

## **STUDY OF RHEOLOGICAL BEHAVIOR OF REPROCESSING HIGH IMPACT POLYSTYRENE**

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**Abstract:** The effect of reprocessing High Impact Polystyrene (HIPS) has been studied in this paper. To simulate recycled HIPS, we reprocessed virgin HIPS through 5 cycles. The HIPS 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. Our results show that viscosity decrease, as the number of reprocessing cycles increases.

### **1. INTRODUCCION**

High Impact Polystyrene is a thermoplastic formed in two phases: a styrene phase and a butadiene phase. Among the diverse applications of this material is its use in the manufacture of packaging materials. This type of product can be characterized as having a short life cycle, and consequently a huge quantity of domestic waste is generated, which must be dealt with to reduce environmental impact.

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 [3] analyzed the influence of the reprocessing cycles on the mechanical properties of polyamide 6 (PA6). Su's work is relevant to our work because he carried out a study of mechanical and rheological properties, although it was with a different material. 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. [2,12] Other authors, including Santana [12] in their work in 2002 and Soriano [3] have carried out similar studies on HIPS. Santana investigated the thermo-mechanical properties of post-consumer HIPS (from disposable cups) through five consecutive injection moulding steps to simulating the recycling cycles. Santana states that tensile strength, modulus of elasticity and elongation at break properties of HIPS were slightly reduced, which indicate an effect of decreasing of molecular weight.

Soriano analyzes influence of the number of processing cycles on the microstructure and macroscopic properties on a HIPS in coextruded sheet, maintaining a constant composition of 70 wt% of virgin HIPS and 30 wt% of recycled HIPS. With respect to the rheological properties, Soriano shows that the viscosity of the material subjected to one processing cycle is higher than of the virgin material, especially at low shear rate, but as shear rate increases, all, curves tend to concur to a similar value and this difference in viscosities becomes very small. After the second and up to the sixth processing cycle, the viscosity decreases. Soriano calculates the value of  $n$  (the model constant which symbolizes the pseudoplastic behavior slope of the material) obtaining a value of 0.31 for virgin material and 0.35 for the sixth processing cycle. This data is calculated from apparent viscosity ( $\eta_{ap}$ ) as Soriano used only one die (L/D 30mm) instead of the three recommended by ISO 11443.

On the other hand, Balard [10] analyzed the compatibility of polycarbonate (PC) with acrylonitrile-butadiene-styrene (ABS) using waste material from the electrical sector,

reaching the conclusion that the composition range comprised between 10 and 20 wt% PC is most interesting in order to obtain an industrial material with balanced properties, for different reasons: firstly, mechanical ductile properties do not decrease. Secondly, processing conditions are similar to other styrenic derivatives and finally, this composition range reflects the generation ratio of these wastes which is close to 4:1 for ABS/PC.

Finally, Navarro [11] and Garcia [1] analyzed 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 terephthalate (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 10.000 s<sup>-1</sup>. 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.

Studies on degradation of polymers are extremely numerous, as are studies on the effect of incorporating other polymers in order to improve and recover properties in the recycled material. But there appear to have been no studies which carry out a long term analysis of the recycling of these previously modified and then recovered polymers. 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 capillary rheometer along with the Bagley and Rabinowitsc corrections.

Some injection processing simulations, such as Autodesk Moldflow Synergy 2012®, use values of the parameters from the Cross-WLF model. Cross [5] and Williams [6] carried out experiments to reproduce the rheological behavior of the materials during the injection process. Reig in his works [7,8] and Boronat [14] applied these models in their studies on reprocessed ABS + PC and ABS respectively. Reig in his work of 2007 determined a Material Processability Index (MPI) from three mixtures of ABS + PC with a different Melt Flow Index (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%.

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.

The objective of this present work is to study the rheological behavior during the recovery process of High Impact Polystyrene waste. We studied the reprocessing phase from virgin material through to the fifth reprocessing cycle.

## **2. EXPERIMENTAL**

To develop this study, we used HIPS 6541 supplied by the company Total Petrochemicals ®. For the extrusion, we used a conventional double spindle extruder at a temperature of 210 °C, with a pelletizer incorporated to obtain the pellet. We carried out five extrusion cycles (R1, R2, R3, R4 and R5) beginning with virgin HIPS (V).

The rheological analysis of all the materials was done using a Thermo Haake Rheoflizer MT® capillary rheometer. The temperature used in the rheometer was 230 °C, 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<sup>-1</sup>. 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

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

$$\eta_{ap} = \frac{\tau_{ap}}{\gamma_{ap}} \quad (1)$$

$$\tau_{ap} = \frac{p \cdot D}{4 \cdot L} \quad (2)$$

Where:  $\tau_{ap}$  is the apparent shear stress [Pa],  $\gamma_{ap}$  is the apparent shear rate [s<sup>-1</sup>], 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.

