Solid State Polymerization: Its Action on Thermal and Rheological Properties of PET/PC Reactive Blends

Luis C. Mendes
Instituto de Macromoléculas Professora Eloisa Mano-IMA, UFRJ

Patrícia S.C. Pereira
Centro Universitário Estadual da Zona Oeste, UEZO

Abstract: The solid state polymerization (SSP) of PET/PC reactive extrusion blends - with and without cobalt catalyst - at different polymer ratios was studied. Thermal and rheological evaluations were performed. DSC results showed changes in the PET’s $T_g$, $T_m$, $T_c$ and $X_c$. The melt flow rate (MFR) decreased for PET and the blends. The intrinsic viscosity increased. The variation in calorimetric and rheological properties might be attributed to the PET’s chain extension reactions – esterification and transesterification. These reactions led to an increase in the PET’s molar mass, consequently shifting the PET’s $T_c$ to lower temperature and PET’s crystallization, besides reducing the blend miscibility and flowability.

Keywords: Rheology, blends, catalysts, PET/PC, thermal properties.

Introduction

Poly(ethylene terephthalate) (PET) and polycarbonate (PC) are commercial polyesters obtained through polycondensation. Their wide application as commodity and engineering polymers is due to their remarkable thermal and mechanical properties. They are easily processing by extrusion, injection, blow-molding and thermoforming. It is well known that condensation polymers can have their degree of polymerization increased by heating in the temperature range between the glass transition temperature ($T_g$) and the crystalline melting temperature ($T_m$). Under these conditions, the polymeric chain end groups have enough mobility to react to each other, generating materials with better physico-mechanical characteristics, due to the increase of the average molar mass. This process is called polymerization/polycondensation in the solid state, or solid state polymerization (SSP). High toughness and modulus nylon-6, nylon-6,6 and bottle grade PET, for instance, are yielded by applying the SSP process. SSP’s reactional parameters - temperature, polymer granules, drag gas or vacuum – still have more influence on the polymerization rate compared with polycondensation in the molten state. In SSP, the temperature – above $T_m$ and below $T_c$ – controls the mobility of the reactive functional end groups of the pre-polymer to react with each other. The temperature must be high enough to induce chain growth but so high as to lead to cyclization and other side reactions. Additionally, the pre-polymer particles can have a critical crystallinity degree in order to avoid their melting, and also the system needs appropriate application of an inert gas or vacuum to release the reactional byproducts.

In SSP studies, the temperature and residence time are generally assessed. Lucas et al. evaluated the influence of both in the SSP to make PET. The study showed that high intrinsic viscosity and consequently high molar mass was achieved due to the increase of both reactional parameters. Regarding the PET/PC blend, research of the SSP process is scarce. Gowd et al. submitted studied the SSP process with several PET/PC oligomer blend compositions. First, the blends were extruded at 250 °C, 100 rpm, at residence time of one minute, in order to minimize the occurrence of transesterification reactions. After that, crystallized blends were subjected to SSP at a range of temperatures and reaction times: 190 °C (1h), 200 °C (1.5h), 210 °C (2.5h), 220 °C (3.0h) and 230 °C (12.0h). The authors noted that the intrinsic viscosity varied with composition, temperature and reaction time.

Considering that dearth of research on SSP with PET/PC blends, the aim of this work was to investigate the effect of solid state polymerization the PET/PC reactive blends on their thermal, mechanical and rheological properties.

Experimental

Materials

PET and PC were supplied by Mossi & Ghisolfi Group and GE Plastics South America, respectively. The MFI PET and density of the PET were 3.0 g.10 min$^{-1}$ and 1.39 g.cm$^{-3}$, respectively. The MFI and density of the PC were 2.5 g.10 min$^{-1}$ and 1.2 g.cm$^{-3}$, respectively. Commercial cobalt acetylacetonate II, produced by J.T.Baker Chemical Co. was used as catalyst.

Blending

PET/PC reactive blending, at different weight fractions, with and without cobalt acetylacetonate II (a transesterification catalyst), was performed in
Extrusão Brasil model DCR 22a, co-rotating twin-screw extruder (L/D = 36 and 22 mm of screw diameter), equipped with a vacuum system, at 190-255 °C and 150 rpm. In order to homogenize the catalyzed blend, a master containing PET and catalyst, in an appropriate proportion, was prepared and the PET amount in the master was discounted for each blend. Before processing, the water was removed from the precursor polymers by drying at 120 °C for 8 hours to prevent hydrolysis during melt processing. After blending, the extrudate was cooled in water (30 °C) and pelletized.

