Effectiveness of the Transesterification Catalyst on the Thermal, Dynamic-Mechanical and Rheological Properties of PET/PC Reactive Melting Blends

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Summary: Reactive poly(ethylene terephthalate) / polycarbonate (PET/PC) melting blends were prepared with different cobalt catalyst and polymer compositions. The presence of catalyst increased the miscibility of the 20/80 (wt%) blend, according to differential scanning calorimetry (DSC) and dynamic-mechanical analyses (DMA). The catalyst also promoted the amorphisation of the PET chains. Besides, the catalyst caused drastic lowering of both moduli (storage and loss) and melt flow rate (MFR) of some blends. The best mechanical and processing properties were achieved for blends without catalyst, indicating that transesterification reactions prejudice mechanical properties.

Keywords: blends; catalyst; PET/PC; properties; rheology

Introduction

Blends of poly(ethylene terephthalate) (PET) and bisphenol-A polycarbonate (PC) have received special attention because of the potential industrial applications. Both homopolymers are widely used as engineering plastics. Particularly, PC has high impact strength and PET displays an excellent solvent resistance. As it is well known, commercial polymer blends are designed to improve the final properties of the parent components, including better processability, higher impact strength, better chemical resistance, etc.[1,2]

The reactive blending of PET and PC constitutes a successful and inexpensive route for production of new materials with improved properties.[3,4] Both polymers are polyesters and can react in the molten state to form block or random copolymers through transesterification, which changes the phase behavior and morphology of the blends.[5–7] PET/PC blends have been extensively studied over the past two decades,[8–12] although most studies have focused on the miscibility,[13–15] phase behavior[16,17] and reactions that occur during melt mixing.[18–22] However, the miscibility properties of the blends are still poorly understood, as some studies[13] indicated that the blends are miscible at higher PET contents (above 70%), while others found that the blends were completely immiscible over the whole range of compositions[12] and entirely miscible after transesterification.[23] For this reason, the main objective of the present manuscript is analyzing how the final properties of the reactive PET/PC blends respond to changes of the blend composition.

Experimental Part

Materials

PET and PC were supplied by Mossi & Ghisolfi Group and GE Plastics South America, respectively. The melt flow index (MFI) of PET and density were equal to 33.0g/10 min and 1.39 g/cm^3, respectively.

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The MFI of PC and density were equal to 2.5g/10min and $1.2\,g/cm^3$, respectively. Commercial cobalt acetylacetonate II produced by J.T.Baker Chemical Co. was used as catalyst.

Blending

Reactive blending of PET/PC was performed in a co-rotating twin-screw extruder (L / D = 36 and 22 mm of screw diameter), equipped with vacuum system, at 150 rpm, with residence time of 2 min and in the temperature range of 190-255 °C. For the reactive blends, a master blend containing a mixture of PET and catalyst was extruded for posterior preparation of the blend. Before processing, water was removed from polymers by drying at 120 °C for 8 hours in order to prevent hydrolysis during melt processing. After blending, the extrudate was cooled in water (30 °C) and pelletized.

Differential Scanning Calorimeter (DSC)

Calorimetric measurements were carried out in a Perkin-Elmer differential scanning calorimeter (DSC-7). The sample was heated from 40 to 300 °C at heating rate of 10 °C/min under nitrogen atmosphere (first scan), kept at 300 °C for 2 min and then cooled down to 40 °C at maximum cooling rate (second scan). A second heating (third scan) was carried out using the same protocol of the first scan. Finally, the sample was cooled down to 40 °C at 10 °C/min (forth scan). The glass transition temperature (T_g), melting temperature (T_m), enthalpy of fusion (ΔH_m), heating and cooling crystallization temperatures (T_{ch} and T_{cc}) were then recorded with data provided by the third and forth scans. For each blend, the degree of crystallization (X_c) of PET was calculated as the ratio of the endothermic peak area (ΔH_m) and the enthalpy of fusion of 100% crystalline PET (136 J/g),[24] taking into account the weight of PET in the blend.