The passage of melted material from a greater to a lesser diameter causes over-pressure which slightly alters the results obtained directly from the capillary 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 capillary wall. Boronat [14] 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, 10,000 [s<sup>-1</sup>]).

Figure 1 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  $\tau$  [Pa], where p is the pressure obtained by the adjustment and we used the corrected L/D ratio, (L/D)<sub>c</sub> which is the L/D distance at which the pressure is zero.

$$\tau = \frac{P}{4[(L/D)+(L/D)_c]} \quad (3)$$

#### 3.2. RABINOWITSC'S CORRECTION.

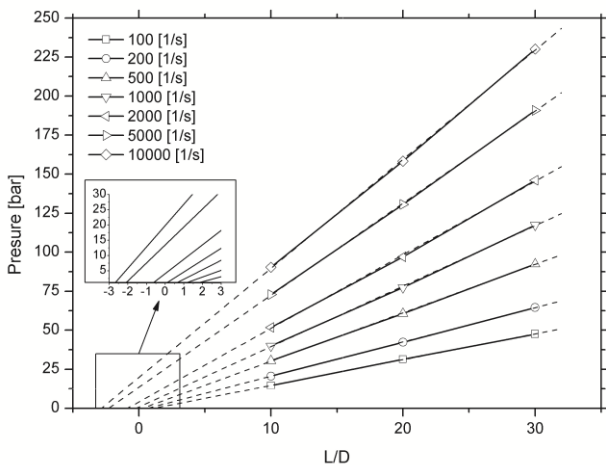
Rabinowitsc's correction allows us to determine the true shear rate  $\gamma$  [s<sup>-1</sup>] using equation (4.) To obtain the data with greater precision, it is necessary to represent graphically the true shear stress log ( $\tau$ ) against the true shear rate log ( $\gamma$ ) (figure 2) and adjust the points of cubic equation (5). In equation (4), for the data of the log  $\tau$ , log  $\tau$ adjust

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.

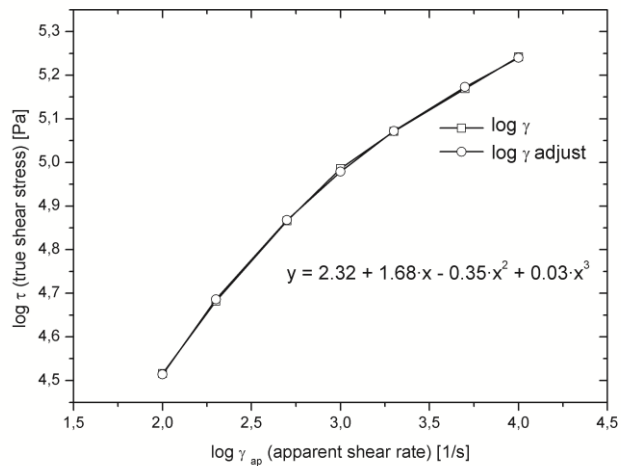
$$\gamma = \frac{\gamma_{ap}}{4} \cdot \left( 3 + \frac{d \log \gamma_{ap}}{d \log \tau} \right) \quad (4)$$

Where  $\gamma_{ap}$  [s-1] is the apparent shear rate.

$$y = a_0 + a_1 \cdot x + a_2 \cdot x^2 + a_3 \cdot x^3 \quad (5)$$



**Figure 1. Bagley's correction for virgin material.**



**Figure 2. Rabinowitsc's correction for virgin material and a die L/D 10.**

### 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 (Figure 3a). From these three curves, one single curve was calculated as a final result. The viscosity curve for 230 °C in 3b is this final curve.

$$\eta = \frac{\tau}{\gamma} \quad (6)$$

### 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 7 allows us to calculate the viscosity of the material at whichever temperature beginning with a viscosity curve of any given temperature.

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

Where  $\eta_0$  [Pa s] is material viscosity under zero-shear-rate conditions,  $\tau^*$  [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).

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

Where  $T_g$  [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 3a), 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.

