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PROCESS BEHAVIOUR OF COMPATIBLE POLYMER BLENDS

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Abstract

It is a common industrial practice to blend virgin polymer with the same polymer recycled from scrap plastic that, in general, has not undergone relevant degradation. In this article, the influence that incorporating recycled material has on injection processes, especially on the rheological behavior of the material was studied. With this aim in mind, a mixture of two materials with the same nature or composition and similar viscosity was used, which is the system that is most commonly seen in industry. The mixture studied is composed of virgin PP (polypropylene) typically found in injection processes, and recycled copolymer PP from scrap plastic. A complete characterization of the materials and applied existing models was carried out in order to predict the mechanical behavior of the mixtures. A model to predict the behavior of the mixtures during processing, based on the rheological characteristics of the materials used was developed. This predictive model has been experimentally validated using filling tests in injection molding machines, as well as by specific simulation software.

Keywords: Viscosity, Mechanical recycling, Blend, Simulation, Rheology

1. Introduction.

Recycled polymers are usually blended with virgin polymers to obtain the best trade-off between cost and final properties ¹⁻⁴.

Moreover, the numerical simulation of the injection moulding process is now extremely helpful to support important decisions in product development ⁵.

The reliability of numerical simulations of the injection moulding process depends mainly on the rheological characteristics of polymers. The rheological characterization of a polymer for injection moulding is commonly carried out by a capillary rheometer ⁶.

When studying a recycled material, it is difficult to carry out an extensive study on characterization due to the huge diversity of components, and its low cost in comparison to virgin material ^{7,8}.

However, the demands of modern production systems make some form of characterization necessary. This characterization must take into account the mechanical, thermal, morphological, etc. properties of the material, as well as ensuring that the recycled material presents no problems during processing and that the transformation of the material can be carried out in the same way as with virgin material ⁹.

With this in mind, our principal aim is to determine, from experimental data, whether it is possible to correctly predict the behavior during processing of a recycled material, and which models can be used. From this data it is then possible to carry out studies on the effect of viscosity on incompatibility of plastic waste material during the recycling process.

In order to study this, one of the simplest systems found in the recycling industry was used, which consists of mixing two materials of the same composition and which have similar viscosity ¹⁰

From this study, the reliability of the predictive models concerning the mechanical behavior of the mixtures was verified, in order to later predict the behavior of the mixtures during processing.

2. Experimental

2.1 Materials

The first component of the system was virgin polypropylene manufactured by Repsol-YPF (PP ISPLEN[®] PB 180 G2M), with a MFI of 20 g/10min, a typical value in injection process.

The second component was recycled copolymer polypropylene in the form of rejected toy components of large size which were transformed through the injection process.

2.2 Characterization

The mechanical properties of the samples were evaluated using an ELIB 30 electro-mechanical universal testing machine by Ibertest (S.A.E. Ibertest, Madrid, Spain), with a load cell of 5 kN. All tests were carried out following UNE-EN ISO 527 standard, at a speed of 30 mm min⁻¹.

Impact strength was determined by using the Charpy impact machine (S.A.E. Ibertest, Madrid, Spain) according to ISO-179.

The values of all the mechanical parameters were calculated as averages over 5 – 7 samples for each composition.

The Thermal characterization was carried out using DSC Mettler-Toledo 821 equipment (Mettler-Toledo Inc, Schwerzenbach, Switzerland). Samples of weight between 8 – 9 mg have been used. A first heating (30°C – 280°C at 10°C min⁻¹) was completed, followed by a cooling process (280°C – 30°C at 10°C min⁻¹) to eliminate the thermal history and by a second heating (30°C – 280°C at 10°C min⁻¹). The T_g values have been

determined from second heating process. The tests were performed in a nitrogen environment (flow rate 50 ml min^{-1}).

Melt flow index measurements were obtained with an extrusion plastometer (Ats Faar S.p.A, Vignate, Italy) equipped with a heating chamber set at 200°C where the blended granules were introduced. After a previously established melting time, the material was forced through a capillary by means of the application of a 5000 g weight.

