Obtaining an Empirical Equation for Correcting the Melt Flow Index of Virgin and Recycled Polypropylene Mixtures and Analysis of Mechanical Properties of the Blends

By Luiz Gustavo Barbosa, Cassiano Rodrigo Dalberto & Edson Luiz Francesquetti

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Keywords: recycled polypropylene, melt flow index, mechanical properties of polymers.

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I. Introduction

Polymeric materials are an important group of the materials engineering because their easy production and wide range of applications. This group includes materials such as plastics and rubbers ranging from low density liquids to rigid solids [1].

The growth in the consumption of plastics in the world is evident. In 1964 around 15 megatons (Mt) were generated, in 2014 this production reached 300 Mt. This production is expected to double again within 20 years, and by the year 2050 it has practically quadruple [2].

Is estimated that if plastics were replaced by other packaging materials, there would be an increase of approximately 60% in the volume of waste produced, 57% electricity consumption over the entire product life cycle and between 78 Mt to 170 Mt of complementary greenhouse gas emissions [3].

Despite the use of plastics in general, more specifically the polymers, to exhibit a decrease in the generation of waste, their discard, as well of other consumable materials, also contributes to the production of urban waste and for the waste in the oceans with the aggravation of not being biodegradable, soon this residue remains for long periods in the nature [4].

One way to mitigate such problem is the reuse of polymeric materials, by secondary or mechanical recycling which according to the Union of the Plastic Material Industry of the State of São Paulo (Sindiplast) and the Environmental Company of the State of São Paulo (CETESB), “[…]is the converting of plastic waste into granules that can be reused by the productive sector to make other products […]” [5].

One of the most used plastics in the world is the polypropylene (PP) wich, due to the great increase in its productive capacity caused its cost to decrease, so it may be used in new much applications. PP has characteristics that allow it to be subjected to many processing techniques such as Injection, Extrusion, Thermoforming, Rotational Molding and Blowing [6]. The main application of PP is in the food sector, representing 32% in products such as: packaging, lids, tupperwares, jars, bottles and gallons. In the consumer goods sector PP represents 17% of the market and is applied in packaging and boxes. In civil construction represents 3% of the market and, among others, it replaces asbestos in fibre cement tiles and water tanks, and it serves as a partial substitute of concrete in slabs with the use of BubbleDeck [7]. Also, it is a raw material for the Pack Less, a plastic pallet. In the automotive sector it represents 9% of the market, being used in dashboards, door panels, bumpers, grilles, for example. [8]. Therefore, all this material when discarded can be recycled and originate new products. In Brazil, about 8.2% of the post-consumer polypropylene is recycled, which is processed into pellets through mechanical recycling and subsequently produces packaging.
automobile components and other recycled products [9].

However, in its use, recycled PP has different properties in relation to virgin. One of these properties is the Melt Flow Index (MFI), defined by many authors as the material's processability index. The value of MFI is important for defining the polypropylene transformation process and also in the processability and quality of the parts produced with this material, being that PP's that have a higher MFI are more suitable for injection processes [10].

In practice, when a polypropylene is recycled presents a higher melt flow index than when virgin. The recycling causes changes in chemical structure, in the melt viscosity, crystallization behaviour, and tensile and fracture properties. The main effect of recycling is the lowering of the melt viscosity, which is attributed to molecular weight decrease and consequently increases the melt flow index [11]. From experience, it is known that changing the MIF can be responsible for problems during the plastics process transforming such as bubbles, fillers, poor filling of the mold, in injected parts in which this material is used.

In this context, and considering the PP's used for making parts in a plastics processing company in the state of Rio Grande do Sul, Brazil, which uses both recycled and virgin PP's, the purpose of this work is to obtain an equation to correct the melt flow index of virgin and recycled polypropylene mixtures in order to keep it within the processability values required by the company and standardize the material used. To verify if the parts injected with the mixture between virgin and recycled PP's attend the technical specifications, the mechanical properties of traction and impact were tested.

It's important to note that recycled polypropylene, in addition to having an interesting ecological bias, is also more economically viable. Therefore, virgin and recycled PP mixtures can attend projects requirements and economic and environmental demands.

II. MATERIALS AND METHODS

a) Materials

Neat polypropylene (PPv), commercial grade PP CP442XP, was provided by Braskem S.A. (Brazil) with a melt flow index of 26 g/10 min (230°C / 2.16 kg), with yield stress of 32 Mpa.

