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Solid State Polymerization of PET/PC Extruded Blend: Effect of Reaction Temperature on Thermal, Morphological and Viscosity Properties

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Abstract: A systematic study of solid state polymerization (SSP), concerning the melt extruded blend of poly(ethylene terephthalate)/polycarbonate (catalyzed PET/PC, 80/20 wt %), as a function of temperature range (180-190°C) for a fixed time (6 h) is presented. The materials obtained were evaluated by differential scanning calorimetry (DSC), thermogravimetry/derivative thermogravimetry (TG/DTG), optical microscopy (OM) and intrinsic viscosity (IV) analysis. After SSP, at all reaction temperatures, PET glass transition and heating crystallization temperatures slightly decreased, melting temperature slightly increased, while degree of crystallinity was practically invariable. The DTG curves indicated that, at least, three phases remained. The OM images revealed that the morphology is constituted of a PET matrix and a PC dispersed phase. In the interfacial region we noticed the appearance of structures like bridges linking the matrix and the dispersed domains. These bridges were correlated to the PET/PC block copolymer obtained during blending in the molten state. IV increased for all polymerization temperatures, due to the occurrence of PET chain extension reactions – esterification and transesterification. The IV range for bottle grade PET was achieved.

Keywords: *SSP, PET/PC, blend, optical microscopy, thermal properties, viscosity.*

Introduction

Solid state polymerization (SSP) is traditionally a post-condensation technique in which polymer or its prepolymer increases in molar mass through reactions among terminal-reactive groups. It can be considered an eco-friendly technique compared to interfacial polymerization, for instance, because it is a solvent-free process and does not release toxic wastes. It is also a relatively simple process since it is carried out by heating the reactants between the polymer glass and melting temperatures, under vacuum or a carrier gas. As a consequence, the polymer chain segments in the amorphous phase become mobile enough to allow reaction among polymer-terminal groups while the segments in the crystalline phase have restricted mobility. The success of SSP depends on the temperature, reaction time, polymer particle size and degree of crystallinity, besides the carrier gas (or vacuum). Condensation polymers, mainly polyamides and polyesters, are candidates for SSP. Poly(ethylene terephthalate) (PET) and polycarbonate (PC) are commercial polyesters with wide applications as commodities and engineering polymers. Both are easy to process and have outstanding thermal and mechanical properties.

The existing literature focuses on several aspects of the post-condensation of PET and PC. Vouyiouka et al. studied the morphological changes of PET prepolymer during SSP. They concluded that secondary crystals are strongly dependent on the SSP temperature[1]. Commercial PET was exposed to ethylene diamine vapors in order to reduce its molecular weight. Subsequent SSP indicated an enhancement of the rate of crystallization[2]. The effect of black activated carbon nanoparticles on solid state polymerization of PET was investigated by Karayannidis and co-authors[3]. They observed an increase of the PET intrinsic viscosity during SSP in the vicinity of the PET's melting temperature. Solid state polymerization of PET copolyester was compared to conventional PET's SSP. It was noted that the presence of a comonomer increased the SSP rate[4]. The action of titanium isopropoxide and antimony trioxide on SSP of PET and PEN oligomers was studied by Sivaram and co-authors[5]. They reported an increase of the crystallization rate but a reduction of the SSP rate for both prepolymers.

The influence of nitrogen sweep and high vacuum on the PET's SSP was reported by Agarwal and co-authors[6]. They observed that when nitrogen was used as the carrier gas, the reaction rate and the extent of molecular weight were somewhat lower compared to SSP under vacuum. Roberts and co-authors[7] studied the SSP of prepolymer of PC with different molecular weights using supercritical carbon dioxide and nitrogen as the carrier fluids. They mentioned a contradictory effect of the molecular weight-carried fluid pair on the increase of molecular weight. A dramatic increase of the polymerization rate of PC's SSP was reported by Kim[8] using a PC prepolymer with a very uniform and porous structure, achieving a dramatic increase in polymerization rate. A study on

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microstrucutre via ^{13}C NMR sequence distribution was conducted on poly(butylene terephthalate) copolymers[9].

Mendes et al.[10-13] have published several studies of PET/PC extruded blends. Rheological, thermal, optical and dynamic-mechanical properties were related to the effectiveness of the transesterification catalyst and morphology of PET/PC reactive melting blends. The effect of melt flow rate of PC, cobalt catalyst and time on properties of PET/PC (80/20 wt%) reactive blending were also investigated. The results have shown there is a decrease in the molar mass of the blends due to the competition among chain degradative reactions – acidolysis and alcoholysis – and transesterification in the molten state. In the present study, solid state polymerization of catalyzed extruded PET/PC blend (80/20 wt.%) was investigated in a range of temperatures in order to increase the blend molar mass. Thermal, morphological and viscosity characteristics were evaluated.

