

# Study of Rheological Behavior During the Recovery Process of High Impact Polystyrene Using Cross-WLF Model

M. A. Peydró, F. Parres, J. E. Crespo, D. Juárez

*Departamento de Ingeniería Mecánica y de Materiales, Universidad Politécnica de Valencia (Campus de Alcoy), Plaza Ferrándiz y Carbonell, s/n 03801 Alcoy, España*

Received 15 July 2010; accepted 24 September 2010

DOI 10.1002/app.33444

Published online 10 December 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** The effect of reprocessing two mixtures: recycled high impact polystyrene (HIPS) with polybutadiene (PB); and HIPS with styrene-ethylene-butylene-styrene (SEBS) have been studied in this article. To simulate recycled HIPS, we reprocessed virgin HIPS through five cycles. The virgin HIPS, the recycled HIPS, and the mixtures have been mechanically and rheologically characterized after the various cycles of reprocessing to evaluate their corresponding properties and correlate them with the number of cycles undergone. To widen our injection simulation analysis by computer (CAE: Computer Aided Engineering) of these new materials with additives, 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 tensile strength increases, while the

lengthening and viscosity decrease, as the number of reprocessing cycles increases. If we mix PB or SEBS with degraded HIPS, the mechanical properties of the virgin material are recovered and the rheological behavior maintains the viscosity values for the mixture with PB but these diminish notably for the mixture with SEBS. The results on mechanical properties show that the mixture with SEBS behaves better than the mixture with PB as the number of cycles increases. The viscosity of the mixture with SEBS diminishes more than the viscosity of the mixture with PB as the number of reprocessing cycles increases. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2400–2410, 2011

**Key words:** polystyrene; blends; reprocessing; viscosity; rheometry

## INTRODUCTION

HIPS 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 et al.<sup>1</sup> 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 et al.'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 five reprocessed.<sup>2,3</sup> Other authors, including Santana and Manrich<sup>2</sup> in their work in 2002 and Soriano et al.<sup>3</sup> have carried out similar studies on HIPS. Santana and Manrich investigated the thermo-mechanical properties of postconsumer HIPS (from disposable cups) through five consecutive injection molding steps to simulating the recycling cycles. Santana and Manrich state 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. The rheological characterization was measured by parallel plates rheometer (different equipment used by us), but the results show the fall of the viscosity.

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 et al. show 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

Correspondence to: M. A. Peydró (mpeydro@mcm.upv.es).

Contract grant sponsor: Polytechnic University of Valencia; contract grant number: 20091056 [First Projects of Investigation (PAID 06-09)].

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 et al. calculate 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 et al. used only one die ( $L/D$  30 mm) instead of the three recommended by ISO 11443.

On the other hand, Balart et al.<sup>4</sup> 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 to obtain an industrial material with balanced properties, for different reasons: first, mechanical ductile properties do not decrease. Second, 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 et al.<sup>5</sup> and Garcia et al.<sup>6</sup> analyzed mixtures of polymers with the aim of improving properties of the recovered material. Navarro et al., 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 5000 and 10,000  $s^{-1}$ . 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.

Studies on degradation of polymers are extremely numerous, as are studies on the effect of incorporating other polymers 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 Moldflow Plastics Inside 6.2<sup>®</sup>, use values of the pa-

rameters from the Cross-WLF model. Cross<sup>7</sup> and Williams et al.<sup>8</sup> carried out experiments to reproduce the rheological behavior of the materials during the injection process. Reig et al. in their works<sup>9,10</sup> and Boronat et al.<sup>11</sup> applied these models in their studies on reprocessed ABS + PC and ABS, respectively. Reig et al. in their work of 2007 determined a Material Processability Index (MPI) from three mixtures of ABS + PC with a different Melt Flow Index (MFI). Reig et al. 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 et al. 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 work is to study the rheological behavior during the recovery process of high impact polystyrene waste, during the three stages of the recovery process. First, we studied the reprocessing phase from virgin material through to the fifth reprocessing cycle. Second, we studied the phase of recovering properties of the material by adding polybutadiene (PB) and styrene-ethylene-butylene-styrene block copolymer (SEBS). Finally, we studied the phase which involves mixing HIPS-PB and HIPS-SEBS.

A further objective of this work is to determine the parameters of the cross-WLF model, both for virgin and recycled to incorporate them into plastic injection simulations.

## EXPERIMENTAL

### Materials

To develop this study, we used HIPS 6541 supplied by the company Total Petrochemicals<sup>®</sup>. HIPS 6541 is a very fluid grade of material. For the mixtures, we used PB supplied by ACTECO<sup>®</sup> (Alcoy, Spain) and SEBS supplied by Applicazioni Plastiche Industriali<sup>®</sup> (Mussolente, Italy).

### Methods and measurements

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). Subsequently, after the fifth cycle, we made mixtures with PB of 1, 2, 4, and 8% by weight (6th cycle). In the same way, we also made mixtures of HIPS with SEBS using the same percentages. Finally, we selected the mixtures with 2% PB and 2% SEBS and carried out four further reprocessing cycles, thus obtaining a material that had undergone 10 reprocessing cycles."

The rheological analysis of all the materials was done using a Thermo Haake Rheoflaxer MT<sup>®</sup> 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 1 mm and with  $L/D$  ratios of 10, 20, and 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.

For the calculation of the  $T_g$  (temperature of vitreous transition), we used a differential scanning calorimeter (DSC) Mettler Toledo, S.A.E.<sup>®</sup>, model 821e, a type of power compensation DSC in compliance with ISO 11357-1 and 11357-4.

For the injection, we used a Meteor 270/75 injector supplied by Mateu and Solé<sup>®</sup> (Barcelona, Spain) at 230°C injection temperature.

