STUDY OF RHEOLOGICAL BEHAVIOR OF REPROCESSING POLYAMIDE 6

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Abstract: The effect of reprocessing Polyamide 6 (PA6) has been studied in this paper. To simulate recycled PA, we reprocessed virgin PA through 5 cycles. The PA has been rheologically characterized after the various cycles of reprocessing in order to evaluate their corresponding properties and correlate them with the number of cycles undergone. In order to widen our injection simulation analysis by computer (CAE: Computer Aided Engineering) of these new materials, it was necessary to determine the viscosity using a mathematical model, in this case the Cross-WLF, to determine the relevant parameters. Our results show that viscosity decrease, as the number of reprocessing cycles increases.

1. INTRODUCTION.

Polyamide 6 (PA6) has been extensively applied in many fields because it possesses a lot of excellent properties, and its consumption will keep growth in the future. Therefore, how to recycle and reuse effectively, as well as restrain their degradation during processing will become interesting subjects for polymer scientists and engineers. Consequently, the influence of reprocessing operations on the characterization of PA6 must be reveal in advance.

The problems which arise in the recovery of polymer materials are basically the variations that occur in their properties, due to either thermic degradation or the presence of impurities. Many studies have been carried out on the degradation of polymers, Su [1] analyzed the influence of the reprocessing cycles on the mechanical properties, rheological properties and changes in structure of PA 6. Su's work is relevant to our work because he carried out a study of mechanical and rheological properties, as we. Su's work is interesting, but we do not consider that reprocessing the material 16 times is very useful, because other studies show that the loss of property occurs in the first 5 reprocessed. Additionally, Su only studies the Melt Flow Index (MFI) and no viscosity.

Moreover, Bonardi [2] in their study of reprocessing of PA 6 shows an interesting behavior, since the viscosity of the material increases as do the reprocessing. This surprising behavior can be explained by the study of Dijkstra [3] which shows that different moisture content of PA 6 can cause behavior contrary. His work shows decreasing viscosities at high humidity content and increasing viscosity for very dry samples.

Maspoch [4] investigated of mechanical and rheological properties of a sample of recycled (comes from fiber grade production waste) and filled (filled with 20% glass beads and 10% glass fiber) PA6, was reported as a function of the number reprocessing operations and of the fraction of recycled material added to the virgin material. Her work showed that the properties of the recycled material remained below the virgin, and the best combination of both appeared to be the mixture with 30 wt.% recycled fraction, which shows a lot of properties similar to three reprocessing operations.

Finally, Navarro [5] mixtures of polymers with the aim of improving properties of the recovered material. Navarro, in his study of the influence of polyethylene (PE) on recycled polyethylene terephtalate (PET) analyzed, among other things, mechanical and rheological properties. His work is of interest to us because he uses the Cross equation to calculate viscosity, although he only uses a die (L/D 10mm) so that the viscosity calculated is

apparent rather than exact. In his study, he obtained values of viscosity that got lower as the percentage of PE in the mixtures was increased. It is also interesting because he also studied in more detail the shear rate interval between 5.000 and 10.000s^{-1}. The study of this interval is important as these values most closely match the conditions to which the material is subject during the injection process.

One of the fundamental properties to consider when studying polymer processing is its rheological behavior. Understanding this parameter is vital to carry out a correct extrusion or injection of the polymer. The real viscosity of a polymer is obtained using a capilliary rheometer along with the Bagley and Rabinowitsc corrections.