Dynamic-Mechanical (DMA)

Dynamic-mechanical properties were performed in a DMA-298 (TA Instruments) on rectangular specimens of 40x10x0.5mm, in bending mode, frequency of 1 Hz, in the temperature range of 50-170 °C, at heating rates of 2 °C/min. The moduli (storage and loss) and Tanδ were then recorded.

Melt Flow Rate (MFR)

The melt flow rate (MFR) was performed in a Dinateste plastometer, according to ASTM D 1238, at 260 °C and weight of 1.2 kg, using samples of 6 g.

Rheology Measurements

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

Results and Discussion

DSC

Table 1 shows the obtained calorimetric data. For blends prepared without catalyst,

Table 1.
Thermal properties of PET/PC blends.

Sample	T_g (°C)		T_g (Fox) (°C)	T_{ch} (°C)	T_m (°C)	X_c (%)
PET	78	–	–	137	247	20
PC	–	153	–	–	–	–
PET/PC 80/20[a]	86	–	95	178	234	19
PET/PC 50/50[a]	82	145	116	172	233	10
PET/PC 20/80[a]	78	149	140	–	–	–
PET/PC 80/20[b]	87	–	95	186	229	10
PET/PC 50/50[b]	97	–	116	–	–	–
PET/PC 20/80[b]	–	138	140	–	–	–

[a]without catalyst; [b]with catalyst

the T_g of PET was shifted to higher temperatures in blends containing up to 50 wt% of PET, but remained constant for smaller PET contents. The T_g of PC was shifted to lower temperatures when detected. The T_{ch} of PET was shifted to higher temperatures, while T_m and X_c decreased. For blends prepared with catalyst, the T_g of PET remained constant when the composition was equal to 80/20, was shifted towards higher temperatures when the composition was equal to 50/50 and was not detected for lower PET contents. The T_g of PC was detected only when the composition was equal to 20/80, while T_{ch} of PET could only be detected when the composition was equal to 80/20, being shifted towards higher temperature. As in the previous cases, T_m and X_c of PET were smaller in the blends.

Modification of the calorimetric data depended on the blend composition when catalyst was not added; however, when catalyst was used, modification of the calorimetric data could only be observed when the PC content was very large. The change of the miscibility behavior can be attributed to chemical reactions, such as acidolysis (reaction between PET terminal-carboxyl and PC carbonate group), alcoolysis (reaction between PET terminal-hydroxyl and PC carbonate group) and transesterification (reaction between PET ester group and PC carbonate group), leading to the formation of PET-PC copolymers, as reported by Lee,[9] Mbarek,[14] Wilkinson[15] and Mendes.[17] According to these authors, chemical reactions can affect the PET crystallizability, reducing its T_m and X_c. According to the Fox miscibility criterion[24] and to the obtained DSC results, the 80/20 and 50/50 blends were partially miscible, while the 20/80 blend was immiscible when prepared without catalyst and miscible when prepared with catalyst.

DMA

Figures 1 and 2 show the Tanδ curves of the prepared blends, while Table 2 presents the T_g measurements taken from the DMA curves. Regarding the blends prepared without catalyst, all Tanδ curves showed two peaks, related to the T_g of PET and PC, respectively.