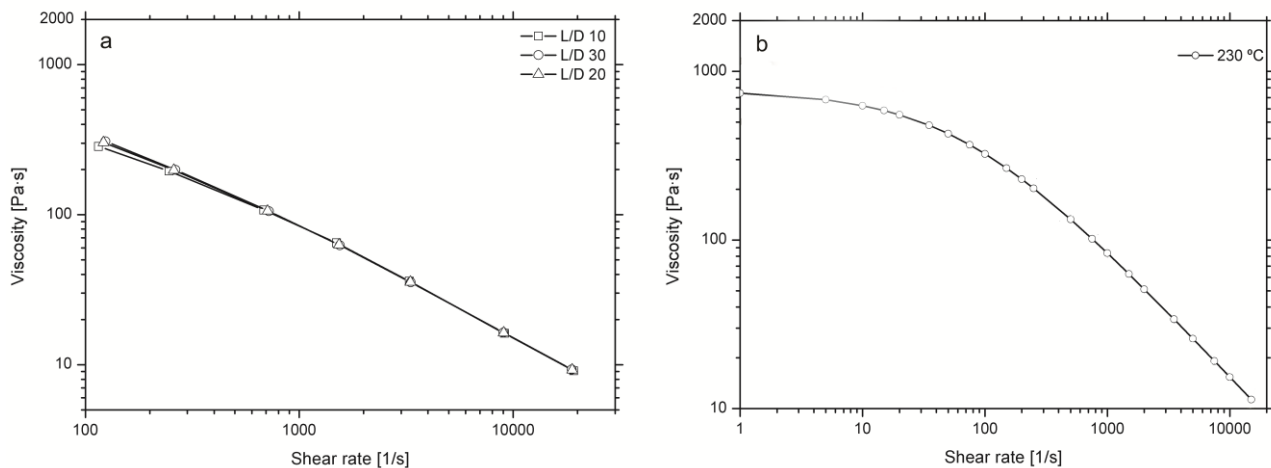
**The independent parameters** of the Cross model are those which only depend on the material and which were obtained from Moldflow 6.1 ® simulation data and from the DSC.  $\tilde{A}_2 = 51.60$  K.  $D_2 = T_g = 86$  °C = 359.15 K.  $D_3 = \frac{\partial T_g}{\partial p} = 0$  K/Pa

**The dependent parameters** of the Cross model which must be calculated are:  $n$  [-];  $\tau^*$  [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.

$$\text{ChiCuadrado}(D_1, A_1, \tau, n, \text{datos}) := \sum_{i=0}^{\text{rows}(\text{datos})-1} \left[ \frac{\left( \text{datos}_{i,2} - \eta(\text{datos}_{i,0}, \text{datos}_{i,1}, D_1, A_1, \tau, n) \right)^2}{\eta(\text{datos}_{i,0}, \text{datos}_{i,1}, D_1, A_1, \tau, n)} \right] \quad (9)$$

Once the parameters were obtained, they were introduced into the data base of as Autodesk Moldflow Synergy 2012®, in order to then obtain the material viscosity graphics (Figure 3b).



**Figure 3. Viscosity of the virgin material.**

### 3. RESULTS AND DISCUSSION

Table 1 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.

**Table 1. Dependant parameters of the Cross-WLF mode**

| Material | n [-]  | t* [Pa] | D1 [Pa·s]              | D2 [°C] | D3 [K/Pa] | A1 [-]  | Å2 [K] | [Pa/s] |
|----------|--------|---------|------------------------|---------|-----------|---------|--------|--------|
| V        | 0.2244 | 50854   | $1.2780 \cdot 10^{13}$ | 359.15  | 0         | 31.9624 | 51.6   | 771.5  |
| R1       | 0.2200 | 52786   | $1.8566 \cdot 10^{11}$ | 359.15  | 0         | 26.2677 | 51.6   | 741.7  |
| R2       | 0.2118 | 55620   | $3.1205 \cdot 10^{11}$ | 359.15  | 0         | 27.0390 | 51.6   | 706.5  |
| R3       | 0.2216 | 53274   | $1.8415 \cdot 10^{14}$ | 359.15  | 0         | 35.7975 | 51.6   | 660.4  |
| R4       | 0.2098 | 54592   | $9.4788 \cdot 10^{13}$ | 359.15  | 0         | 34.8571 | 51.6   | 679.3  |
| R5       | 0.2161 | 53724   | $9.4113 \cdot 10^{14}$ | 359.15  | 0         | 38.0400 | 51.6   | 647.5  |

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.