The rheological characterization was carried out as described under the ISO 11443 standard, using a capillary rheometer, (Rheoflizer Typ 556-0101, ThermoHaake Inc, Germany). Test parameters were as follows:

- Test dies (Diameter/Length): 1/10; 1/20; 1/30 mm
- Test temperature: 200°C and 230°C
- Test shear rate: $100 - 10000 \text{ s}^{-1}$
- Previous compression: 20 bar during 30 sec
- Previous decompression: 10 bar during 30 sec
- Pressure sensor used: 1400 Bar
- Melting Time: 5 min

Given the wide range of test temperatures according to the ISO 11443 standard, previous tests were carried out in order to determine the optimum parameters.

Tests for each sample were carried out in the three dies to obtain the real shear stress. The Bagley correction¹¹ was used. The real shear rate was also obtained, to which the Rabinowitsch correction¹² was applied. In this way the real viscosity was obtained.

High shear rate values ($\dot{\gamma}$) were established, ranging between 102 and 104 (s^{-1}). The study of this interval is important as these values most closely match the processing conditions for the material ^{2,13}.

2.3 Process and simulation.

The preparation of the mixtures was carried out using a double screw extruder with five temperature zones (170/190/210/220/230°C) to ensure correct dispersion of the components in the blend 14. A co-rotation extruder Collin ZK 25 (Collin extrusions Ltd, Warwickshire, UK) with 25 mm diameter screw and a length – diameter ratio of 24 was used.

To add the components to the blend, two volumetric dispensers were used.

For the mechanical characterization, samples were obtained conforming to ISO-527 and ISO-179.

The mould used for the injection has been a laboratory mould for tensile samples of one cavity.

The injection process was performed in a MATEU-SOLÉ 270/75 injection machine (MATEU-SOLÉ, Barcelona, Spain) at a screw temperature of 230°C and mould temperature 30°C .

Plastic flow analysis simulations were carried out using the commercial computer-aided engineering software, Moldflow Plastics Insight (release 6.2), which theoretical basis of calculation is based on Cross-WLF rheological model.

3. Results and discussion

3.1 Materials characterization.

In the case of virgin polypropylene PP ISPLEN® PB 180 G2M, the physical / mechanical properties necessary for the study were provided by the manufacturer (Table 1).

Table 1

Similarly, the rheological parameters of the material used as references for the Cross-WLF model were also supplied by the manufacturer (Table 2)

Table 2

where: 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.

\tilde{A}_2 (K), A_1 (-), are the WLF parameters.

n , is the model constant which symbolizes the pseudoplastic behavior of the material

τ^* [Pa], is the model constant that shows the shear stress rate, from which the pseudoplastic behavior of the material starts.

D_1 [Pa•s], is the model constant which registers the viscosity of the material, under zero-shear-rate conditions, at the glass transition temperature of the material and at atmospheric pressure.

In the case of recycled PP, the material came from injection molding process in the toy industry, which means that it had undergone a thorough characterization prior to being used (Table 3).

Table 3

The thermal properties of the material were determined using differential scanning calorimetry (DSC), having first carried out a study of crystallinity (Figure 1).

To determine variations in the level of crystallinity a first heating (30–280 °C at 10 deg min⁻¹) was completed, followed by a cooling process (280–30 °C at 10 deg min⁻¹) to eliminate the thermal history, and was finished with a second heating (30 °C at 280 °C at 10 deg min⁻¹). The tests were performed in a nitrogen environment (flow rate 50 ml min⁻¹).

From the study of the fusion energy values from the two heating cycles carried out it was deduced that the material had a slow and controlled cooling during transformation, as the crystallinity values (with respect to the theoretical maximum value of PP) were very similar in both cycles (Table 4).

This crystallinity was as expected, given that the material came from injection molded parts of large size, where cooling times are usually long in order to avoid shrinkage problems in the parts and part distortion during ejection.

Table 4

Figure 1

In second place, to determine the degree of degradation of recycled PP, the conditions of the thermal analysis were varied, in this case using a single thermal ramp which began at 30 °C and finished at 260 °C at a rate of 10 °C min⁻¹, but in this case in oxygen atmosphere (Figure 2).