Some injection processing simulations, such as Moldflow Plastics Inside 6.2 ®, use values of the parameters from the Cross-WLF model. Cross [6] and Williams [7] carried out experiments to reproduce the rheological behavior of the materials during the injection process. Boronat [8] and Reig in his works [9],[10] applied these models in their studies on reprocessed ABS + PC and ABS respectively. Boronat´s study is interesting because he calculated the Cross dependant parameters of his mixtures and shows how variations in these affect viscosity. At the same time, he showed that increasing the temperature has a greater influence on the degradation of ABS than increases in the shear rate. Reig in his work of 2007 determined a Material Processability Index (MPI) from three mixtures of ABS + PC with a different MFI. Reig calculated the Cross parameters for each mixture and uses the methodology for the design of experiments (DOE). The variables reused in the DOE were the variables from injection processing (filling time, melt temperature, coolant temperature, packing pressure level and filling-packing switch-over). For all of this, Reig used the computer simulation of the injection process to determine that the ideal PC content in the ABS/PC blend is 3.6%.

The objective of this present work is to study the rheological behavior of PA 6 from virgin material through to the fifth reprocessing cycle.

Finally, a further objective of this present work is to determine the parameters of the Cross-WLF model, both for virgin and recycled in order to incorporate them into plastic injection simulations.

2. EXPERIMENTAL

2.1 Materials and preparation of specimens

To develop this study, we used PA6 Heramid S Neg 233 supplied by the company Radici Plastic ®.

For the injection, we used a Meteor 270/75 injector supplied by Mateu & Solé® (Barcelona, Spain) at 240 ºC injection temperature. We carried out five injection cycles (R1, R2, R3, R4 and R5) beginning with virgin PA (V).

2.2 Methods and Measurements.

The rheological analysis of all the materials was done using a Thermo Haake Rheoflixer MT® capillary rheometer. The temperature used in the rheometer was 240 ºC, which is well within the recommended range of the manufacturer. The shearing speeds used in the study were in the range 100 to 10,000 s^{-1}. The rheometer was equipped with three separate dies, all with a diameter of 1mm and with L/D ratios of 10, 20 y 30. The tests were carried out in compliance with ISO 11443. The viscosity values for each die correspond with the average of the five experimental tests.

3. METHODOLOGY FOR VISCOSITY CALCULATION

Capilliary rheology allows us to obtain the apparent viscosity (η_{ap}) of the polymer under test without any difficulty using the following equations and a constant temperature:

$$\eta_{ap} = \frac{\tau_{ap}}{\gamma_{ap}}$$

(1)

(2)

$$\tau_{ap} = \frac{p \cdot D}{4 \cdot L}$$

Where: τ_{ap} is the apparent shear stress [Pa], γ_{ap} is the apparent shear rate [s^{-1}], p is the test pressure in pascals, D is the diameter of the die in mm y L is the length of the die in mm.

In the graphs in Figures 1a, 1b and 1c are observed in the rheometer pressures obtained with the die of L / D 10, 20 and 30 respectively for the six materials.
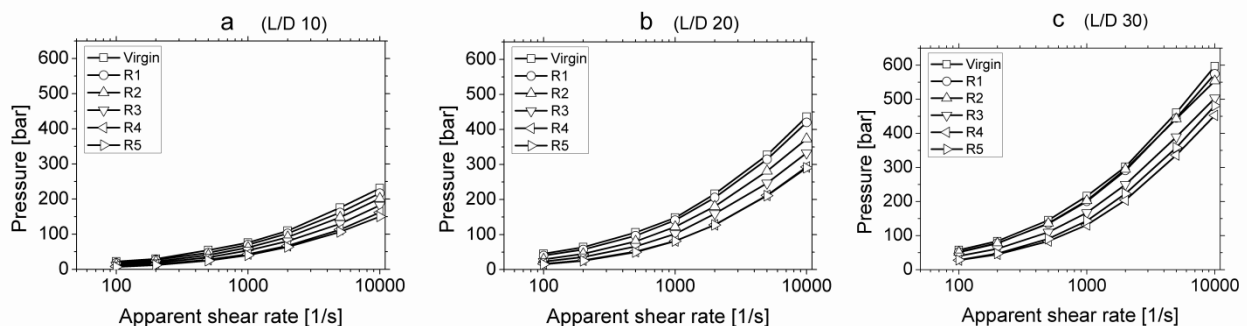

Figure 1 Pressures obtained in the capillary rheometer for the three dies and the six materials.

