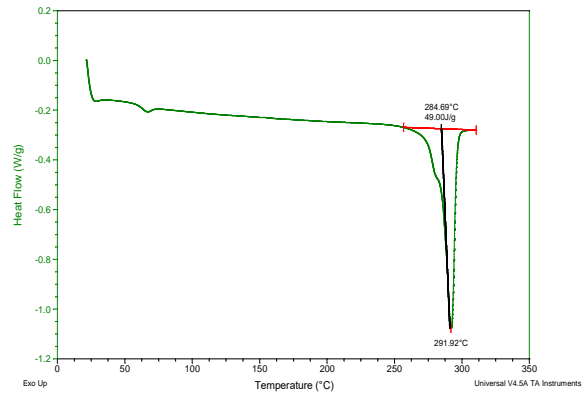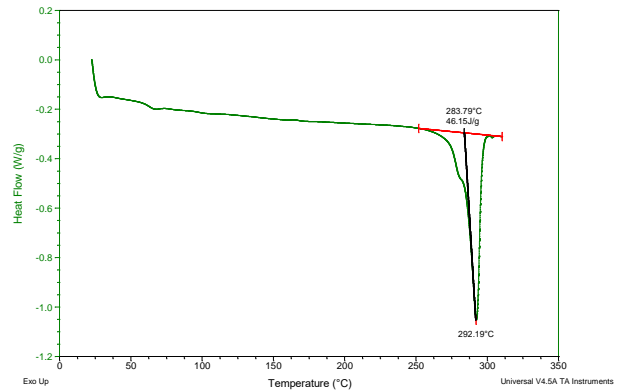| Initials	Polyamide
AS – Before the dryer	PA46
DS – After the dryer	PA666

Figure 3 - PA46 AS
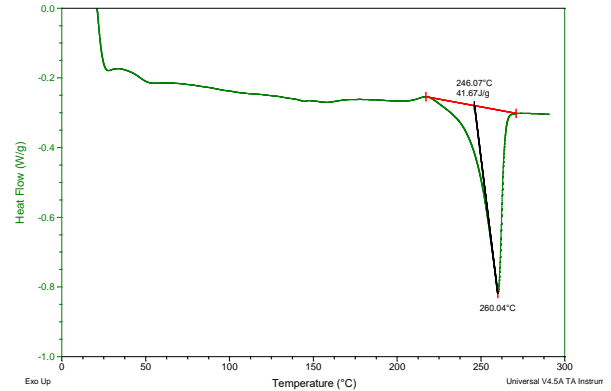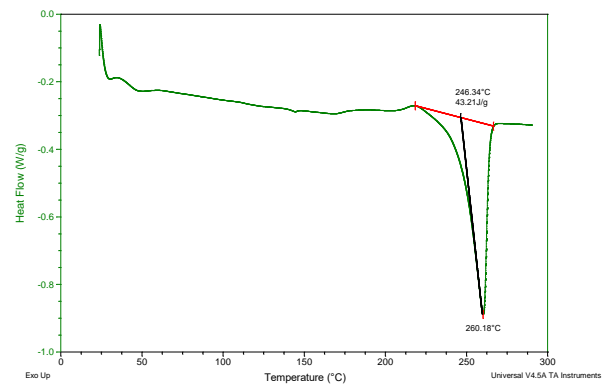
Figure 4 - PA46 DS

Figure 5 - PA666 AS

Figure 6 - PA666 AS

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The DSC curves show the glass transition and the peak crystalline melt, typical signals of a semicrystalline polymer.

As evidential evidence only a peak melting for a PA66 + PA6, which confirms that it is a random copolymer.

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However, there was variation in the latent heat value.

The latent heat of fusion, or enthalpy involved during the melting process (ΔHf), absorbed during crystalline melting or released during the crystallization process.

If the presence of moisture changes the degree of crystallinity, this results in a change in the enthalpy of melting. [53]

Assuming that the differences in melting enthalpy reflect the variation of the crystallinity induced and the weight caused by the presence of water, it is possible to estimate the percentage of moisture initially present

As such the H% present in the grain was calculated, resulting in 10% moisture in PA46 and 4% PA66+PA6.