For the mechanical characterization, we used a universal traction machine ELIB 30 (S.A.E. Iberstest, Madrid, Spain) in compliance with ISO 527.

## 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, and  $L$  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 calcu-

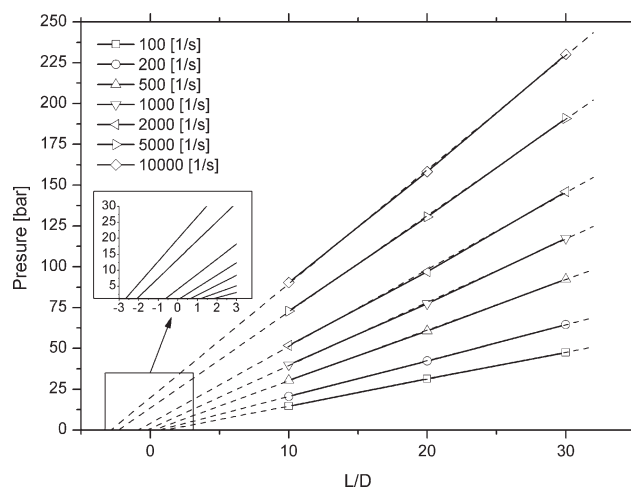


Figure 1 Bagley's correction for virgin material.

late 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 et al.<sup>11</sup> used these corrections in his work on reprocessing of ABS.

### Bagley's correction

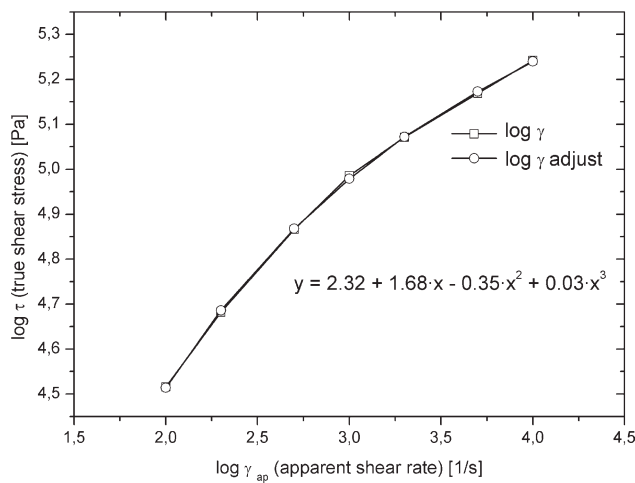
The application of this method required that we use the polymer at a particular temperature and with three dies with different length/diameter ratios ( $L/D = 10$ ,  $L/D = 20$ ,  $L/D = 30$ ), to obtain the pressure in each die at different shear rate (100, 200, 500, 1000, 2000, 5000, 10,000 [s<sup>-1</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 Eq. (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,  $(L/D)_c$  which is the  $L/D$  distance at which the pressure is zero.

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

### Rabinowitsch's correction

Rabinowitsch's correction allows us to determine the true shear rate  $\gamma$  (s<sup>-1</sup>) using Eq. (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  $\log(\gamma)$  (Fig. 2) and adjust the points of cubic Eq. (5). In Eq. (4), for the data of the  $\log \tau$ ,  $\log \tau_{adjusted}$  adjusted for the curve of Eq. (5). In 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  $L/D = 20$  and 30.



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

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

where  $\gamma_{ap}$  ( $s^{-1}$ ) is the apparent shear rate.

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

### Calculation of viscosity

The viscosity was calculated with the quotient between shear stress and shear rate, as seen in Eq. (6). As with the calculation of viscosity, three dies were used, we also obtained three viscosity curves for each material [Fig. 3(a)] From these three curves, one single curve was calculated as a final result. The viscosity curve for 230°C in Figure 3(b) is this final curve.

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

### 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 [eqs. (7) and (8)]. The Cross model<sup>7</sup> 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).

$$\begin{aligned} \eta_0 &= D_1 \cdot e^{\frac{-A_1 \cdot (T - \tilde{T})}{A_2 + (T - \tilde{T})}}, \text{ si } T \geq \tilde{T} \quad (8) \\ A_2 &= \tilde{A}_2 + D_3 \cdot p \\ \tilde{T} &= D_2 + D_3 \cdot p \end{aligned}$$

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.

### Calculation method

After obtaining the three viscosity curves [Fig. 3(a)], 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<sup>®</sup> simulation data and from the DSC [Fig. 4].  $\tilde{A}_2 = 51.60$  K.  $D_2 = T_g = 86^\circ\text{C} = 359.15$  K.  $D_3 = \frac{\partial T_g}{\partial p} = 0$  K/Pa