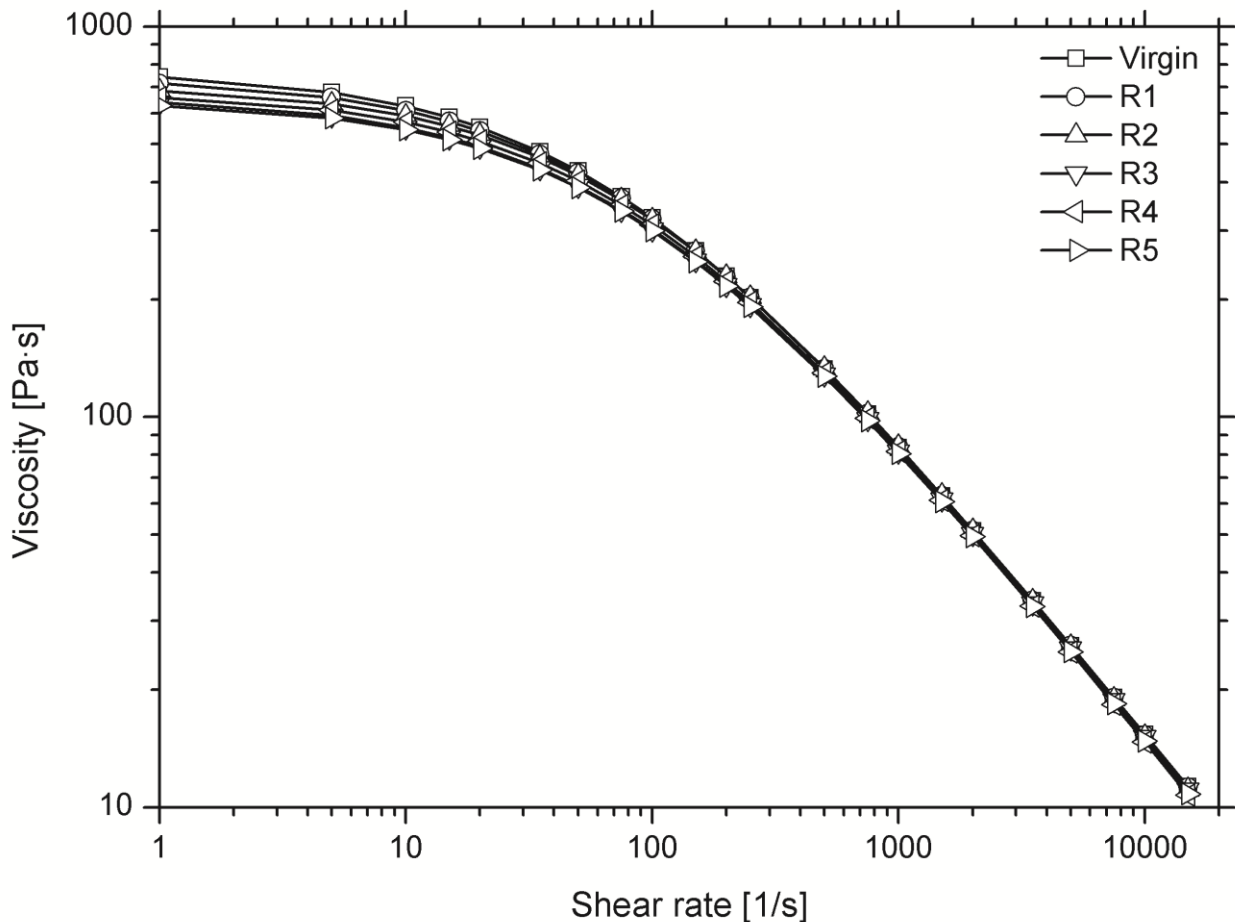
The variation of the value  $\tau^*$ , which shows the shear stress rate from which the pseudoplastic behavior of the material begins, increases slightly with each cycle. This behavior causes the viscosity curve to move to the right, causing a slight increase in viscosity, considered to be a negative 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  $\eta_0$ , viscosity of the material at zero shear rate was calculated with the Williams-Landel-Ferry equation (7). As can be seen in Table 1, there is a slight drop in this value.

Of the three parameters n,  $\tau^*$  y  $\eta_0$ , 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<sup>-1</sup>. The reduction in n (which increases the slope of the curve) and the increase in

$\tau^*$  (which moves the curve to the right) cause the curves to cross and join in the area of high shear rate ( $1,000 \text{ s}^{-1}$  and above). This behavior can be seen in the graphics of Figure 4.



**Figure 4. Viscosity of virgin and reprocessed material**

Viscosity is a property that is extremely sensitive to variations in molecular weight. This behavior which sees falls in viscosity is due to degradation of the material (breaks in the polymer chains which then become shorter), as the material is repeatedly reprocessed (extruded and pelletized). Santana [12] obtained a similar result when reprocessing HIPS. The viscosity of HIPS diminishes with repeated cycles, although the final data is not comparable given that a slit die rheometer at  $200 \text{ }^\circ\text{C}$  was used. Navarro [11] showed that the study of shear rate in the interval  $5,000 \text{ s}^{-1}$  and  $10,000 \text{ s}^{-1}$  is of great importance, as these values are reached by the plastic during the injection process.

#### **4. CONCLUSIONS**

We studied the effects of reprocessing on HIPS thermoplastic material. Our study was centered on the rheological behavior. Viscosity diminishes with each reprocessing cycle. At the fifth cycle, at zero shear rate, the viscosity falls by around 16%. 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. This effect has more influence than the crosslinking of the butadiene, which should increase viscosity. This is because the reprocessing in the extruder took place at a

relatively low temperature, 210 °C, which meant that there was not a great deal of crosslinking, given that this phenomenon only begins to occur at about 190 °C.

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