B. DMA

The DMA curves obtained for each sample, PA46 and PA666, approved by quality control and sample lead (scrap) are shown below for further comparison. The temperature of each assay varied between -22 and 250 ° C. The curves were analyzed with the *Universal Analysis 2000 program of TA Instruments.*

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Figure 8 - Samples of PA 46 rejected

Figure 7 – Sample aprroved of PA46
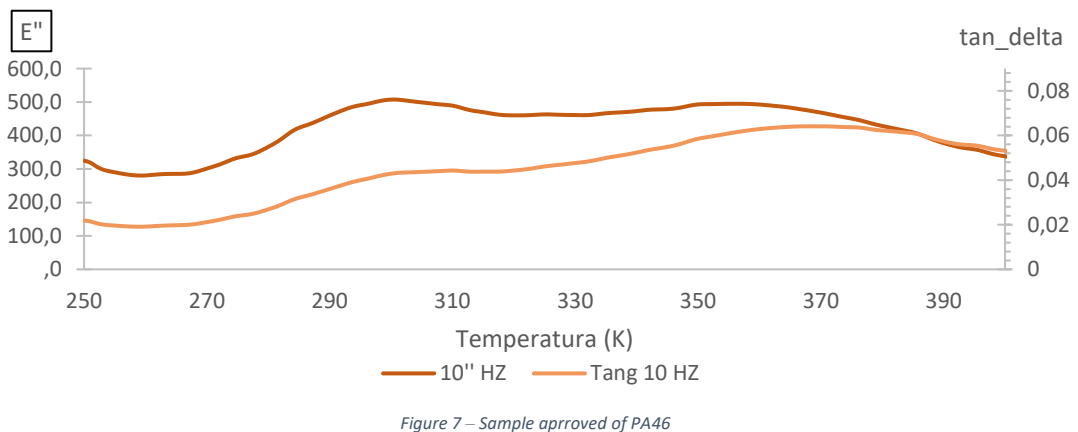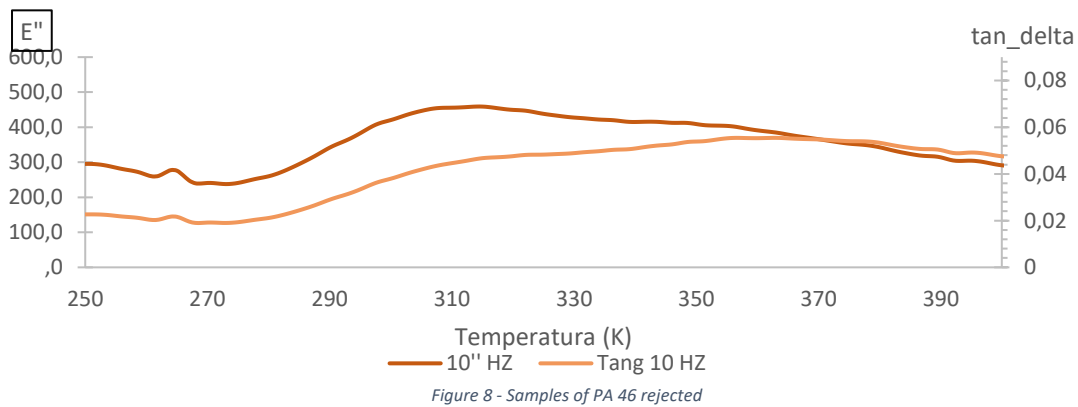
By the analysis of both figures, we observe a noticeable change of the elastic component of the Young's modulus at 250K which is to 15GPa in the unreacted specimen and 13GPa in the accepted specimen and also change in the tan δ peaks, about 310K in one