Experimental

Materials

Poly(ethyelene terephthalate) (PET) and polycarbonate (PC) were supplied by Mossi & Ghisolfi Group and GE Plastics South America, respectively. Cobalt acetylacetonate II, transesterification catalyst, supplied by J.T.Baker Chemical Co., was used as received.

Blending

Before blending, the precursor polymers were dried at 120ºC for 8 hours in an oven with air circulation to prevent degradation. A co-rotating twin-screw extruder equipped with a vacuum system - L/D ratio = 36, 22 mm screw diameter, with 3 heating zones (190, 222.5 and 255°C), screw speed of 150 rpm - was used to blend the PET/PC (80/20 wt.%) with cobalt acetylacetonate II. After blending, the extrudate was cooled in water (30°C) and pelletized.

Solid state condensation (SSP)

After preliminary experiments, the SSP conditions were settled: 180-190°C, 6 hours and 0.08 bar of vacuum. Post-condensation was applied to the blend and the precursor polymers. The sample was classified according to the SSP temperatures (°C): A0 (blank); A1 (180.0); A2 (182.5); A3 (185.0); A4 (187.5); A5 (190.0).

Differential scanning calorimetry (DSC)

A Perkin-Elmer differential scanning calorimeter (DSC-7) was used to evaluate the thermal transitions. First, the sample was heated from 40 to 300°C at a heating rate of 10°Cmin^{-1}, under nitrogen atmosphere. After two minutes at 300°C – necessary to eliminate the thermal history – the sample was quenched down to 40°C. Then the sample was heated again to 300°C at a rate of 10°Cmin^{-1}, under nitrogen, and finally was cooled to 40°C at 10°Cmin^{-1}. The glass transition and melting temperatures, T_g and T_m, respectively, were measured from the curves. The heating crystallization temperatures, T_{ch} were determined. The PET's degree of crystallinity (X_c) was calculated from the ratio of PET endothermic peak area (ΔH_m) in the blend and the enthalpy of fusion of 100% crystalline PET (136 J g^{-1})[14], taking into account the weight of PET in the blend.

Thermogravimetry/derivative thermogravimetry (TG/DTG)

Thermogravimetry/derivative thermogravimetry (TG/DTG) was performed with a TA Instruments model Q1000 DSC. The test conditions were 30 to 700°C, at a rate of 10°C.min^{-1}, under nitrogen atmosphere. The T_{onsetr}, T_{max} and T_{final}, respectively the onset, maximum and final degradation temperatures, were determined.

Optical microscopy (OM)

The phase constitution of the blend was evaluated with a Zeiss optical microscope from a sample squeezed between thin glass plates. The assembly was placed over the microscope's hot plate and the sample morphology was monitored by heating/cooling cycles.

Intrinsic viscosity (η)

The intrinsic viscosity [η] was measured based on the ASTM D 4603 standard[15] using an Ubbelohde 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

Research on solid sate polymerization of PET/PC catalyzed extruded blend is scarce. Ramesh and Gowd[16] investigated the morphological consequences of the interchange reaction of melting blend of PET and PC oligomers, during SSP. They described that a copolymer was produced through a simultaneous SSP and ester-carbonate interchange reaction. More recently, Mendes and Pereira[17] published an article on SSP of PET/PC reactive blends, with and without cobalt catalyst, at different polymer ratios, focusing on rheological and thermal properties.

Thermogravimetry

The data from the present study help to better understand the SSP process of PET and PC melting blend. Figure 1 and Table 1 show the DTG curves and thermogravimetric data, respectively. The DTG curves showed three distinct peaks, which are related to at least three phases. The first one was attributed to the PET/PC block copolymer generated during molten state processing. The intermediate (more intense) peak represents the thermal degradation of PET rich phase while the last one (at higher temperature) was correlated to the degradation of PC rich phase. T_{onset}, T_{max} and T_{final} were practically invariable. The results indicated that during SSP, the blend did not have any additional degradation.