Polypropylene from secondary recycling (PPr) with a many different melt flow index: 5.91, 5.93, 7.70, 8.23, 8.36 and 12.29 g / 10 min (230°C / 2.16 kg) was provided by Coplast - LTDA from Manaus city (Amazonas, Brazil).

b) Methods

i. Mixture preparation

The materials used for the measure of the melt flow index were blended in the proportions shown in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPv100</td>
<td>100 Virgin (%) 100 Recycled (%)</td>
</tr>
<tr>
<td>PPr10</td>
<td>90 Virgin (%) 10 Recycled (%)</td>
</tr>
<tr>
<td>PPr20</td>
<td>80 Virgin (%) 20 Recycled (%)</td>
</tr>
<tr>
<td>PPr30</td>
<td>70 Virgin (%) 30 Recycled (%)</td>
</tr>
<tr>
<td>PPr40</td>
<td>60 Virgin (%) 40 Recycled (%)</td>
</tr>
<tr>
<td>PPr100</td>
<td>100 Virgin (%) 0 Recycled (%)</td>
</tr>
</tbody>
</table>

The specimens for the tensile and impact tests were injected in the proportional for 30% of virgin PP and 70% of recycled PP, following the dimensional requirements of ASTM D638-02a and ASTM D256-02, respectively. Table 2 shows the parameters used during their injection.

<table>
<thead>
<tr>
<th>Injection Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum holding pressure (MPa)</td>
<td>35</td>
</tr>
<tr>
<td>Maximum injection pressure (MPa)</td>
<td>50</td>
</tr>
<tr>
<td>Maximum back pressure (MPa)</td>
<td>8</td>
</tr>
<tr>
<td>Decompression pressure (MPa)</td>
<td>55</td>
</tr>
<tr>
<td>Injection time (s)</td>
<td>5</td>
</tr>
<tr>
<td>Temperature of zones 1 to 4 (°C)</td>
<td>200</td>
</tr>
<tr>
<td>Temperature of zone 5 (injection) (°C)</td>
<td>195</td>
</tr>
</tbody>
</table>
Obtaining an empirical equation for correcting the melt flow index of virgin and recycled polypropylene mixtures and analysis of mechanical properties of the blends

ii. Obtaining an equation to melt flow index of virgin and recycled polypropylene mixture

The obtaining of an equation relating the melt flow index with the different proportions of PPv and PPr, was carried out empirically, carrying out tests with the different mixtures. After the rheological tests were performed, MFI x %PPV graphics were generated, and so the linear equations and the general equation was obtained of the melt flow index as a function to percent of virgin polypropylene in the mixtures.

c) Characterization

i. Melt Flow Index - MFI

The experiment was accomplished in IFRS – Campus Farroupilha, in Farroupilha city (Rio Grande do Sul, Brazil), using an INSTRON CEAST equipment, type 7023, at a temperature of 230°C, 2.16 kg and 420 seconds to stabilization in according to ASTM D1238.

ii. Differential Scanning Calorimetry (DSC)

The crystallization (Tc) melting (Tm) temperatures, and percentual of Polypropylene and polyethylene were measured by differential scanning calorimetry on a DSC 6000 PerkinElmer. Samples of 8 mg were analyzed under nitrogen atmosphere under a flow rate of 20 mL/min. In order to erase their thermal history, samples were initially heated at 30°C to 200°C with rates of 50°C/min and kept at 200°C for 2 min. Then, they were cooled down to 30°C with rates of 20°C/min to determine the crystallization temperature. A second heating to 200°C with rates of 20°C/min was conducted to evaluate the melting temperature of the composite.