case and the other 300K. The curves d tan δ show that there are microstructural differences between the accepted and rejected specimen, which may eventually result from different cooling modes in the mould during the injection cycle. The changes are somewhat surprising in the Young's modulus, they are likely to be correlated with the arrangement and orientation of the glass fibres in the injected specimen. Such changes are usually due to changes in the casting of the molten material in the mould during filling.
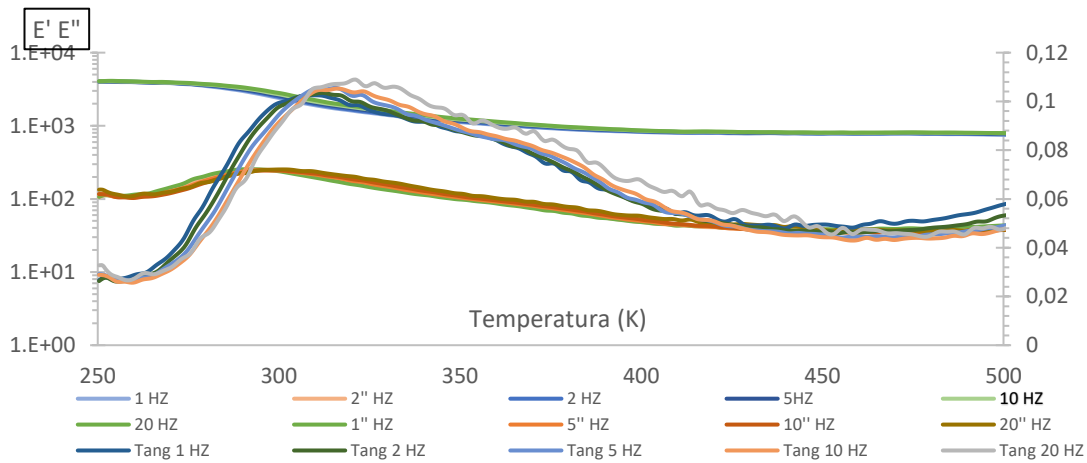

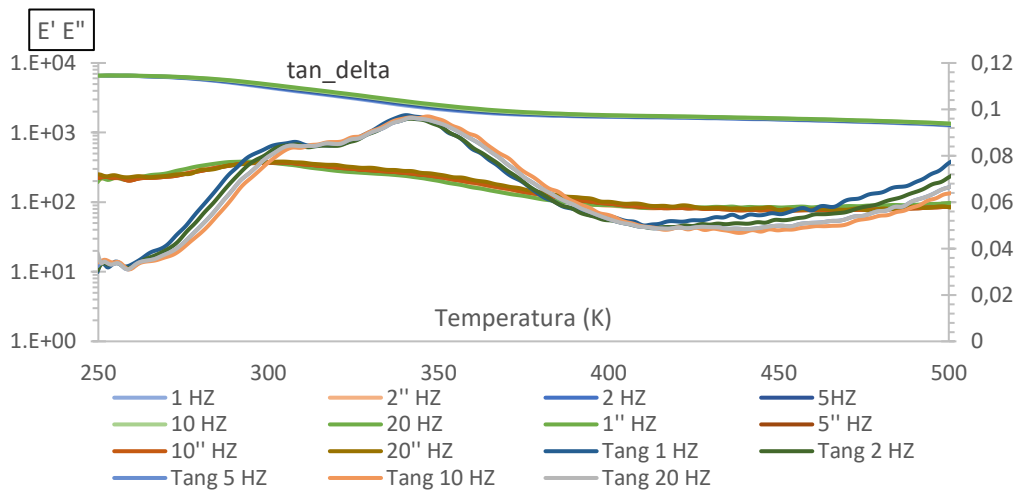*Figure 9 - DMA of a PA666 sample approved*

Figure 10 - DMA of a PA666 sample rejected

The differences between accepted and rejected samples are mainly notorious in cures that show the temperature as a function of tan δ. In the rejected specimens two peaks are observed; which has the lowest temperature corresponds to polyamide 66 and the one which is the highest temperature to polyamide 6.

The presence of two partially overlapping peaks indicates that there are richer zones in the polyamide 66 and other polyamide 6 richest specimens. It is known that in the random copolymers AB the arrangement of the monomers A and B in the chain is not totally random (the probability of the monomer A is proportional to the A content in the chain) but also

depends on the reactivity during the copolymerization (the reactivities of AA, BB and AB are not the same). In the present case where the polyamide-6 content is 10% and the polyamide 66 content is 90%, it is likely that regions rich enough in monomer 66 may exist so that there may be crystallization, and less likely to be regions rich enough in monomer 6 and in monomer 6. In the case contemplated in this hypothesis, nonconformity could be attributed to the way the polymerization of the raw material was carried out, although further testing is necessary. It may also be the case that the cooling in the injection mold has been a little slower causing segregation

C. Drying test

A study was performed on the drying time required to optimize the injection process, since the presence of moisture causes anomalies in the parts. The polyamide was initially saturated in water. Heating was then carried out in an oven (at 80°C), to which samples were drawn along the heating.