Differential scanning calorimetry

Figure 2 and Table 2 show the calorimetric curves and data, respectively. Before SSP, the PET showed glass transition, heating crystallization and melting temperatures and 20% degree of crystallinity. Due to its amorphous nature, the PC showed only the T_g. In the blend, the PET's T_g and T_{ch} were shifted to higher temperatures while its T_m decreased. The reason for the changes in PET's characteristics can be attributed to the production of *in situ* PET/PC block copolymer – compatibilizing – during the molten state. The PC's T_g was overlapped by the PET's T_{ch} so it could not be determined. The solid state polymerization had an influence on pure PET. It was noticed a sharp increase in the PET's degree of crystallinity, which can be interpreted as indicating both an additional increase of molar mass and enhancement of PET's nucleation/crystal growth processes. In the blend, PET's T_g and T_{ch} decreased slightly. A small increase of PET's melting temperature was observed. The PET's degree of crystallinity was almost invariable.

A transesterification reaction between (PET-ester (-[O=C]-O) and PC-carbonate (-O-[C=O]-O) linkages and a esterification reaction among (PET-carboxyl terminal group (-[C=O]-OH) and PET-hydroxyl terminal group (-OH) with the PC carbonate group (-O-[C=O]-O), commonly called acidolysis and alcoholysis reactions, respectively, were the main reactions that occurred in the PET/PC molten blend. The transesterification reaction leads to an increase both of compatibility and molar mass of the polycondensates polymers in the molten state. Although causing an increase in compatibility, acidolysis and alcoholysis are degradative reactions that decrease the molar mass of the blend. SSP is a technical appeal to achieve an increase of molar mass. In this study, these reactions did not operate during SSP. If they had occurred, an increase of T_g and reduction of T_m would have been observed. Considering the calorimetric data of the blend, it can suppose that PET's chain extension reactions – esterification and transesterification – occurred during SSP. These reactions increase the influence of the PET on the blend's properties. The reactions are shown schematically in Figure 3.

Optical microscopy

Through the OM images, the optical study in the molten state and after solidification allowed determining the blend matrix and dispersed phase. Figure 4 shows the blend morphology before SSP while Figure 5 depicts the blend behavior after SSP. In all situations, after cooling no crystallization occurred inside the droplets, which was interpreted as PC domains. On the other hand, crystallization was detected outside them, indicating that PET was the matrix. There was a tendency for disappearance of small drops (coalescence). There was still an interfacial region between matrix and droplets in which we observed the appearance of structures like bridges linking the matrix and dispersed domains. These bridges were correlated to the PET/PC block copolymer achieved during molten blending, playing a compatibilizing role as can be seen from OM images.

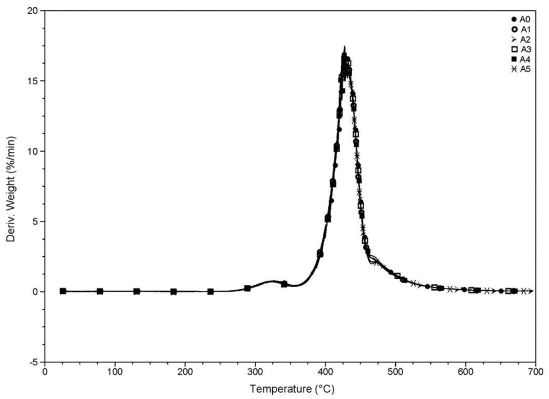

Figure 1. DTG curves of the materials, before and after SSP.

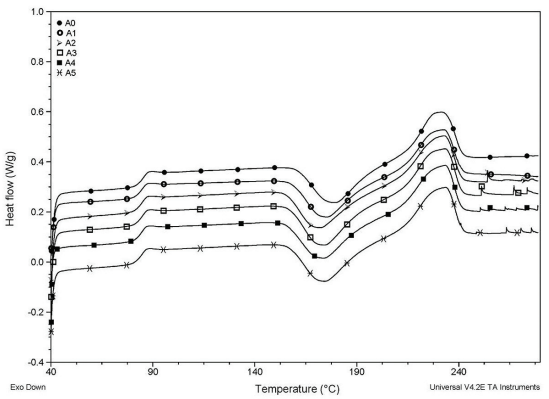

Figure 2. DSC curves of the materials, before and after SSP.

Table 1. DTG degradation data of the materials, before and after SSP.

Sample	Degradation temperature (°C)		Maximum degradation temperature (°C)	
	T_{onset}	T_{final}	$T_{máx}$ PET rich phase	$T_{máx}$ PC rich phase
A0	408	536	327 / 426	470
A1	408	540	326 / 426	468
A2	408	538	319 / 427	475
A3	408	535	324 / 427	475
A4	407	540	325 / 428	468
A5	407	528	326 / 427	475

Table 2. DSC properties of the materials, before and after SSP.