**Solid State condensation (SSP)**

PET, PC and PET/PC blends were submitted to the SSP process in a stainless steel reactor equipped with heating system, vacuum pump and a manometer, at 180 °C during 6 hours, at 0.08bar of vacuum. The conditions were adjusted after several preliminary experiments.

**Differential scanning calorimetry (DSC)**

Calorimetric measurements were carried out with a Perkin-Elmer differential scanning calorimeter (DSC-7). Two cycles of heating and cooling were applied. The first heating cycle was performed from 40 to 300 °C at a heating rate of 10 °C/min⁻¹ (1st scan), under nitrogen atmosphere, kept for 2 minutes in order to eliminate the thermal history, and then cooled (first cooling cycle) to 40 °C at maximum equipment cooling rate (2nd scan). The third cycle of heating (3rd scan) was carried out following the same protocol of the first one. Finally, the fourth cycle was applied, cooling to 40 °C at 10 °C/min⁻¹ (4th scan). The glass transition and melting temperatures, T_g and T_m, respectively, were measured from the curves. The heating and cooling crystallization temperatures, respectively, T_ch and T_cc, were determined when it was possible. For each blend, the PET’s degree of crystallization (X_c) was calculated from the ratio of PET endothermic peak area (ΔH_m) in the blends and the enthalpy of fusion of 100% crystalline PET (136 J.g⁻¹)[16], taking into account the weight of PET in each blend. As proposed by Santana et al.[17], the degree of participation (herein called of effectiveness degree - ε_j) of each component in the PET-rich phase and PC-rich phase was calculated.

**Rheology measurements**

The rheological properties were investigated in a Rheometrics model AR2000 dynamic oscillatory rheometer equipped with parallel plates (D=25 mm, gap=1 mm), in the frequency range from 350 to 10 rad.s⁻¹, at 270 °C, under nitrogen atmosphere. Before the rheological measurements, all materials were dried at 120 °C for 8 hours.

**Melt flow rate (MFR)**

The melt flow rate (MFR) was measured with a Dinastete plastometer, using the ASTM D 1238[18] standard as guidance. The test conditions were 260 °C and 1.2 kg and the result was the average of five measurements.

**Intrinsic viscosity (η)**

The intrinsic viscosity (η) was measured based on the ASTM D 4603 standard[19] using an Ubbelode viscometer, with a phenol-TCE mixture (60/40 v/v) as solvent, at 30 °C. The result was the average of two measurements.

**Results and Discussion**

**Differential scanning calorimetry (DSC)**

Figure 1 and 2 shows the DSC curves of the materials before SSP: 80/20 (A-without catalyst; D-with catalyst) 50/50 (B-without catalyst; E-with catalyst), 20/80 (C-without catalyst; F-with catalyst).

![Figure 1. Second heating DSC curves of the materials before SSP: 80/20 (A-without catalyst; D-with catalyst) 50/50 (B-without catalyst; E-with catalyst), 20/80 (C-without catalyst; F-with catalyst).](image-url)
Mendes, L. C.; Pereira, P. S. C. - Solid state polymerization: its action on thermal and rheological properties of PET/PC reactive blends

in the blends when it could be calculated. In some cases, it overlapped the PET’s heating crystallization temperature, so it was not possible to determine it. After SSP, there was no tendency concerning a change of the PET’s $T_g$. This property decreased for the 50/50 blend, with and without catalyst, while it is constant for the blend with the lowest amount of PET. For the PET rich blends, the PET’s $T_g$ showed an increase and remained constant for the uncatalyzed and catalyzed materials, respectively. The catalyst seems not to act during SSP. Because of overlapping of the the PET’s $T_{ch}$ values, the PC’s $T_g$ could not be determined in the majority of the cases.

Heating crystallization temperature ($T_{ch}$)

For all blends, the values of $T_{ch}$ were shifted to higher temperatures, before and after SSP, independent on the presence of catalyst. The PC’s molecules always retard the PET’s crystallization but their effect is lesser after SSP – lower $T_{ch}$ values were achieved.

Crystalline melting temperature ($T_m$)

The values of $T_m$ were very similar before and after SSP indicating that the crystal thickness was not affected after the post-condensation process.

Crystallinity degree ($X_c$)

The SSP showed a strong influence on the PET’s $X_c$ – it increased for all blends – behavior similar that for the neat PET.