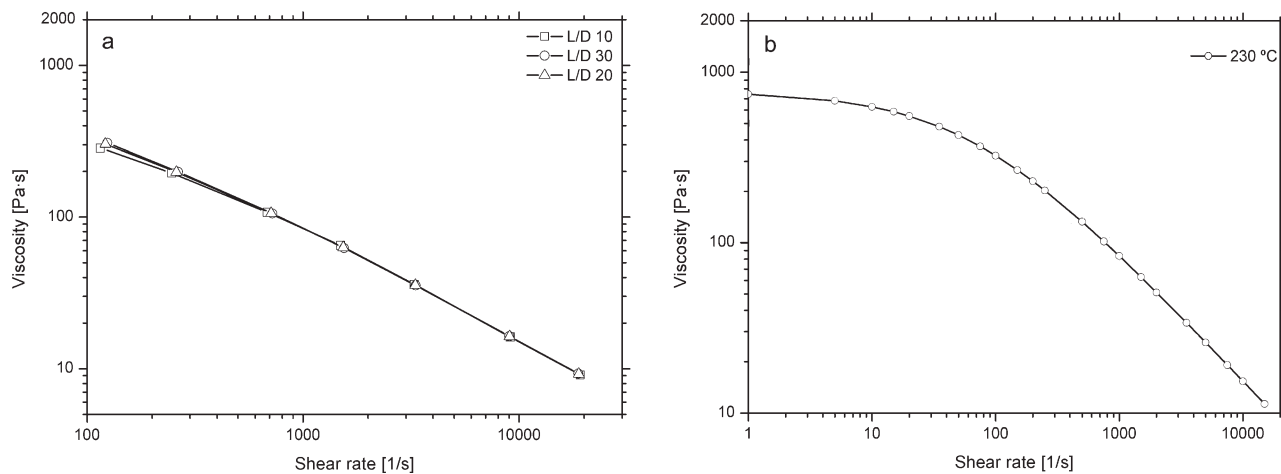
The dependent parameters of the cross model which must be calculated are:  $n$ (–);  $\tau^*$ (Pa);  $D_1$ (Pa/s);  $A_1$ (–).

To calculate these parameters, we used the MathCad 2001<sup>®</sup> program for the interaction and separation of data from the three dies. The equation for this calculation can be seen in Eq. (9).

$$\begin{aligned} \text{ChiCuadrado}(D1, A1, \tau, n, \text{datos}) &= \sum_{i=0}^{\text{rows}(\text{datos})-1} \\ &\times \left[ \frac{(\text{datos}_{i,2} - \eta(\text{datos}_{i,0}, \text{datos}_{i,1}, D1, A1, \tau, n))^2}{\eta(\text{datos}_{i,0}, \text{datos}_{i,1}, D1, A1, \tau, n)} \right] \quad (9) \end{aligned}$$

Once the parameters were obtained, they were introduced into the data base of Moldflow Plastics





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

Inside 6.2 to then obtain the material viscosity graphics. Figure 5 shows the viscosity of virgin material at three different temperatures.

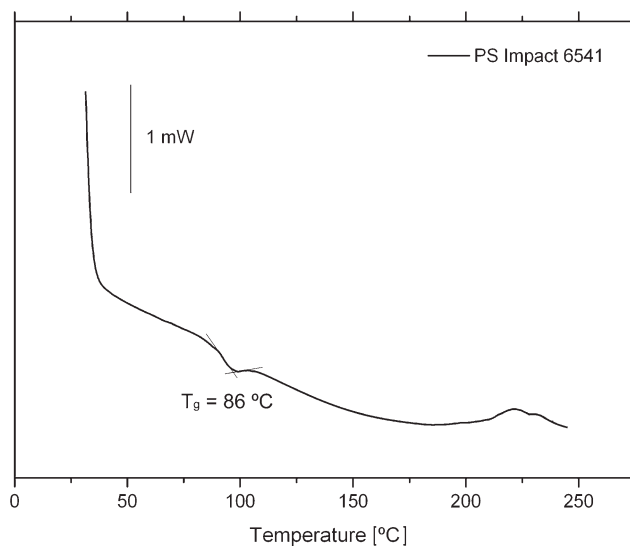
## RESULTS AND DISCUSSION

### Study of virgin material and its degradation when reprocessed

#### Analysis of mechanical properties

The mechanical properties of any material are fundamental for its use in any particular application. The traction test is extremely important because it allows us to understand properties such as tensile strength and elongation at break.

Thermal degradation as a consequence of recycling processes causes changes in the internal structure of the polymer and these changes in turn cause variations in its mechanical properties.

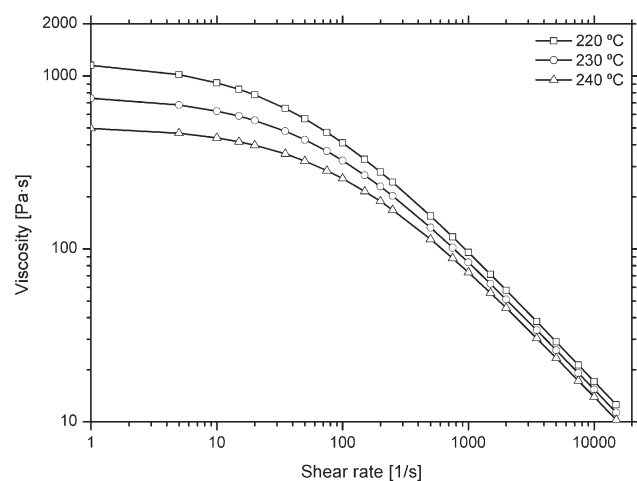


**Figure 4** DSC of virgin HIPS

In the study carried out on HIPS, Table I showing the values of tensile strength with the extrusion cycles reveals an increasing lineal evolution in the values. Furthermore, the evolution of the elongation values with extrusion cycles is different to those obtained with the ultimate strength; in this case, the loss of elongation is very significant between the first and third cycles, whereas after these extrusion cycles the values remain constant.

Initially, the variations produced in the HIPS are not significantly noteworthy, and this behavior is logical given that the temperatures used in the extrusion process are not particularly high. Kalfoglou and Chaffey<sup>12</sup> showed that large variations only take place in the mechanical properties of HIPS when extremely high temperatures are used (290°C).

In spite of using relatively low extrusion and injection temperatures, the presence of a butadiene phase causes a degree of crosslinking of the chains, and as a consequence, an increase in rigidity in the HIPS.