Figure 2

The value of Onset Oxidation Temperature (OOT) indicates that we have a material that has not had much thermal degradation during processing, since the value obtained is similar to a standard non-stabilized PP used in injection molding^{15,16}.

Concerning the rheological properties of the material, it is obtained a melt flow index of 12.9 g/10 min .

Following this, it is obtained the real viscosity curve through a capillary rheology test (Figure 3). The test temperature was set at 230°C, a typical value for transformation of this type of material.

Figure 3

3.2 Calculation of mechanical behavior

Some theoretical models have been used to predict behaviour of polymeric blends ^{17,18}. A model, based on Takayanagi ¹⁹ has been used to evaluate quite accurately mechanical performance of blends. This model, known as Equivalent Box Model (EBM), considers that certain fractions of each material contribute to mechanical properties as in series work, while other fractions contribute in parallel.

The contribution of these fractions to the final value of the studied property is determined according to the general Rule of Mixtures.

The equations deduced by the model to calculate Young's modulus and Tensile strength are as follows:

$$E_b = (E_1 \cdot v_{1p} + E_2 \cdot v_{2p}) + \frac{v_s^2}{\left[\left(\frac{v_{1s}}{E_1} \right) + \left(\frac{v_{2s}}{E_2} \right) \right]} \quad (1)$$

$$\sigma_{R(\min)} = \sigma_1 \cdot v_{1p} + \sigma_2 \cdot v_{2p} + A \cdot \min(\sigma_1, \sigma_2) \cdot v_s \quad (2)$$

Where :

v_{1p} , v_{2p} are the fractions of each component working in parallel.

v_{1s} , v_{2s} are the fractions of each component working in series.

$$v_p = v_{1p} + v_{2p}$$

$$v_s = v_{1s} + v_{2s}$$

A , represented the intensity of the adhesion/interaction forces in the interface (the value 1 was used in our case because the materials are completely compatible)

The determination of series and parallel fractions for each one of the components in the blend, depends on the critical values defined by percolation theory, v_{crit} and T (percolation threshold and critical exponent respectively). Therefore, prediction of mechanical properties is based on the determination of these critical values by identifying the most appropriate lattice for the system (square, triangular, hexagonal, 3D lattices...). Many studies have focussed on the determination of these critical values and generally, values based on three dimensional geometries give good results, specially in

heterogeneous isotropic materials²⁰. Therefore, for three-dimensional domains of spherical type of discreet nature, percolation theory establishes percolation threshold $v_{crit} = 0,156$, while value of the universal exponent, T is located in the range $1,7 < T < 1,9$; many systems use a T value of 1,8 with excellent results²¹⁻²³.

Therefore, with a 50 / 50 blend and using the critical exponent commonly used, we obtain a value for $V_{1p} = V_{2p} = 0,2$ and for $V_S = 0,6$

Applying equations 1 and 2 to the system being studied, composed of 50% each of virgin polypropylene PB 180 G2M and recycled PP, values for Young's modulus and Tensile strength which were very similar to those obtained experimentally were obtained (Table 5).

Table 5.

3.3 Process behavior.

The most important parameter when characterizing a material during injection processes is its rheological behavior.

In the current work, two materials with a high compatibility index were rheologically characterized, in order to later develop a model which would allow us to evaluate the behavior of the blend during its process of transformation.

This model would later be verified experimentally using specific simulation software.

3.3.1 Rheological properties of materials

There are currently on the market various software programs specifically developed for injection simulation, and these incorporate models to evaluate the viscosity of a material.

The rheological model most extensively used is the Cross-WLF ²⁴, which offers a very close approximation to the behavior of the real material, relating viscosity to other parameters such as temperature, shear rate and pressure.

The model is as follows:

$$\eta = \frac{\eta_0}{1 + \left(\frac{\eta_0}{\tau^*} \cdot \dot{\gamma} \right)^{1-n}} \quad (3)$$

Where η_0 (Pa.s) is the viscosity under zero-shear-rate conditions, τ^* (Pa) is the model constant which shows the shear stress rate, which is the starting point for the pseudoplastic behavior of the material, and n is the model constant which symbolizes the pseudoplastic behavior of the material.