The percentage of polyethylene (PE) and polypropylene (PP) in the composite was calculated using the melt enthalpy reference value obtained from the curves of the samples analyzed. To obtain the results, the method developed by Zamin [12] was used, in which, by the ratio \( Y = \frac{\Delta H_{PE}}{\Delta H_{PP}} \), is possible to determine PE percentage in the material, by the equation 1:

\[
Y = 0.001X^2 - 0.0029X + 0.0804 \quad (1)
\]

Where:

\( Y \) = (\( \Delta H_{PE} / \Delta H_{PP} \)) ratio

\( X1 (+) \) = Percentage of PE in te material

\( X2 (-) \) = Disregard

iii. Fourier Transforms Infrared Spectroscopy – FTIR

Fourier transform infrared (FTIR) spectroscopy analysis was performed using a PerkinElmer Frontier spectrophotometer with an attenuated total reflectance (ATR) accessory. Each spectrum was obtained using five scans ranging from 4000 to 600 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\).

iv. Mechanical properties

The tensile test were performed according to ASTM D638-02a, operating at a speed of 5 mm/min and at room temperature. Five specimens of each mixture were tested and then the mean values of elastic modulus, yield strength and yield strain were obtained. To perform the tensile tests a universal testing machine model WDW100E, made by Time Group was used, located in the test laboratory of the IFRS – Campus Erechim, controlled by WinWDW software, and has a 100kN load cell and a strain gauge.

Impact tests were performed according to ASTM D256-02 in a controlled environment, with a room temperature of 23 ± 2°C and a relative humidity of 50 ± 10%. The impact strength value was obtained by the ratio of the average energy absorbed by 8 specimens tested according to the dimensions specified in the standard. The tests were performed with a Zwick Izod impact testing machine, located at the IFRS - Farroupilha Campus. The hammer used for the test provides 4.0 J of energy and was released from a height of 610 mm in relation to base.

III. Results and Discussion

a) Differential Scanning Calorimetry

The Table 3 show the results of melting enthalpy (\( \Delta H \)), melting temperature (Tm), crystallization temperature and percentage of polyethylene in the material. The table shows that the melting temperatures of the materials have not changed since it is a blend, both were close to those found in the literature, HDPE 125 °C to 135 °C and PP 160 °C to 170 °C [12, 13].

<table>
<thead>
<tr>
<th>Sample</th>
<th>MFI (g/10min)</th>
<th>Tm PP (°C)</th>
<th>Tm PE (°C)</th>
<th>( \Delta H_{PP} ) (J/G)</th>
<th>( \Delta H_{PE} ) (J/G)</th>
<th>Tc (°C)</th>
<th>( Y = \frac{\Delta H_{PE}}{\Delta H_{PP}} )</th>
<th>% PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPr2</td>
<td>5.912</td>
<td>162.83</td>
<td>128.88</td>
<td>42.08</td>
<td>22.09</td>
<td>118.09</td>
<td>0.525</td>
<td>22.19</td>
</tr>
<tr>
<td>PPr4</td>
<td>8.36</td>
<td>162.34</td>
<td>128.03</td>
<td>46.72</td>
<td>20.35</td>
<td>118.16</td>
<td>0.436</td>
<td>19.51</td>
</tr>
<tr>
<td>PPr5</td>
<td>7.70</td>
<td>163.12</td>
<td>128.86</td>
<td>43.38</td>
<td>19.48</td>
<td>118.14</td>
<td>0.449</td>
<td>20.19</td>
</tr>
</tbody>
</table>
The values shown in Table 3 indicate that the material supplied by the Coplast company is not only composed of polypropylene, but has 20% polyethylene. Therefore, the MFI variation does not depend on the percentage of polyethylene present in the composition of the material.

b) Fourier Transform Infrared Spectroscopy – FTIR

The FTIR-ATR spectra of the recycled polypropylenes (PPr) are presented in Figure 1. The FTIR spectra PPr matrices show characteristic bands of PP [14], with stretching of CH and CH₂ bonds between 2965 and 2820 cm⁻¹, and asymmetric and symmetrical deformations of CH and CH₃ at 1447 and 1378 cm⁻¹, respectively. Still in Figure 1, it is possible to observe that in PPr4 there are changes in the range from 3600 to 3000 cm⁻¹, related to the O-H groups, showing a peak that may be an indication of a lot of humidity in this sample. It's difficult to distinguish between PP and PE just by the FTIR test, as both have similar bands; which proves the presence of both materials is the DSC test.

In the graph of Figure 1 it is also possible to observe the presence of calcium carbonate in the material, through the absorption bands at 873 and 719 cm⁻¹, which are characteristic of CaCO₃ [16]. The PP's bands are in accordance with the ones found in the literature and can be seen in Table 4.