**Figure 5** Viscosity of virgin material at 220°C, 230°C, and 240°C.

TABLE I  
Resistance to Stress and Elongation at Break of the Virgin Material  
and Reprocessed Material

Material	V	R1	R2	R3	R4	R5
Tensile strength [MPa]	13.58	13.84	14.29	15.02	15.16	15.91
Elongation at break [%]	9.80	9.67	9.00	8.25	8.00	8.00

Michaeli et al.<sup>13</sup> carried out studies in this field and observed that significant variations in mechanical properties do not occur as a result of the slight interlacing of butadiene chains at processing temperatures of around 190°C. Soriano et al.<sup>3</sup> studied the results of this crosslinking effect which is produced when the temperature of the thermoplastic is increased time after time on reprocessed HIPS obtained by coextrusion, and the same conclusion was reached.

#### Analysis of rheological properties

Table II 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  $\tau^*$ , 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 Math-Cad 2001<sup>®</sup> 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 Eq. (7). As can be seen in Table II, there is a slight drop in this value.

Of the three parameters  $n$ ,  $\tau^*$ , and  $\eta_0$ , 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 (1000 s<sup>-1</sup> and above). This behavior can be seen in the graphics of Figures 6 and 7.

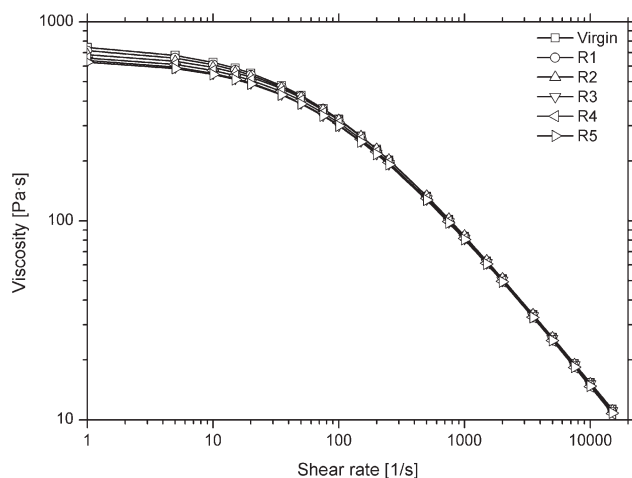
Viscosity is a property that is extremely sensitive to variations in molecular weight. This behavior which sees falls in viscosity is due to degradation of the material (breaks in the polymer chains which then become shorter), as the material is repeatedly reprocessed (extruded and pelletized). Santana and Manrich<sup>2</sup> 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°C was used. Navarro et al.<sup>5</sup> showed that the study of shear rate in the interval 5000 and 10,000 s<sup>-1</sup> is of great importance, as these values are reached by the plastic during the injection process. Figure 7 shows the fall in viscosity at these shear rate with an increase in number of cycles.

#### Effect of incorporating PB and SEBS on the properties of degraded HIPS

To degraded material (R5), we added 1, 2, 4, and 8% PB and then did exactly the same for SEBS. For each

TABLE II  
Dependant Parameters of the Cross-WLF Model

Material	$n$ (-)	$\tau^*$ (Pa)	$D_1$ (Pa/s)	$D_2$ (°C)	$D_3$ (K/Pa)	$A_1$ (-)	$\bar{A}_2$ (K)	$\eta_0$ (Pa/s)
V	0.2244	50,854	$1.2780 \times 10^{13}$	359.15	0	31.9624	51.6	771.5
R1	0.2200	52,786	$1.8566 \times 10^{11}$	359.15	0	26.2677	51.6	741.7
R2	0.2118	55,620	$3.1205 \times 10^{11}$	359.15	0	27.0390	51.6	706.5
R3	0.2216	53,274	$1.8415 \times 10^{14}$	359.15	0	35.7975	51.6	660.4
R4	0.2098	54,592	$9.4788 \times 10^{13}$	359.15	0	34.8571	51.6	679.3
R5	0.2161	53,724	$9.4113 \times 10^{14}$	359.15	0	38.0400	51.6	647.5



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

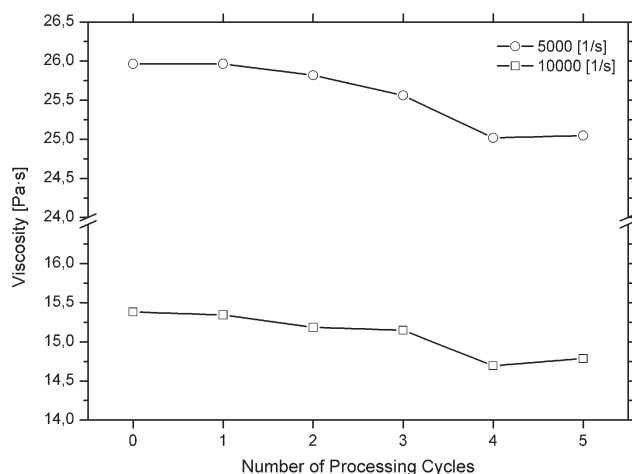
of these mixtures, we carried out mechanical and rheological characterizations.

#### Analysis of mechanical properties

The loss of ductility in the recycled HIPS limits its use in some applications. Given that a change in properties is basically due to interlacing of butadiene chains, the addition of polybutadiene is common at an industrial level to increase the flexibility of the recycled HIPS. The quantities generally used are around 2% by weight with respect to the HIPS.

Our study takes this a step further and makes comparisons between PB and SEBS with different percentages by weight (1, 2, 4, and 8%).