To determine the viscosity of the material under zero-shear-rate conditions, Williams-Landel-Ferry expression ²⁵ was used.

$$\eta_0 = D_1 \cdot e^{\frac{-A_1 \cdot (T - T^*)}{A_2 + (T - T^*)}} \quad \text{if } T \geq T^* \quad (4)$$

Where ;

$$A_2 = \tilde{A}_2^0 + D_3 \cdot p$$

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

$\tilde{T}_g(K)$ is the glass transition temperature of the material depending on the pressure, D_2 (K) is the model constant that marks the glass transition temperature at atmospheric pressure, D_3 (K/Pa) is the model constant which symbolizes the temperature variation of the material during transformation in function of pressure, D_1 (Pa.s) is the model constant which shows viscosity of the material under zero-shear-rate conditions, at the glass transition temperature of the material and at atmospheric pressure, and finally A_1 and \tilde{A}_2 (K) are the model constants.

Therefore, it was necessary to know seven parameters to model the system, three of which (D_2 , D_3 and \tilde{A}_2) belong to each type of polymer (PP, ABS, PE, etc.), and the remaining four (n , τ^* , D_1 , A_1) are specific to each grade of material.

In the case of virgin PP, these parameters were supplied by the manufacturer (Table 2).

In the case of recycled PP, the parameters of the Cross-WLF model were obtained from the real viscosity curve. From this curve, after the corresponding corrections, the four parameters particular to the model (n , τ^* , D_1 , A_1) were obtained, carrying out an adjustment using Chi squared minimization criteria. This adjustment was carried out using the numerical analysis software Origin[®], thus obtaining an extremely high correlation value between estimated and real values.

The remaining three (D_2 , D_3 and \tilde{A}_2), are constant for any PP.

Thus, the parameters obtained for the recycled material are those shown in Table 6.

Table 6

3.3.2 Calculating the rheological behavior of blends

Rheological studies of a material require very specific equipment which is generally only within the reach of polymer manufacturers and research laboratories.

On occasions those carrying out the transformation need to know the rheological behavior of a blend of polymers, but only have available to them the specifications supplied to them by the manufacturers.

The present study proposes a method for calculating rheological behavior of a polymer mixture based on the rheological characteristics of each individual component.

Basing this study on the Cross-WLF equation and on knowledge of the physical significance of the different parameters, a model a model was proposed in which, applying the blending law, we calculate the different parameters of the model for a particular mixture.

The representation of the viscosity curve against shear rate is logarithmic, and with this fact as a starting point, the parameters τ^* and $D1$ can be calculated as follows:

$$\log \tau^* = \phi_1 \log \tau_1^* + \phi_2 \log \tau_2^* \quad (5)$$

$$\log D1 = \phi_1 \log D1_1 + \phi_2 \log D1_2 \quad (6)$$

Where Φ is the fraction in weight of each component and $\Phi_1 + \Phi_2 = 1$.

In the same way, and observing that the parameters n and A_1 appear in the Cross-WLF equation as exponent, the calculation can be expressed as:

$$n = \phi_1 n_1 + \phi_2 n_2 \quad (7)$$

$$A_1 = \phi_1 A_{1_1} + \phi_2 A_{1_2} \quad (8)$$

Where Φ is the fraction in weight of each component and $\Phi_1 + \Phi_2 = 1$.

The remaining three parameters of the equation (D_2 , D_3 and \tilde{A}_2) have constant values whenever we are dealing with different grades of the same material.

With the aim of verifying the proposed model, these calculations were applied to a 50/50 blend of each of the materials proposed in the study. In this case, we obtained from the Cross-WLF equation (Table 7) parameters whose graphic representation shows a very good approximation to the real rheological behaviour of the blend, showing only slight variations in the initial part of the curve (Figure 4). Both curves, as expected, rheological behavior that has values somewhere between those of the individual initial materials for the whole range of shear rates studied.

Table 7

Figure 4

3.3.3 Validation of the rheological model of the blends.

The rheological model has been validated experimentally, through mold filling tests using injection machines. For this, a laboratory mold with normalized test samples was used. In this case, the tensile sample is injected, which allowed better observation of the advance of the flow of material.