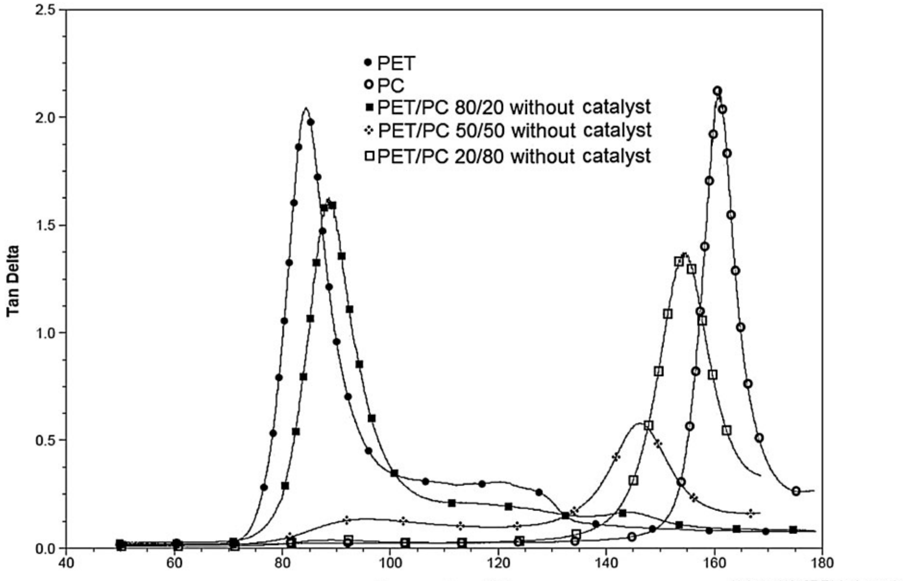

Figure 1.
Tanδ curves of PET, PC and blends prepared without catalyst.

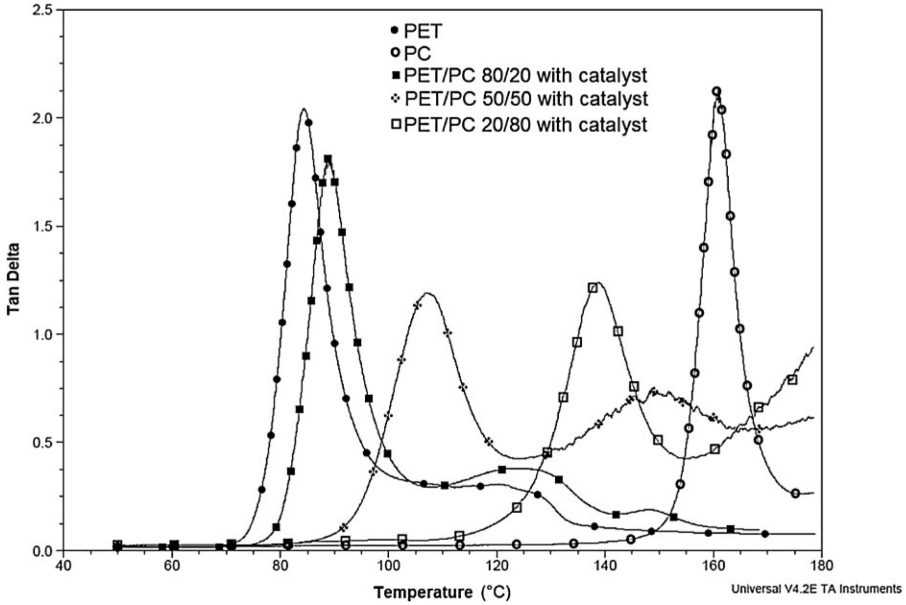

Figure 2.
Tanδ curves of PET, PC and blends prepared with catalyst.

The T_g values presented the same trends described previously. Regarding the blends prepared with catalyst, all Tanδ curves presented two peaks, with the exception of the blend containing the highest PC content. In this case, the T_g of PET were similar to the ones obtained without catalyst and presented similar trends, although the T_g was not detected in the 80/20, 50/50 and 20/80 blends. The T_g of PC was shifted to lower temperatures in all cases. Obtained results indicate that the T_g values change mostly as a function of the blend composition, although the presence of catalyst increased the miscibility of the 20/80 blend.

Although the DMA results have shown some positive effect of the catalyst on the miscibility when the PC content was large, the opposite trend was observed for the dynamic-mechanical properties presented in Table 3, as both the storage and loss moduli decreased drastically when catalyst was added to the blend. The drop of the storage modulus was in the range 20-39%, whereas the loss modulus decreased

Table 2.
T_g values as obtained through DMA.