For both compounds, PB and SEBS, the evaluation of the values of the different mechanical properties (tensile strength and elongation at break) is very similar, with the ductility of the mixtures increasing in function of the PB or SEBS content. First, tensile strength falls



**Figure 7** Viscosity of virgin and reprocessed material at shear rate of 5,000 and 10,000  $\text{s}^{-1}$ .

**TABLE III**  
Tensile Strength and Elongation at Break of Virgin Material, R5, and of the Eight Mixtures

Material	Tensile strength (MPa)		Elongation at break (%)	
V	13.58		9.80	
R5	15.91		8.00	
	Tensile strength (MPa) with PB	Tensile strength (MPa) with SEBS	Elongation at break (%) with PB	Elongation at break (%) with SEBS
R5+1%	15.96	15.29	11.10	8.63
R5+2%	14.78	14.58	12.05	10.50
R5+4%	14.11	14.28	12.98	11.13
R5+8%	13.65	14.20	14.80	11.60

gradually until it reaches values closest to those of virgin HIPS with a content of 8% (Table III).

In contrast, the addition of SEBS and PB causes the opposite effect on elongation at break, where in this case the values increase significantly even with relatively low percentages; surpassing the initial properties of the virgin HIPS with 1% of PB and 2% of SEBS.

The incorporation of PB and SEBS in HIPS after the fifth extrusion allows the recovery of the initial properties of virgin HIPS to a degree, and in some cases, even surpass them. Initially, the addition of 2% PB and SEBS allows the recovery of the original properties of HIPS, due to the elastic character of PB and SEBS.

Tasdemir and Karatop<sup>14</sup> observed this same behavior when mixing small quantities of SIS or SBS with a mixture of ABS/PC. SIS and SBS have very similar properties to SEBS. Santana and Manrich<sup>15</sup> obtained similar results when they incorporated 5, 6, and 7% SEBS to a mixture of PP/HIPS.

#### Analysis of rheological properties

Table IV shows the cross WLF values and the viscosity of the material at zero shear rate. The variation in the value of  $n$  increases slightly for the mixture with 2% PB and remains constant for 4 and 8% PB. This slight increase in  $n$  produces a slight reduction in the curve slope which indicates a slight increase in viscosity at the same zero shear rate, but this variation is minimal. Concerning the mixtures with SEBS, we saw that this value increases slightly for 1% and remains more or less constant for the rest. This slight reduction in the curve also means a slight increase in viscosity.

The variation in the value of  $\tau^*$  diminishes with R5. All the mixtures with PB have similar values which are very close to those of virgin material. This

TABLE IV  
Dependent Parameters of the Cross-WLF Model and Viscosities at Zero Shear Rate

Material	$n$ (-)	$\tau^*$ (Pa)	$D_1$ (Pa/s)	$D_2$ ( $^{\circ}$ C)	$D_3$ (K/Pa)	$A_1$ (-)	$\tilde{A}_2$ (K)	$\eta_2$ (Pa/s)
V	0.2244	50,854	$1.2780 \times 10^{13}$	359.15	0	31.9624	51.6	771.5
R5	0.2161	53,724	$9.4113 \times 10^{14}$	359.15	0	38.0400	51.6	647.5
R5+1% PB	0.2145	51,683	764.1	359.15	0	0.11285	51.6	699.4
R5+2% PB	0.2239	50,663	428.6	359.15	0	-0.5858	51.6	656.0
R5+4% PB	0.2184	50,382	605.0	359.15	0	-0.0855	51.6	644.3
R5+8% PB	0.2204	51,274	$1.314 \times 10^{14}$	359.15	0	35.3877	51.6	637.4
R5+1% SEBS	0.2452	49,640	$1.6399 \times 10^{14}$	359.15	0	36.0268	51.6	496.7
R5+2% SEBS	0.2346	53,542	$7.2883 \times 10^{13}$	359.15	0	35.0449	51.6	454.8
R5+4% SEBS	0.2240	52,229	$3.6119 \times 10^{13}$	359.15	0	33.9803	51.6	493.6
R5+8% SEBS	0.2416	47,335	$2.6218 \times 10^{13}$	359.15	0	33.6123	51.6	469.8

behavior causes the curve to move to the left for all the mixtures, causing a slight reduction in viscosity. Concerning the mixtures with SEBS, again the values are similar and there is no recognizable trend. We should highlight the fact that for the mixtures of 1 and 8% SEBS this value is the same as that of virgin material, while for the mixtures with 2 and 4% the value is closer to that of R5, but the variations are again minimal.

The variation in the value of  $\eta_0$  was calculated with the Williams–Landel–Ferry Eq. (7). The adhesion of PB to degraded HIPS (R5) causes a very slight fall in this value, but all values are similar to R5. Concerning the mixtures with SEBS, we saw the exact opposite. First, there was a significant reduction in this value for all the mixtures compared R5 and virgin material, and second, that the percentage of SEBS made no difference, as all the mixtures have the same viscosity value at zero shear rate.

$\eta_0$ , as was observed with virgin and reprocessed material, is the determining factor when calculating the viscosity curves. We saw that the mixtures with 1% PB were somewhat higher than the rest of the mixtures of PB, which all showed similar value. This can be seen in Figure 8, the viscosity graph. With respect to the mix-

tures with SEBS, the behavior of the four mixtures is similar at low shear rates, from 0 to  $200 \text{ s}^{-1}$ . The viscosity is less than with virgin or R5 material (influenced by the value of  $\eta_0$ ) and as the shear rate increases, this difference diminishes (influenced by  $n$  which makes the curve diminish). This can be seen in Figure 9.

The shear rate was again studied for the interval between 5000 and  $10,000 \text{ s}^{-1}$ . Figure 10 shows that the adhesion for 1 and 2% for both materials to R5 has practically no effect on viscosity, while for mixtures of 4 and 8%, this is reduced. We can also see that for the SEBS mixtures, the fall is more marked (up to 6.2%) than with the PB (4.4%).