The changes of the blends’ calorimetric properties could have occurred for different reasons. During the blending process, the increase of the PET’s $T_g$ along with the decrease of the PC’s $T_g$, could have been caused by reactions such as transesterification (reaction between PET-ester (-[O=C]-O) and PC- carbonate (-O-[C=O]-O) linkages) and esterification (reactions between PET-carboxyl terminal group (-[C=O]-OH) and PET-hydroxyl terminal group (-OH) with the PC carbonate (-O-[C=O]-O) link), known as acidolysis and alcoholysis reactions, respectively.

These reactions are widely recognized as responsible for the changes in PET/PC blend’s miscibility during blending in the molten state. In the SSP process, besides those reactions, PET-carboxyl, hydroxyl and ester (-[C=O]-OCH$_2$CH$_2$OH) terminal groups may react to each other – esterification and transesterification (chain extension reactions), respectively – leading to an increase of the molar mass. The variation of the $T_m$ can be explained in terms of the competition among all feasible reactions cited. In situations where there is a decrease of the PET’s
T_g along with an increase of the PC’s T_g, it can be inferred that the chain extension reactions prevailed in detriment of the acidolysis and alcoholysis ones. The uncatalysed 80/20 blend was the only case where the PET’s T_g showed an increase, attributed to the transesterification reaction between PET-ester and PC-carbonate linkages along the polymer chains. As in all other cases, the PET’s T_g either decreased or remained the same, so it can be deduced that the transesterification reaction between PET and PC did not occur during SSP. This indicates that the catalyst was inactive during SSP. Therefore, the variation of the blends’ calorimetric properties – T_g, T_ch and X_c – can be attributed to PET’s chain extension reactions. These reactions could have led to the increase of the molar mass of the PET’s chains, the shift of the PET’s T_g to lower temperature and the reduction of the effect of the PC chains inside the PET’s phase on the blend miscibility and PET’s crystallization.

The effectiveness degree - \( \epsilon_d \) - and the glass transition temperature (T_g) of the materials are listed in Table 2. For uncatalysed blends, the \( \epsilon_d \) did not show any tendency, before and after SSP.

The behavior was dictated for each composition. After SSP, blends rich in PET and PC showed increasing in the \( \epsilon_d \) value as result of the esterification and transesterification reactions between end-groups of PET chains and also end-groups of PET chains with end-groups of copolymer PET/PC. Only the PET/PC 50/50 blend showed decreasing of the \( \epsilon_d \) value which could indicate a demixing process. Concerning the catalysed blends, the PET/PC 50/50 blend showed again anomalous behavior. The \( \epsilon_d \) values for blends rich in PET and PC could be considered similar, before and after SSP. By this form, it would be reasonable to think that the cobalt catalyst did not play any role during SSP.

### Rheology measurements

The values of the storage and loss moduli before and after SSP were plotted (Figures 3 and 4, respectively). The curves overlapped, which confirms the inertia of the catalyst in the SSP conditions.

Table 3 shows the G’ and G” as a function of the frequency, before and after SSP. For both precursor polymers, there was a decrease after the post condensation process, which can be attributed to some thermal degradation.

Concerning the blends, before SSP, the G’ value seems to be influenced by the amount of PC – uncatalysed

<table>
<thead>
<tr>
<th>PET/PC blend</th>
<th>PET rich phase</th>
<th>PC rich phase</th>
<th>Before SSP</th>
<th>After SSP</th>
<th>Before SSP</th>
<th>After SSP</th>
</tr>
</thead>
<tbody>
<tr>
<td>80/20^a</td>
<td>89</td>
<td>147</td>
<td>98</td>
<td>145</td>
<td>3.31</td>
<td>36.00</td>
</tr>
<tr>
<td>50/50^a</td>
<td>94</td>
<td>146</td>
<td>85</td>
<td>152</td>
<td>14.13</td>
<td>18.57</td>
</tr>
<tr>
<td>20/80^a</td>
<td>81</td>
<td>155</td>
<td>81</td>
<td>152</td>
<td>11.35</td>
<td>0</td>
</tr>
<tr>
<td>80/20^b</td>
<td>89</td>
<td>148</td>
<td>88</td>
<td>147</td>
<td>3.02</td>
<td>35.76</td>
</tr>
<tr>
<td>50/50^b</td>
<td>107</td>
<td>145</td>
<td>86</td>
<td>138</td>
<td>18.82</td>
<td>30.89</td>
</tr>
<tr>
<td>20/80^b</td>
<td>81</td>
<td>140</td>
<td>81</td>
<td>139</td>
<td>44.44</td>
<td>0</td>
</tr>
<tr>
<td>PET</td>
<td>81</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PC</td>
<td>-</td>
<td>158</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a - without catalyst / b - with catalyst.
Mendes, L. C.; Pereira, P. S. C. - Solid state polymerization: its action on thermal and rheological properties of PET/PC reactive blends

The G’ reached a maximum value for the uncatalysed blend with 50 wt.% of PC. There was marked action of the catalyst on the blends – the G’ value drastically decreased for the catalyzed blends. Similarly, after SSP, the same influences remained with respect to G’ but a tendency to decrease was observed in the majority of cases. Similar behavior was observed regarding G”.