It is important to note that the existing water absorption concerns only polyamide, eliminating the contribution of GF, since it does not absorb water.
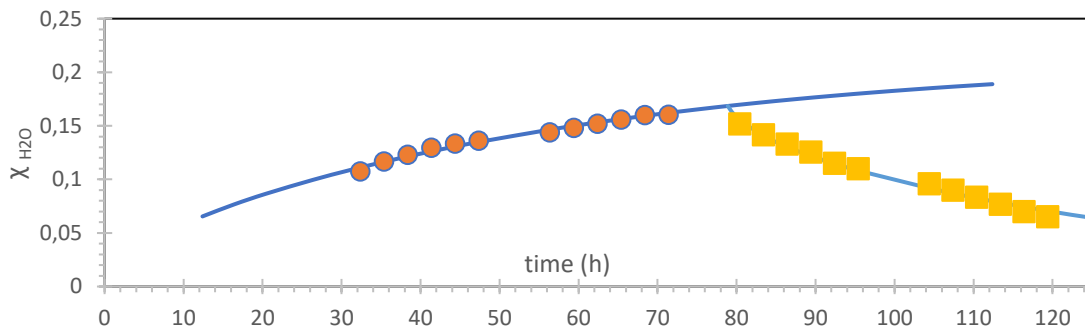

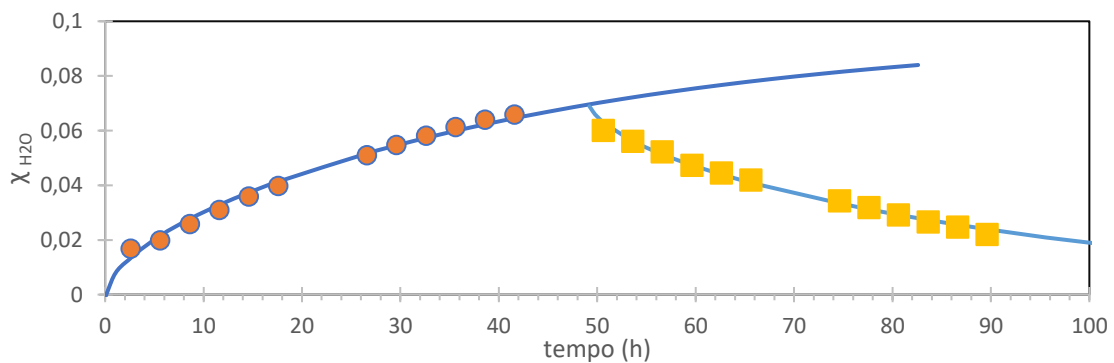Figure 11 - Drying test for PA46 (Simple Diffusion)

Figure 12 - Drying test for PA66+PA6 (Simple Diffusion)

A analysing the graph, it is possible to verify the saturation of the material and subsequent comparison with the drying. Comparing the PA66 + PA6 copolymer with the PA46 polymer, it would be predicted that PA46 would have a lower fraction of H_2O, since it is a more crystalline material. However, this does not happen, which may be due to the high density of the amorphous phase and because diffusion also occurs at the interface between the polyamide and the GF. The absorption of water in the polyamides occurs mainly in the amorphous phase due to the high

diffusion of the water molecules, compared to the crystalline phase, following the diffusion model.

The diffusion model an exponential function, characterized by a rapid growth followed by a very slow stabilization until reaching a plateau, the saturation. Mittag-Leffler function:

$$E_\propto(x) = \sum_{k=0}^{\infty} \frac{x^k}{\Gamma(\alpha k+1)} \qquad 1.1$$

According to literature for intermediate values of Mittag-Leffler and Padé approximations, it is possible to have a standard function for the humidification and dehumidification of the polyamide.