#### Study of properties of degraded HIPS/SEBS and degraded HIPS/PB blends after several reprocessing cycles

The addition of compounds to recycled polymers has, in most cases, beneficial effects on the recycled material. However, a fact that is often neglected when studying the recycling of such materials is the effect that these compounds may have when the material is submitted to a number reprocessing cycles.

In the previous section we studied the effect of incorporating PB and SEBS on the properties of

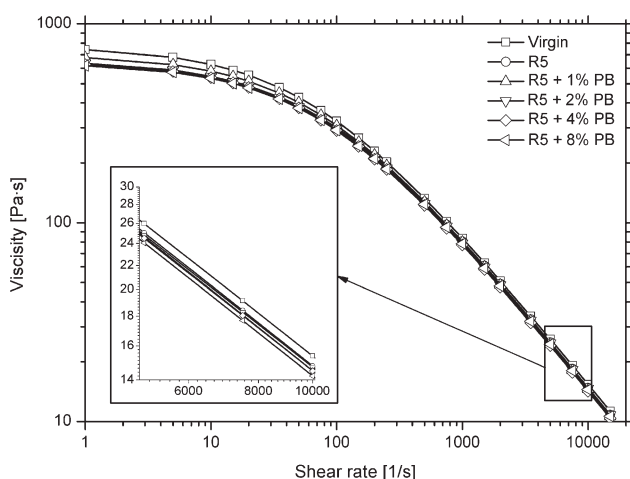


Figure 8 Viscosity of R5 and its mixtures with PB.

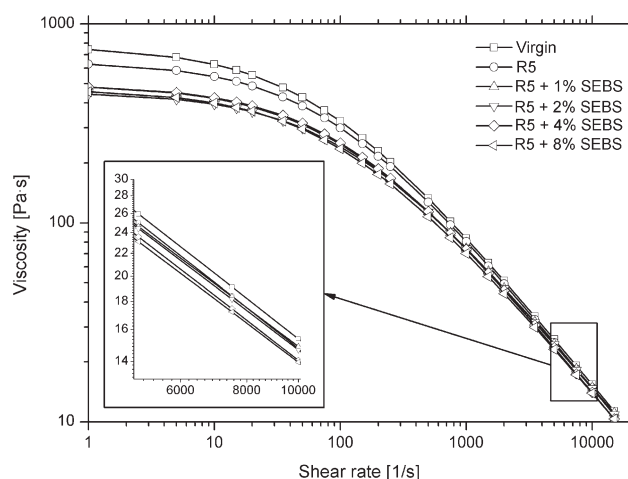
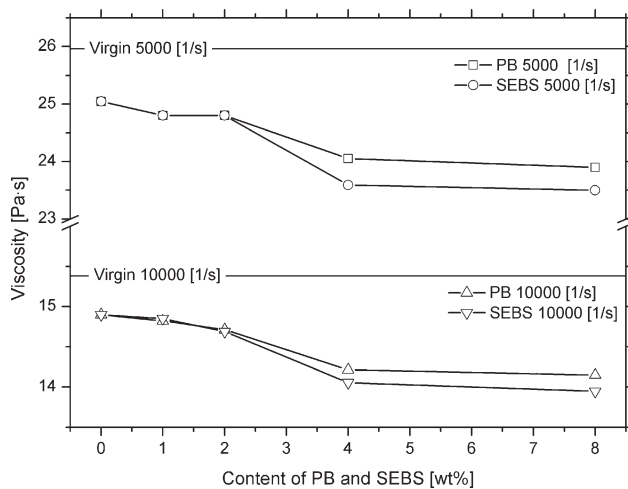


Figure 9 Viscosity of R5 and its mixtures with SEBS.





**Figure 10** Viscosity of R5 and its mixtures with SEBS and PB at 5,000 and 10,000  $\text{s}^{-1}$ .

degraded HIPS. In this section, we will analyze the mechanical and rheological properties of these blends after multiples extrusion cycles.

#### Analysis of mechanical properties

In the case of a 2% addition of SEBS and PB to the HIPS extruded 5 times, the evolution of the tensile strength values is different. The values corresponding to the addition of SEBS remain practically constant, whereas with the addition of PB, we saw a slight increase in tensile strength with each new extrusion cycle (Table V).

On the other hand, what is referred to as lengthening at break in the samples showed values that remained practically constant during the first few cycles, but after the third cycle, the values decreased slightly (Table V).

#### Analysis of rheological properties

Table VI shows the values of the cross-WLF model and the viscosity of the material at zero shear rate.

**TABLE VI**  
Dependant Parameters of the Cross-WLF Model and Viscosities at Zero Shear Rate

Material	$n$ (-)	$\tau^*$ (Pa)	$D_1$ (Pa/s)	$D_2$ ( $^{\circ}\text{C}$ )	$D_3$ (K/Pa)	$A_1$ (-)	$\tilde{A}_2$ (K)	$\eta_0$ (Pa/s)]
V	0.2244	50,854	$1.2780 \times 10^{13}$	359.15	0	31.9624	51.6	771.5
R5	0.2161	53,724	$9.4113 \times 10^{14}$	359.15	0	38.0400	51.6	647.5
R5+2% PB	0.2239	50,663	428.6	359.15	0	-0.5858	51.6	656.0
R5+2% PB_R1	0.2352	47,900	$8.9238 \times 10^{13}$	359.15	0	34.7990	51.6	667.4
R5+2% PB_R2	0.2295	48,551	$1.9081 \times 10^{14}$	359.15	0	35.8446	51.6	660.9
R5+2% PB_R3	0.2266	51,277	$3.9885 \times 10^{12}$	359.15	0	30.7383	51.6	592.9
R5+2% PB_R4	0.2189	54,324	$3.0175 \times 10^{14}$	359.15	0	36.7014	51.6	556.2
R5+2% SEBS	0.2346	53,542	$7.2883 \times 10^{13}$	359.15	0	35.0449	51.6	454.8
R5+2%SEBS_R1	0.2285	57,291	$5.1422 \times 10^{12}$	359.15	0	31.5711	51.6	414.0
R5+2% SEBS_R2	0.2363	55,460	$1.7146 \times 10^{13}$	359.15	0	33.2827	51.6	391.6
R5+2% SEBS_R3	0.2356	54,509	$3.8082 \times 10^{13}$	359.15	0	34.3412	51.6	399.0
R5+2% SEBS_R4	0.2394	54,743	$9.6750 \times 10^{14}$	359.15	0	38.8015	51.6	380.0