The passage of melted material from a greater to a lesser diameter causes over-pressure which slightly alters the results obtained directly from the capilliary rheometer. This variation can be corrected using Bagley's correction. The melted polymers are fluid and not Newtonian and the equations used to calculate viscosity must also be adjusted. One of the most commonly used corrections is that of Rabinowitsch, using which it is possible to obtain the true shear rate at the capilliary wall. Boronat [8] used these corrections in his work on reprocessing of ABS.

3.1. Bagley's correction.

The application of this method required that we use the polymer at a particular temperature and with three dies with different length / diameter ratios (L/D =10, L/D = 20, L/D = 30), to obtain the pressure in each die at different shear rate (100, 200, 500, 1000, 2000, 5000, 10000 [s^{-1}]).

Figure 2 shows the linear trend for the pressure as a function of the *L/D* ratio of the dies used and in which we can see the adjustment produced for *L/D* = 0. The Bagley method corrects the over-pressure related to an apparent increase in die length. Thus, with equation 3, we calculated the true shear stress τ [Pa], where p is the pressure obtained by the adjustment and we used the corrected *L/D* ratio, *(L/D)c* which is the *L/D* distance at which the pressure is zero.

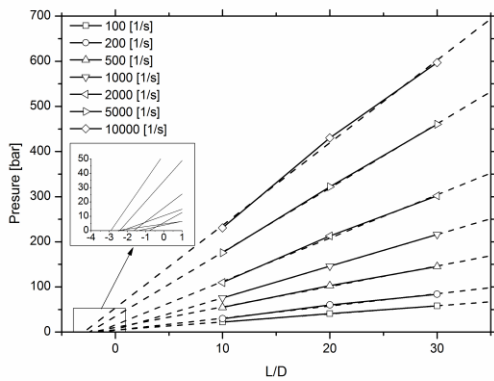$$\tau = \frac{P}{4\left[(L/D) + (L/D)_c\right]}$$

(3)

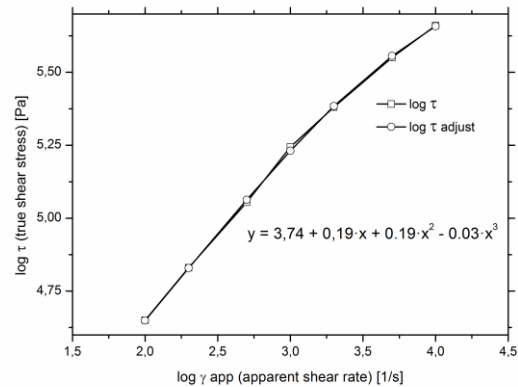**Figure 2. Bagley's correction for virgin material.**

Figure 3. Rabinowitsc's correction for virgin material and a die L/D 10.

3.2. Rabinowitsc's correction.

Rabinowitsc's correction allows us to determine the true shear rate γ [s-1] using equation (4). To obtain the data with greater precision, it is necessary to represent graphically the true shear stress log (τ) against the true shear rate log (γ) (figure 3) and adjust the points of cubic equation (5). In equation (4), for the data of the log τ, log $\tau_{adjusted}$ for the curve of equation (5). In this figure 2, we can see that the equation used is perfectly adjusted to the points calculated for the virgin material and die L/D 10. This was also calculated for L/D 20 y 30.

$$\gamma = \frac{\gamma_{ap}}{4} \cdot \left(3 + \frac{d \log \gamma_{ap}}{d \log \tau}\right) \tag{4}$$

Where γ_{ap} [s-1] is the apparent shear rate.