These tests were carried out using the three materials characterized:

- Virgin Polypropylene Repsol-YPF PB 180 G2M
- Recycled Polypropylene sourced from injection processes.
- Blend of 50% by weight of both materials.

To carry out the filling tests, flow rate as the parameter under study is selected, maintaining the rest of the parameters (screw temperature and mold temperature) constant.

As two similar grades of polypropylene are used, the transformation parameters supplied by the manufacturers of the virgin material (Table 8) were chosen in all the tests.

Table 8

To determine the different flow rates, a first test was carried out to obtain the minimum flow rate at which the mold is completely filled and the injection time needed to do so.

Later, filling tests were carried out, keeping the injection time constant but progressively reducing the flow rate until no flow of material was observed inside the cavity.

This operating procedure was followed in the same way for the three materials proposed. In each of the tests, samples from a series of five injections were obtained from which the average weight was calculated.

Running parallel to the filling tests in the injection machine, simulations of the process using the Moldflow[®] program were carried out with the aim of comparing the experimental and theoretical flow advance rates. With this in mind, the injection parameters used in the machine were introduced into the simulation along with the rheological characteristics of each of the materials, obtained from the Cross-WLF model parameters.

From each of the simulations, the theoretical advance of the flow and the theoretical weight of injected material were obtained for each of the flow rates proposed.

Comparing the experimental flow (top image) with the theoretical (bottom image), it is observed that in the case of virgin PP, these are very similar for the whole range of flow rates (Figure 5).

Figure 5

Similarly, in the case of recycled material, a good correlation between the experimental flows and theoretical flows was observed, with the exception of a small difference at

low flow rates (Figure 6), due to the fact that these speeds control of the injection is quite difficult, and the quantity injected into the mold is small.

Figure 6

Finally, from the study of flow advance of a 50/50 blend PPs, it could be deduced that the model proposed offers a close approximation to real rheological behavior of the blend, as experimental and theoretical flows that were very similar were seen clearly, even at low injection flow rate (Figure 7).

Figure 7

In order to make a quantitative comparison between the experimental and simulated flows, the average shot weight of the injected material under the different conditions proposed was obtained (Figure 8).

Figure 8

If the evolution of the weights obtained from the injection machine experiments is studied, it was possible to see how in the case of the blends, the values follow more closely the trend seen in the recycled material, while the trend for virgin material is a little different.

On the other hand, if the difference in weights between experimental tests and simulations it is analyzed, it can be seen that the area of greater error corresponds with the average flow rates, reaching in all three cases absolute errors of less than 1 gram .

Analyzing the relative error, it can be generally seen that for the three materials, it is higher at lower injection flow rate, due to the fact that these speeds control of the injection is quite difficult, and the quantity injected into the mold is small. Therefore in practical terms, the error produced in this area is not considered significant. As the speed was increased, the error stabilized, giving values that oscillate between 0.5% and 9%. Once again, the lowest values for relative error came from recycled material.

To summarize, relatively small errors were obtained (around 10%), and the values for these were independent of the origin of the rheological parameters used in the simulation, which were:

- supplied by the manufacturer
- obtained from the rheological characterization of the material
- calculated from the rheological characteristics of the individual components of the blend.

4. Conclusions

The value of Onset Oxidation Temperature (OOT) of the recycled polypropylene used in the blends, indicates that we have a material that has not had much thermal degradation during processing. The high crystallinity values obtained show that the material had a slow and controlled cooling during transformation.

The equivalent box model (EBM) with the parameters developed by Kolarik is appropriate for the mechanical characteristics of the system. The comparison between simulation and experimental results allowed validation of the model both for the Young's modulus and Tensile strength, in which very similar values were obtained in both cases.

The model proposed to calculate rheological behavior was shown to be correct as it gave rheological curves that fall between those of the two initial materials.

The rheological model proposed was shown to work accurately for the three materials studied, and a good correlation between experimental and simulation flows was observed.

Relatively small errors were obtained (below 10%) between weights of injected material obtained experimentally and via simulation, and these values were shown to not be very sensitive to the origin of the rheological parameters used in the simulations.

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