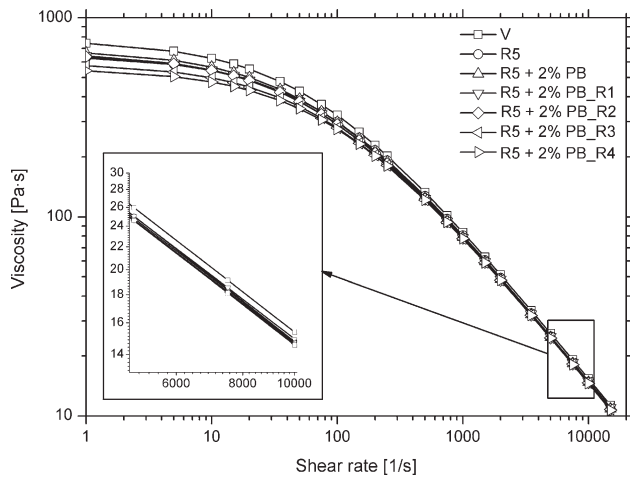
**TABLE V**  
Tensile Strength and Elongation of Virgin Material, R5, and Mixtures at 2%

Material	Tensile strength (MPa)	Elongation at break (%)		
V	13.58	9.80		
R5	15.91	8.00		
Material	Tensile strength (MPa) with PB	Tensile strength (MPa) with SEBS	Elongation at break (%) with PB	Elongation at break (%) with SEBS
R5+2%	14.78	14.57	12.05	10.50
R5+2%_R1	16.05	14.27	11.60	10.40
R5+2%_R2	16.14	14.14	11.60	10.33
R5+2%_R3	16.47	14.04	11.13	9.83
R5+2%_R4	17.00	14.00	10.00	9.50

The variation in the value of  $n$  diminishes slightly with further cycles for the mixtures with PB. This slight increase in the curve slope means a slight reduction in viscosity. For the mixtures with SEBS, the effect is the opposite, where we saw a gradual increase with further cycles. This reduction in the curve slope means a slight increase in viscosity.

The variation in the values for  $\tau^*$  increases with the number of cycles, with the final value equaling that of R5 for the mixtures with PB. This increase in  $\tau^*$  causes the graph curve for viscosity to move to the right in all the mixtures, causing a slight increase in viscosity as the number of reprocessing cycles increases. For the mixtures with SEBS, the effect is the opposite, in which case we saw with an increase in number of cycles, that this value diminishes slightly, equaling those of R5 and R5 + 2% SEBS.

The value of  $\eta_0$  diminishes considerably for all reprocessed material in comparison with virgin material. We also saw that for the mixture with PB that this value is constant for the first and second cycle, and decreases steadily with the fourth and fifth

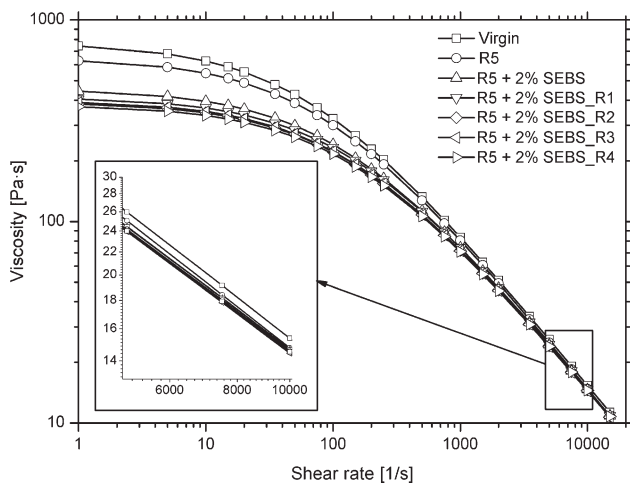


**Figure 11** Viscosity of V, R5, R5+2% PB through various cycles.

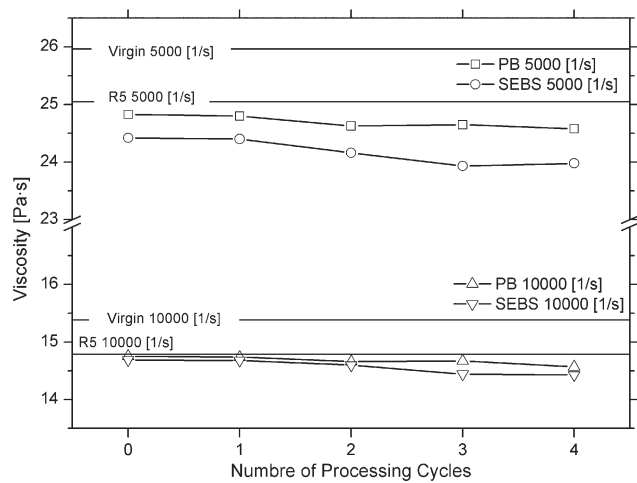
cycles. For the mixture with SEBS, we saw a strong reduction in values for all reprocessed material compared to virgin material and R5 which was much more pronounced than the mixture with PB. On the other hand, the reprocessed material with SEBS has little or no effect on the fall in viscosity, and the values remain more or less constant