$$y = a0 + a1 \cdot x + a2 \cdot x2 + a3 \cdot x3 \tag{5}$$

3.3. Calculation of viscosity.

The viscosity was calculated with the quotient between shear stress and shear rate, as seen in equation (6). As with the calculation of viscosity, three dies were used, we also obtained three viscosity curves for each material. From these three curves, one single curve was calculated as a final result. The viscosity curve for 240 ºC in figure 4b is this final curve.

$$\eta = \frac{\tau}{\gamma} \tag{6}$$

3.4. Determination of dependent parameters from the Cross-WLF model; determination of viscosity of the material.

The viscosity value obtained is the result of the complete process at a constant temperature. Viscosity varies with temperature (equations 7 and 8). The Cross model 9 allows us to calculate the viscosity of the material at whichever temperature beginning with a viscosity curve of any given temperature.
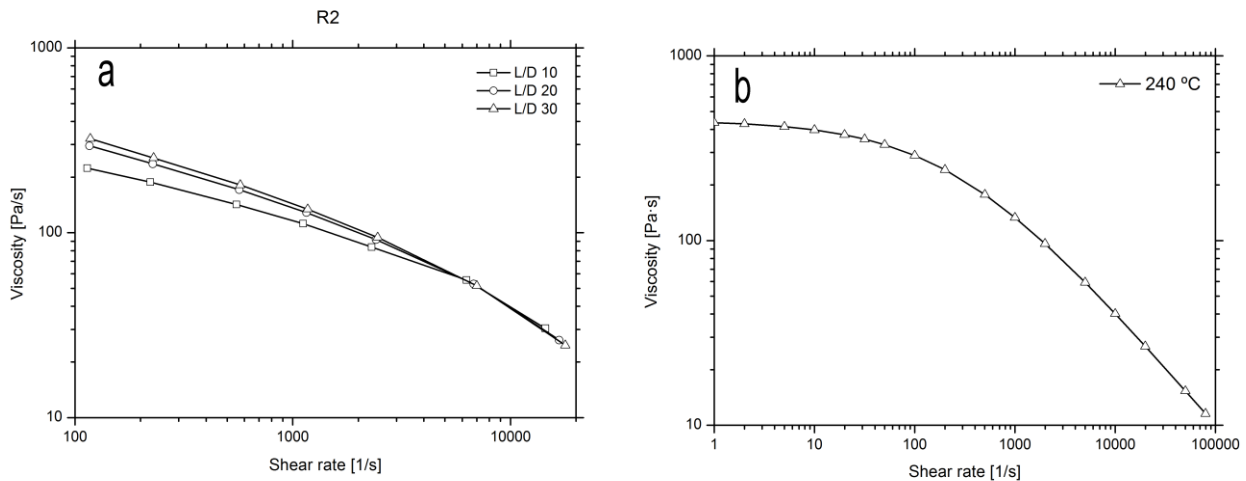
Figure 4. Viscosity of the R2 material.

$$\eta = \frac{\eta_0}{1 + \left(\dfrac{\eta_0}{\tau^*} \cdot \gamma \right)^{1-n}} \qquad (7)$$

Where η_0 [Pa s] is material viscosity under zero-shear-rate conditions, τ^* [Pa] is the model constant that shows the shear stress rate, from which the pseudoplastic behavior of the material starts, n [−] is the model constant which symbolizes the pseudoplastic behavior slope of the material as: $(1-n)$.

To determine the viscosity of the material with zero shear, we used the Williams-Landel-Ferry expression (8).

$$\eta_0 = D_1 \cdot e^{\frac{-A_1 \cdot \left(T - \tilde{T} \right)}{A_2 + \left(T - \tilde{T} \right)}} \quad , \text{ si } T \geq \tilde{T} \qquad (8)$$

$$A_2 = \tilde{A}_2 + D_3 \cdot p$$

$$\tilde{T} = D_2 + D_3 \cdot p$$

Where $\tilde{T}$ [K] is the glass transition temperature of the material, depending on the pressure. D_2 [K] is the model constant which registers the glass transition temperature of the material at atmospheric pressure. D_3 [K/Pa] is the model constant which symbolizes the variation of the glass transition temperature of the material, according to the pressure. D_1 [Pa s] is the model constant which registers the material viscosity, under zero shear rate conditions, at material glass transition temperature and at atmospheric pressure. A_1 [−] is the model constant that shows the temperature dependence of material glass transition temperature under zero shear rate conditions. $\tilde{A}_2$ [K] is a model parameter that depends on the type of material that has been considered.