Figure 4. G” of the materials at 10 rad/s.

Table 3. G’ and G” of the materials at 10 rad/s.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Before SSP</th>
<th>After SSP</th>
<th>Before SSP</th>
<th>After SSP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G’</td>
<td>G’</td>
<td>G”</td>
<td>G”</td>
</tr>
<tr>
<td>PET</td>
<td>92.56</td>
<td>88.01</td>
<td>2881</td>
<td>1861</td>
</tr>
<tr>
<td>PC</td>
<td>4830</td>
<td>3357</td>
<td>10060</td>
<td>8298</td>
</tr>
<tr>
<td>PET/PC 80/20</td>
<td>1810</td>
<td>1366</td>
<td>16710</td>
<td>16280</td>
</tr>
<tr>
<td>PET/PC 50/50</td>
<td>3780</td>
<td>3276</td>
<td>18280</td>
<td>21950</td>
</tr>
<tr>
<td>PET/PC 20/80</td>
<td>2769</td>
<td>3322</td>
<td>3252</td>
<td>3233</td>
</tr>
<tr>
<td>PET/PC 80/20</td>
<td>677.7</td>
<td>579.1</td>
<td>901</td>
<td>2407</td>
</tr>
<tr>
<td>PET/PC 50/50</td>
<td>236.7</td>
<td>491.3</td>
<td>2067</td>
<td>1470</td>
</tr>
<tr>
<td>PET/PC 20/80</td>
<td>346.6</td>
<td>236.4</td>
<td>2067</td>
<td>1470</td>
</tr>
</tbody>
</table>

a - without catalyst / b - with catalyst.

Figure 5. Melt flow rate (MFR) of the PET, PC and PET/PC without catalyst before and after SSP.
Unexpectedly, there was a tendency for reduction of the moduli of the blends after SSP. This can be explained by the occurrence of the reactions –transesterification, acidolysis and alcoholysis – or also thermal degradation due to the test conditions, namely prolonged high temperature (270 ºC) and shearing action. In the molten state, all these reactions contributed to deteriorate the polymers’ molar mass, although there was a gain in miscibility.

Table 4. Intrinsic viscosity $[\eta]$ of the materials, before and after SSP, and its variation.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Before SSP [dL/g]</th>
<th>After SSP [dL/g]</th>
<th>Percentage change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>0.81</td>
<td>0.96</td>
<td>19</td>
</tr>
<tr>
<td>PC</td>
<td>1.58</td>
<td>1.57</td>
<td>-1</td>
</tr>
<tr>
<td>PET/PC 80/20a</td>
<td>0.61</td>
<td>0.65</td>
<td>7</td>
</tr>
<tr>
<td>PET/PC 50/50a</td>
<td>1.03</td>
<td>0.83</td>
<td>-19</td>
</tr>
<tr>
<td>PET/PC 20/80a</td>
<td>1.17</td>
<td>1.35</td>
<td>16</td>
</tr>
<tr>
<td>PET/PC 80/20b</td>
<td>1.63</td>
<td>1.92</td>
<td>18</td>
</tr>
<tr>
<td>PET/PC 50/50b</td>
<td>0.70</td>
<td>1.21</td>
<td>66</td>
</tr>
<tr>
<td>PET/PC 20/80b</td>
<td>0.56</td>
<td>0.86</td>
<td>54</td>
</tr>
</tbody>
</table>

a – without catalyst / b - with catalyst.

The MFR and intrinsic viscosity of the PET and blends decreased and increased, respectively.

Conclusion

The post-condensation reaction of poly(ethylene terephthalate)/polycarbonate blends (PET/PC), with and without catalyst, was evaluated. The variation of PET’s $T_g$, $T_{ch}$, and $X_c$ indicated that during SSP only PET’s esterification and transesterification reactions happened. A convergent finding was found based on the rheological study. The MFR and intrinsic viscosity of the PET and blends decreased and increased, respectively.

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