Table 4: FTIR absorption bands assigned to PP and PE present in the samples

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Peak Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP Pe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2952, 2918 and 2838</td>
<td>CH stretching</td>
<td>[14]</td>
</tr>
<tr>
<td>2720</td>
<td>CH bending and CH₃ stretching</td>
<td>[15]</td>
</tr>
<tr>
<td>1456</td>
<td>CH₃ asymmetric deformation</td>
<td>[15]</td>
</tr>
<tr>
<td>1376</td>
<td>CH₃ symmetric deformation</td>
<td>[15]</td>
</tr>
<tr>
<td>1165</td>
<td>Bending vibration of tertiary carbon</td>
<td>[15]</td>
</tr>
<tr>
<td>974, 841 and 808</td>
<td>CH₂ deformation out-of-plane</td>
<td>[15]</td>
</tr>
<tr>
<td>873</td>
<td>C-O, calcite, CaCO₃</td>
<td>[17]</td>
</tr>
<tr>
<td>719</td>
<td>CO₃ stretching</td>
<td>[18]</td>
</tr>
</tbody>
</table>

c) Melt Flow Index

To evaluate the melt flow index of the raw material with which the company works, rheology tests were carried out on them, the first tests being carried out using 100% of the recycled material (PPr100) and 100% of the virgin material (PPv100). The PPv100 presented a MFI of 26 (g/10 min) according to the value provided by Braskem.

As the MFI considered ideal is between 9 and 13 (g/10 min) for injection processes in the company requesting the research, to obtain the equation and analyze the mechanical properties, recycled polymers with MFI above 9 (g/10 min) were not used in mixtures with PPv100. The Table 5 shows the measured values of melt flow index and the nomenclature used for each raw material studied.
Table 5: Measured values of MFI and the nomenclature used for each raw material studied

<table>
<thead>
<tr>
<th>MFI measured (g/10 min)</th>
<th>MFI PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.00</td>
<td>MFI PPv100</td>
</tr>
<tr>
<td>12.286</td>
<td>MFI PPr1</td>
</tr>
<tr>
<td>5.912</td>
<td>MFI PPr2</td>
</tr>
<tr>
<td>5.93</td>
<td>MFI PPr3</td>
</tr>
<tr>
<td>8.36</td>
<td>MFI PPr4</td>
</tr>
<tr>
<td>7.70</td>
<td>MFI PPr5</td>
</tr>
<tr>
<td>8.23</td>
<td>MFI PPr6</td>
</tr>
</tbody>
</table>

The Table 6 shows the results of melt flow index of the recycled polymer samples with different percentages of virgin.

Table 6: Results of MFI of the recycled polymer samples with different percentages of virgin

<table>
<thead>
<tr>
<th>Percentage of virgin PP (% PPv)</th>
<th>MFI PPr2 (g/10 min)</th>
<th>MFI PPr3 (g/10 min)</th>
<th>MFI PPr4 (g/10 min)</th>
<th>MFI PPr5 (g/10 min)</th>
<th>MFI PPr6 (g/10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.912</td>
<td>5.93</td>
<td>8.36</td>
<td>7.70</td>
<td>8.23</td>
</tr>
<tr>
<td>10</td>
<td>7.45</td>
<td>7.2</td>
<td>9.33</td>
<td>8.64</td>
<td>9</td>
</tr>
<tr>
<td>20</td>
<td>8.83</td>
<td>8.15</td>
<td>9.47</td>
<td>10.06</td>
<td>9.28</td>
</tr>
<tr>
<td>30</td>
<td>9.5</td>
<td>9.64</td>
<td>10.4</td>
<td>11</td>
<td>10.68</td>
</tr>
<tr>
<td>40</td>
<td>10.4</td>
<td>11.13</td>
<td>12.81</td>
<td>12.45</td>
<td>12.71</td>
</tr>
<tr>
<td>50</td>
<td>12.1</td>
<td>13.3</td>
<td>14.446</td>
<td>13.9</td>
<td>13.67</td>
</tr>
<tr>
<td>60</td>
<td>14.1</td>
<td>13.3</td>
<td>14.88</td>
<td>14.92</td>
<td>14.91</td>
</tr>
</tbody>
</table>

d) Obtaining the melt flow index equation for blends of virgin and recycled polypropylene

The Figure 2 shows the graph with the straight lines of each blend relating the melt flow index to virgin polypropylene percentage. MFila being the straight line obtained by mixing with MFI PPR2, MFib is the straight line obtained by mixing with MFI PPR3, MFic the straight line obtained by mixing with MFI PPR4, MFId the straight line obtained by mixing with MFI PPR5 and MFie is the straight line obtained by mixing with MFI PPR6.