3.5. Calculation method.

After obtaining the three viscosity curves (figure 4a), it was necessary to calculate the collective viscosity of the material, for which two methods were used. The first was the chi squared test and the second was squared minimums. After the study, we found the chi squared method adjusts better. The determination of viscosity was carried out using the independent parameters of the Cross WLF model.

The independent parameters of the Cross model are those which only depend on the material and which were obtained from Moldflow 6.1 ® simulation data and from the DSC. $\tilde{A}_2$ = 51.60 K. D_2, = T_g = 50 ºC = 323.15 K.

$$D_3 = \frac{\partial T_g}{\partial p} = 0k/PA$$

The dependent parameters of the Cross model which must be calculated are: n [-]; τ * [Pa]; D_1 [Pa•s]; A_1 [-].

In order to calculate these parameters we used the MathCad 2001 ® program for the interaction and separation of data from the three dies. The equation for this calculation can be seen in equation 9.

$$\text{ChiCuadrado}(D1, A1, \tau, n, \text{datos}) := \sum_{i=0}^{\text{rows(datos)}-1} \left[\frac{\left(\text{datos}_{i,2} - \eta\left(\text{datos}_{i,0}, \text{datos}_{i,1}, D1, A1, \tau, n\right)\right)^2}{\eta\left(\text{datos}_{i,0}, \text{datos}_{i,1}, D1, A1, \tau, n\right)} \right] \tag{9}$$

Once the parameters were obtained, they were introduced into the data base of Moldflow Plastics Inside 6.2® in order to then obtain the material viscosity graphics. Figure 5 shows the viscosity of virgin material at three different temperatures.
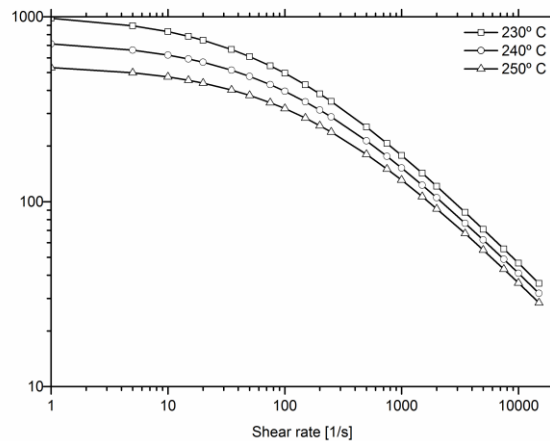

Figure 5. Viscosity of virgin material at 230 ºC, 240 ºC and 250 ºC.

4. RESULTS AND DISCUSSION

Table 2 shows the values of the Cross-WLF model and the viscosity of the material at zero shear rate. These values are very important in enabling us to carry out an accurate injection simulation using data on reprocessed material, given that no other data base exists.

The variation in the value n, (a constant of the model represented as (1-n) which describes the pseudoplastic behavior of the material) diminishes slightly with each new reprocessing cycle. This slight increase in the slope of the curve causes a slight reduction in viscosity under the same conditions of zero shear rate.

The variation of the value τ^*, which shows the shear stress rate from which the pseudoplastic behavior of the material begins, increases slightly with each cycle. This behavior causes the viscosity curve to move to the right, causing a slight increase in viscosity, considered to be a negative aspect of the material's behavior.