Sample	T_g Fox (°C)	T_g DMTA (°C)	
PET	–	81	–
PC	–	–	158
PET/PC 80/20[a]	95	89	147
PET/PC 50/50[a]	116	94	146
PET/PC 20/80[a]	140	78	155
PET/PC 80/20[b]	95	89	148
PET/PC 50/50[b]	116	107	145
PET/PC 20/80[b]	140	–	140

[a]without catalyst; [b]with catalyst

Table 3.
Mechanical properties as obtained through DMA.

Sample	Storage modulus[c] (MPa)	Loss modulus[c] (MPa)
PET	1000	150
PC	1800	110
PET/PC 80/20[a]	1400	110
PET/PC 50/50[a]	1500	170
PET/PC 20/80[a]	1000	11
PET/PC 80/20[b]	550	18
PET/PC 50/50[b]	1200	80
PET/PC 20/80[b]	350	9

[a]without catalyst; [b]with catalyst; [c]value at 50 °C

Table 4.
MFR of PET, PC and blends.

Amostras	MFR (g/10min)
PET	77 ± 0,3
PC	5,0 ± 0,1
PET/PC 80/20[a]	50 ± 0,1
PET/PC 5050[a]	29 ± 0,4
PET/PC 20/80[a]	16 ± 0,2
PET/PC 80/20[b]	36 ± 0,4
PET/PC 50/50[b]	40 ± 0,3
PET/PC 20/80[b]	54 ± 0,1

[a]without catalyst; [b]with catalyst

18-82%. The decrease of the loss modulus also depended on the blend composition, being lower for blends containing higher amounts of PC. Thus, it seems that addition of catalyst and occurrence of transesterification reactions are not beneficial for the final mechanical performance of the blends.

MFR

Table 4 shows the MFR values of the obtained materials. In both cases, the MFR values of the blends were between the MFR values of the homopolymers; however, the MFR values decreased with the increase of the PC content in blends prepared without catalyst, while the opposite behavior was observed when catalyst was added.

The additivity rule was used to compare the theoretical MFR values with experimental ones, as shown in Figure 3. For blends prepared without catalyst, measured MFR values were close to calculated values, while distinct behavior was observed when catalyst was added. It seems that transesterification reactions promoted by the catalyst caused the lowering of the molar mass and the consequent increase of the MFR.

Rheological Measurements

Figures 4 and 5 present the rheological behavior of the prepared blends. PET samples presented the typical Newtonian behavior, while PC samples presented the characteristic pseudoplastic behavior. The viscosity plots of the blends prepared without catalyst were averages of viscosity plots of the homopolymers, as reported by Carrot.[25] Regarding the blends prepared with catalyst, all viscosity plots were are shifted towards lower values, as also described by Nabar and coworkers,[26] and did not depend significantly on the blend composition. As described previously, it seems that transesterification reactions promoted by the catalyst caused the lowering of the molar mass and the consequent decrease of the viscosity values.

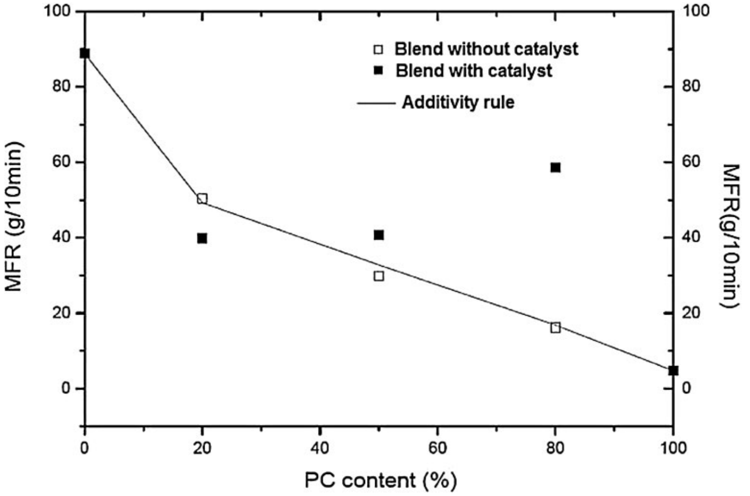

Figure 3.
MFR of PET, PC and blends.