Figure 2: Graph with the straight lines of each blend relating the melt flow index to virgin polypropylene percentage
From the graph in Figure 2 is possible to observe an increase in the melt flow index of the mixtures proportional to virgin polypropylene percentage, that can be approximated to a straight line for all mixtures. Thus, the line equations for the mixtures are as follow:

Line equation \(MF_{a}\):

\[
MF_{a} = 5.9637 + 0.12645x \quad R=0.98952 \quad (1.1)
\]

Where:
- \(MF_{a}\): Melt Flow Index of the mixture (g/10min)
- \(x\): Percentage of PPv in the mixture (%)
- \(R\): Correlation coefficient of the line (1)

Line equation \(MF_{b}\):

\[
MF_{b} = 5.8947 + 0.12489x \quad R=0.99824 \quad (1.2)
\]

Where:
- \(MF_{b}\): Melt Flow Index of the mixture (g/10min)
- \(x\): Percentage of PPv in the mixture (%)
- \(R\): Correlation coefficient of the line (1)

Line equation \(MF_{c}\):

\[
MF_{c} = 7.4517 + 0.12286x \quad R=0.98963 \quad (1.3)
\]

Where:
- \(MF_{c}\): Melt Flow Index of the mixture (g/10min)
- \(x\): Percentage of PPv in the mixture (%)
- \(R\): Correlation coefficient of the line (1)

Line equation \(MF_{d}\):

\[
MF_{d} = 7.7825 + 0.11797x \quad R=0.99382 \quad (1.4)
\]

Where:
- \(MF_{d}\): Melt Flow Index of the mixture (g/10min)
- \(x\): Percentage of PPv in the mixture (%)
- \(R\): Correlation coefficient of the line (1)

Line equation \(MF_{e}\):

\[
MF_{e} = 7.9047 + 0.11139x \quad R=0.97113 \quad (1.5)
\]

Table 7 shows that with the increase in the melt flow index of polypropylene, the yield strength of the polypropylene also rises. In a comparison between the two mixtures made PP\(_{M1}\) and PP\(_{M2}\) it is possible to visualize an increase of 4.35% in the yield strength. The virgin material has a value of about 50% above that presented by the mixture between PP\(_{v}\) and PP\(_{r}\) of IF = 10.691 (g/10 min). For the chosen mixtures the values of

Through the results, the general equation obtained to increase the Melt Flow Index between PPv and PPr mixtures, which is show below:

\[
MF_{Im} = MF_{Ir} + 0.120712x \quad R=0.988468 \quad (1.6)
\]

Where:
- \(MF_{Im}\): Melt Flow Index of the mixture (g/10min)
- \(MF_{Ir}\): Melt Flow Index of the recycled polypropylene (g/10min)
- \(x\): Percentage of PPv in the mixture (%)
- \(R\): Correlation coefficient of the line (1)
elastic modulus (E) are very close, so both samples have the same stiffness. It is also observed that both mixtures have lower E values than virgin material and therefore are less rigid.

As for the yield strain, was observed in Table 7 that the values found for both PP_M1 and PP_M2 are equal. As with the elastic modulus, the highest deformation value is in the virgin material, about 23.5% in relation to PP_M2.

When observed the results of the energy absorbed in the impact, also in Table 7, is possible to verify that both mixtures of virgin and recycled polymer absorb little energy under impact when compared to 100% virgin material.

IV. Conclusions

In the present work, the mixtures of virgin and recycled polypropylene were analyzed in order to obtain an equation to basically correct the melt flow index required by the company to correct the injection process. The results showed that there is a proportional relationship between the melt flow index and the amount of virgin polymer in the mixture. Therefore, for correction and elevation of the melt flow index of recycled polymer, a certain amount of virgin polymer must be inserted to reach the desired index for processing. The evaluation of the mechanical properties showed that the mixtures of virgin and recycled polypropylene maintains rigidity similar that samples with 100% virgin polypropylene, but under impact the mixtures presents a drastic drop in the absorbed energy. Therefore, for applications that require impact the mixtures presents a drastic drop in the absorbed energy. Therefore, for applications that require impact, recycled polymers would have their use compromised.

Acknowledgements

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