The parameter D_1 (a constant of the model which shows the viscosity of the material in zero shear rate conditions, and at the transition temperature and atmospheric pressure) and the parameter A_1 (a constant of the model which shows the sensitivity of the viscosity at zero shear rate at the temperature) are not represented as the model

developed with MathCad 2001 ® can give the same viscosity values for different pairs of D_1 and A_1.

The variation in the value η_0, viscosity of the material at zero shear rate was calculated with the Williams-Landel-Ferry equation (7).There is a slight drop in this value.

Table 2. Dependant parameters of the Cross-WLF model

Material	n [-]	τ^* [Pa]	D1 [Pa·s]	D2 [ºC]	D3 [K/Pa]	A1 [-]	Ã2 [K]	η_0 [Pa/s]
V	0.3551	90457	$1.11791 \cdot 10^{15}$	323.15	0	35.65	51.60	745.63
R1	0.3635	87007	$9.80508 \cdot 10^{14}$	323.15	0	35.57	51.60	696.45
R2	0.3663	115504	$1.37925 \cdot 10^{15}$	323.15	0	36.57	51.60	446.21
R3	0.3498	133992	$9.87610 \cdot 10^{14}$	323.15	0	36.56	51.60	322.03
R4	0.3843	118250	$2.10833 \cdot 10^{14}$	323.15	0	34.94	51.60	245.78
R5	0.4027	115452	$2.07138 \cdot 10^{14}$	323.15	0	35.12	51.60	209.60

Of the three parameters n, τ^* and η_0, it is the last which makes the viscosity of the material diminish slightly as the number of cycles increases, above all at low shear rate up to 200 s^{-1}. The reduction in n (which increases the slope of the curve) and the increase in τ^* (which moves the curve to the right) cause the curves to cross and join in the area of high shear rate (1,000 s^{-1} and above). This behavior can be seen in the graphics of Figures 6.

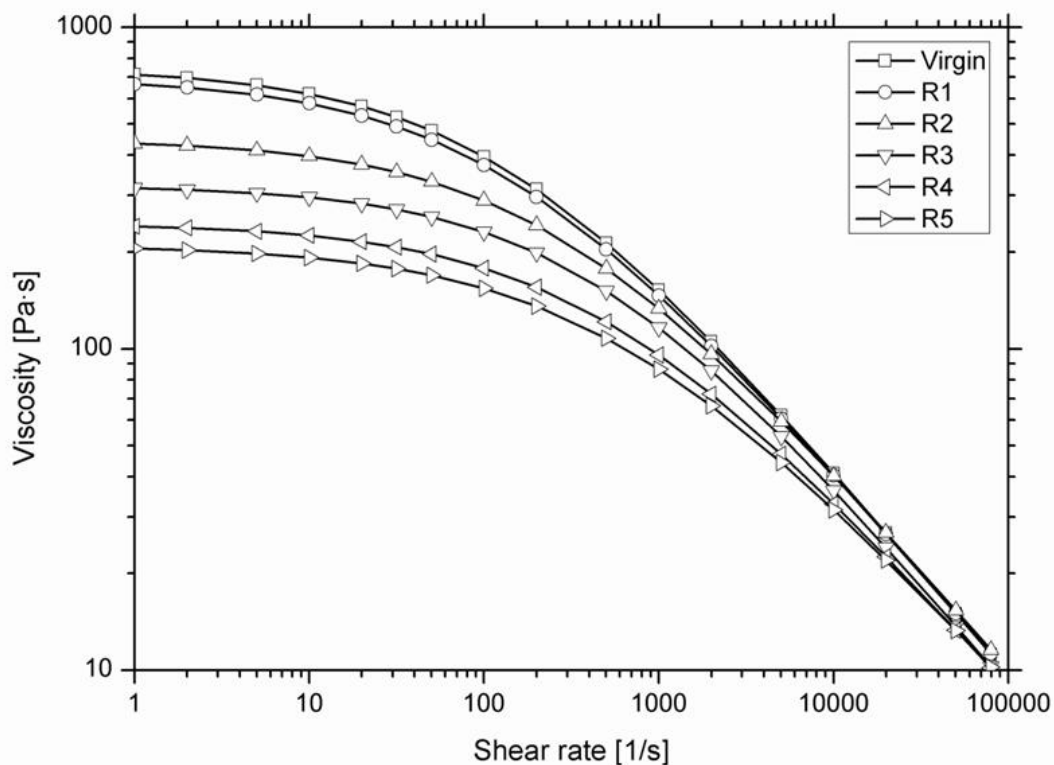**Figure 6. Viscosity of virgin and reprocessed material.**