Thus, with the function normalized by the Padé approximations, it was possible to compute the α and the characteristic time, for each polyamide under the conditions that were analyzed.
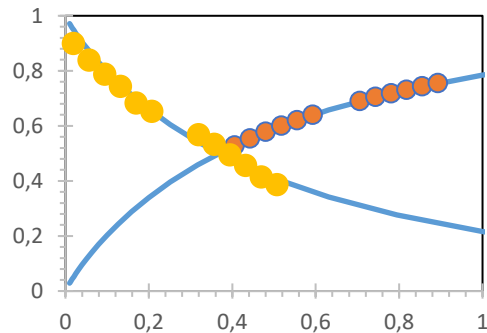

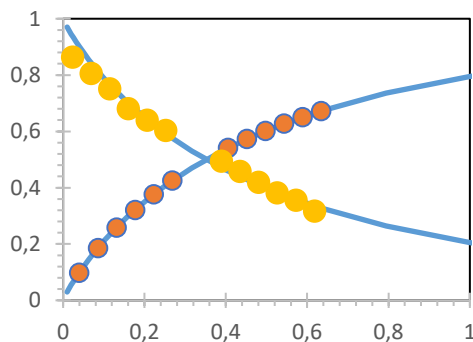Figure 13 - Mittag-Leffler with approximations from Padé to PA46

Figura 14 - Mittag-Leffler with approximations from Padé to PA66+PA6

Since α = 1 gives the simple diffusion equation, parameter (1-α) measures the degree of distance from simple diffusion (non-local cooperative diffusion) and can be called the degree of cooperativity. The values α found for the parameter α (close to 0.7) show that the diffusion process has a significant cooperative diffusion component. It is interesting to note that the degrees of cooperativity found for polyamides (46) and (66.6) are rather close in suggesting that the elemental mechanisms will not be substantially different in one case or another, as would be expected given the fact that polyamides are chemically near.

It is also interesting to note that the results obtained are in accordance with the experimental observation of the abnormally high values α obtained for the saturation time during humidification, which will also correspond to values higher than expected in the case of drying. In the case of injection molding, the drying times of non-specified wetting granules are likely to be highly dependent on the initial moisture contents.

The alpha parameter that varies between 0 and 1 can be used to define a cooperativity index that weighs cooperativity and the nonlocal character, in this case of diffusion, and which is equal to 1-α. Thus, if α = 1, the Mittag-Leffler function reduces to the exponential function, which is the characteristic function of a simple diffusion process, as the alpha value decreases increases the cooperative index. In the cases considered the alpha values, they were respectively 0.67 and 0.69 for PA46 and PA66 + PA6, which means that the degrees of cooperativity are very similar to what was expected given the similarity of the materials.

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IV. Conclusion

It is concluded with this work that the presence of water in the test pieces influence, in a lot, the quality of each moulded piece. This, therefore, the smaller the amount of water present in the polyamide, the better the parts

obtained, with respect to the configuration and response of the part.

Through the DSC analysis and performed calculations it was possible to verify that the results obtained by this technique show that PA66 + PA6, which confirms that it is a random copolymer. Through calculations it was possible to verify that the PA46 has about H% = 10 and the PA66 + PA6 of H% = 4, which causes a decrease of the properties of the polyamides.

The DMA technique evidences a difference between rejected and accepted samples, because the rejected samples have two peaks in tan δ, possibly due to the poor copolymerization of PA66 and PA6 (since it is made with a ratio of 9: 1 in w / w), a random copolymerization was demonstrated. In the polymer PA46 the process of alteration of the chemical microstructure is notorious, it may be due to changes in the lining of the molten material in the mould during filling or to the effect of molecular weight change (presence of moisture).

In the drying test alpha values α were respectively 0.67 and 0.69 for PA46 and PA66 + PA6, which means that degrees of cooperativity are very similar. This test also suggests that drying on the order of 8h may not be enough.

V.   Future works

As the presence of water in the polyamides, from the industrial point of view, presents a great loss, it is necessary to determine it before the injection process. As such, it will have to be a rather simple and rapid analysis, as is the case of the Karl Fischer method. This method can determine, in several types of material, water contents lower than 50ppm. Since the intensity of the titration stream is low, one can determine the amount of water in just 10 minutes. It is an absolute method that does not require calibration, which makes it a very simple technique.[12]

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