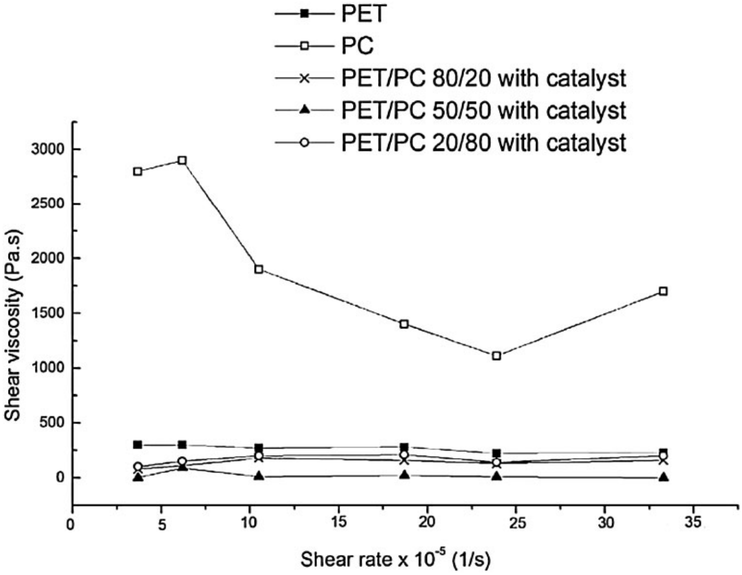

Figure 4.
Viscosity x shear rate of PET, PC and blends without catalyst.

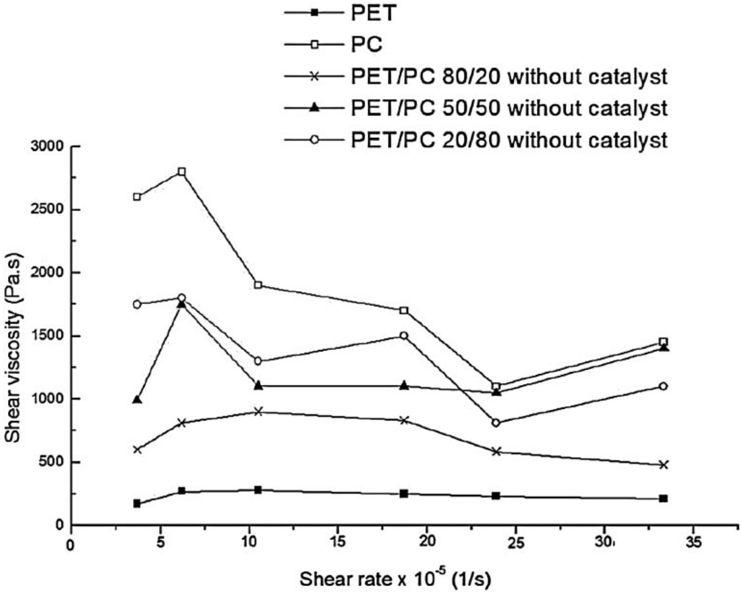

Figure 5.
Viscosity x shear rate of PET, PC and blends with catalyst.

Conclusion

Reactive poly(ethylene terephthalate)/polycarbonate (PET/PC) melting blends were prepared with different cobalt catalyst and polymer compositions and characterized through thermal, dynamic-mechanical and rheological analyses. It was shown that the catalyst affected the miscibility of the blend only when the PET/PC composition was equal to 20/80 wt%. In all cases, moduli were affected negatively by the cobalt catalyst. Besides, the addition of catalyst caused dramatic reduction of the shear viscosity and increase of the MFR. It is beleived that transesterification reactions promoted by the catalyst caused the lowering of the molar mass and the consequent decrease of the viscosity values and increase of the MFR values. Therefore, addition of catalyst must be considered with care during preparation of PET/PC blends.

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