Figure 11 shows the viscosity graph for the PB mixture. The behavior of the reprocessed material shows lower viscosity with each cycle. For low shear rates of 0 to 1000 s<sup>-1</sup>, and 1° and 2° mixtures, the values are the same as R5, while the others are clearly lower. For higher shear rates, from 1000 s<sup>-1</sup> onwards, the viscosities of all the reprocessed materials are similar but below those of R5 and virgin material. Figure 13 shows the viscosities for rates of 5,000 and 10,000 s<sup>-1</sup>.

The graph for SEBS mixtures can be seen in Figure 12. This material also displays lower viscosity with each cycle. We can also see the same as



**Figure 12** Viscosity of V, R5, R5+2% SEBS through various cycles.



**Figure 13** Viscosity of the mixtures of R5+2% reprocessed at 5,000 s<sup>-1</sup> and 10,000 s<sup>-1</sup>.

occurred with the study of degraded HIPS with different percentages of SEBS, that at low shear rates from 0 to 200 s<sup>-1</sup>, there is a considerable reduction in viscosity (influenced by the fall in the value of  $\eta_0$ ) and as the shear rate increases, this difference diminishes (influenced by the increase of  $n$ , which reduces the slope of the curve).

This fall in viscosity helps the injection process for plastics, as less pressure is needed to achieve the same results as with virgin material. However, too great a reduction in viscosity can lead to defective pieces due to flash. As viscosity is a function of temperature, to increase viscosity it is necessary only to reduce the temperature. The shear rate 5000 s<sup>-1</sup> is very common in thermoplastic injection processes. Using Eq. (6), we calculated the viscosity for virgin material at this shear rate, obtaining a value of 25.90 Pa/s. We also carried out the same calculation for the material R5 + 2% SEBS\_4R but this time varying the temperature. With a reduction of 5°C, that is an injection temperature of 225°C, we obtained a similar viscosity value of 25.80 Pa/s.

### CONCLUSIONS

We studied the effects of reprocessing on HIPS thermoplastic material. Our study was centered on the two most important properties of the material: mechanical resistance and viscosity. The results show that with respect to mechanical behavior, tensile strength increases by around 15%, while lengthening at break is reduced by 18%. As already commented, this behavior is caused by the crosslinking effect which is produced in thermoplastics when the temperature is raised time after time. Concerning 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.

We also saw the effect of mixing different percentages of PB and SEBS with HIPS that had been reprocessed five times, to try and recover the properties of virgin material. We again obtained information on mechanical resistance and rheological behavior (determining the dependent parameters of Cross-WLF model). The results show that with these mixtures, we can recover the mechanical behavior of virgin material, while for rheological behavior, the values for PB remain the same and for SEBS they diminish considerably.

Finally, we chose HIPS mixtures with 2% PB and 2% SEBS and we carried out further reprocessing cycles to study how the incorporation of PB and SEBS might affect recycling of this material in the future. Our results show that the mixture with SEBS behaves better with regard to tensile strength and lengthening, than the PB mixture. PB, and not SEBS, is the material that is normally used in industry to create HIPS. With respect to viscosity, again it was lower for SEBS than PB. We also saw that the viscosity diminishes more with each reprocessing cycle.

Reprocessing HIPS with SEBS reduces the viscosity. This means that the injection process is easier, 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 to 225°C. 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.

## References

1. Su, K. H.; Lin, J. H.; Lin, C. C. *J Mater Process Technol* 2007, 192, 532.
2. Santana, R. C.; Manrich, S. *Prog Rubber Plast Recycling Technol* 2002, 18, 99.
3. Soriano, F.; Morales, G.; de Leon, R. D. *Polym Eng Sci* 2006, 46, 1698.
4. Balart, R.; Lopez, J.; Garcia, D.; Salvador, M. D. *Eur Polym J* 2005, 41, 2150.
5. Navarro, R.; Ferrandiz, S.; Lopez, J.; Segui, V. J. *J Mater Process Technol* 2008, 195, 110.
6. Garcia, D.; Balart, R.; Parres, F.; Lopez, J. *J Appl Polym Sci* 2007, 106, 20.
7. Cross, M. M. *J Colloid Sci* 1965, 20, 417.
8. Williams, M. L.; Landel, R. F.; Ferry, J. D. *J Am Chem Soc* 1955, 77, 3701.
9. Reig, M. J.; Segui, V. J.; Ferrandiz, S.; Zamanillo, J. D. *J Polym Eng* 2007, 27, 29.
10. Reig, M. J.; Segui, V. J.; Zamanillo, J. D. *J Polym Eng* 2005, 25, 435.
11. Boronat, T.; Segui, V. J.; Peydro, M. A.; Reig, M. J. *J Mater Process Technol* 2009, 209, 2735.
12. Kalfoglou, N. K.; Chaffey, C. E. *Polym Eng Sci* 1979, 19, 552.
13. Michaeli, W.; Höcker, H.; Berghaus, U.; Heidemeyer, P.; Klee, D.; Günzel, R.; Rathmer, P. *Plastverarbeiter* 1990, 41, 102.
14. Tasdemir, M.; Karatop, S. *J Appl Polym Sci* 2006, 101, 559.
15. Santana, R. M. C.; Manrich, S. *J Appl Polym Sci* 2003, 87, 747.