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5. CONCLUSIONS.

We studied the effects of reprocessing on PA 6 thermoplastic material. Our study was centered on the one most important properties of the material: viscosity property. The results show, viscosity diminishes with each reprocessing cycle. At the fifth cycle, at zero shear rate, the viscosity falls by around 72%. This effect is caused by the reduction in the molecular weight caused by degradation of the material due to breaks in the polymer chains, which become shorter as the material is repeatedly reprocessed.

Furthermore, the effects of moisture on the polymer make this work as a plasticizer and further reduce the viscosity. However, in injection molding processes using shear rate of 5000 s^{-1} to 10.000 s^{-1} and these rates decreased viscosity is lower at 28% and 23% respectively. This drop in viscosity is beneficial in plastic injection, because, with less injection pressure can achieve the same results as the virgin material, but also means that as the material is more fluid, more defective pieces are generated (appearance of flash).

As the ultimate objective is to recover the original properties of virgin material, the solution is simply to reduce the injection temperature from 230 ºC to 225 ºC. Thus we achieve an energy saving (representing lower environmental impact) as well as optimum re-use of recycled material instead of virgin material, further reducing the impact on the environment.

5. REFERENCES

[1] Su, K. H., J. H. Lin and C. C. Lin, (2007), Influence of reprocessing on the mechanical properties and structure of polyamide 6. Journal of Materials Processing Technology, 192, 532-538.
[2] Bonardi, A., R. Cilloni, V. Paganuzzi and N. Grizzuti, (2003), Effects of degree of recycling on the rheology and processability of thermoplastic polymers. Journal Of Polymer Engineering, 23, 79-94.
[3] Dijkstra, D. J., (2009), Guidelines for rheologocal characterization of polyamite melts. Pure and Applied Chemistry, 81, 339-349.
[4] Maspoch, M. L., H. E. Ferrando and J. I. Velasco, (2003), Characterisation of filled and recycled PA6. Macromolecular Symposia, 194, 295-303.
[5] Navarro, R., S. Ferrandiz, J. Lopez and V. J. Segui, (2008), The influence of polyethylene in the mechanical recycling of polyethylene terephtalate. Journal of Materials Processing Technology, 195, 110-116.
[6] Cross, M. M., (1965), Rheology of Non-Newtonian Fluids - a New Flow Equation for Pseudoplastic Systems. Journal of Colloid Science, 20, 417-437.
[7] Williams, M. L., R. F. Landel and J. D. Ferry, (1955), Mechanical Properties of Substances of High Molecular Weight .19. the Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-Forming Liquids. Journal of the American Chemical Society, 77, 3701-3707.
[8] Boronat, T., V. J. Segui, M. A. Peydro and M. J. Reig, (2009), Influence of temperature and shear rate on the rheology and processability of reprocessed ABS in injection molding process. Journal of Materials Processing Technology, 209, 2735-2745.
[9] Reig, M. J., V. J. Segui, S. Ferrandiz and J. D. Zamanillo, (2007), An evaluation of processability by injection molding of ABS/PC blends obtained from recycled materials. Journal of Polymer Engineering, 27, 29-54.
[10] Reig, M. J., V. J. Segui and J. D. Zamanillo, (2005), Rheological behavior modeling of recycled ABS/PC blends applied to injection molding process. Journal of Polymer Engineering, 25, 435-457.