Sample	T_g PET phase (°C)	T_g PC phase (°C)	T_{ch} (°C)	T_m (°C)	X_c (%)
Before SSP					
PET	78	---	137	247	20
PC	---	158	---	---	---
A0	85	nd	179	231	19.5
After SSP					
PET	78	---	134	245	27
PC	---	158	---	---	---
A1	84	nd	175	233	18.9
A2	84	nd	172	233	19.8
A3	84	nd	174	233	20.6
A4	84	nd	174	233	18.6
A5	84	nd	174	234	19.5

nd means not detected.

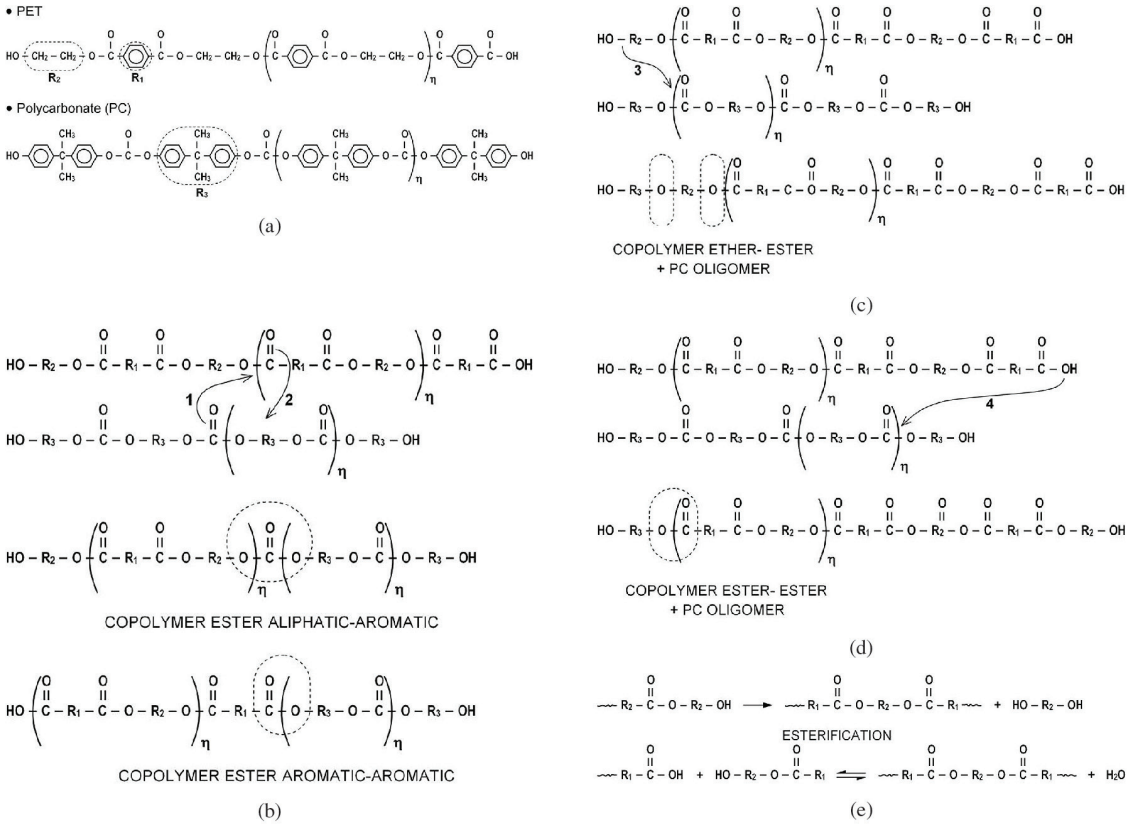

Figure 3. Schematic representation of the main reactions at molten state – (a) PET and PC chains; (b) transesterification; (c) alcoholyisis; (d) acidolyisis; and main reactions at SSP (e) transesterification / polycondensation.

Intrinsic viscosity

Table 3 presents the intrinsic viscosity [η] values of the blend, before and after SSP. Except for PC, an increase of [η] is shown for the PET and the blend, for each temperature. This suggests that the PC did not undergo post-condensation reaction under the conditions applied in this study. On the contrary, the PET-carboxyl, hydroxyl and ester (-[C=O]-OCH_2CH_2OH) terminal groups reacted to each other through esterification and transesterification (chain extension reactions). These reactions led to an increase of the molar mass of the PET's chains and influenced the blend characteristics. There was a tendency for increasing viscosity with temperature. At the highest temperature, the [η] increased almost 40% compared to the blank. The IV values attained the range for PET-carbonated soft drink bottles[18]. Then, the SSP of PET/PC (80/20) blend was successful.

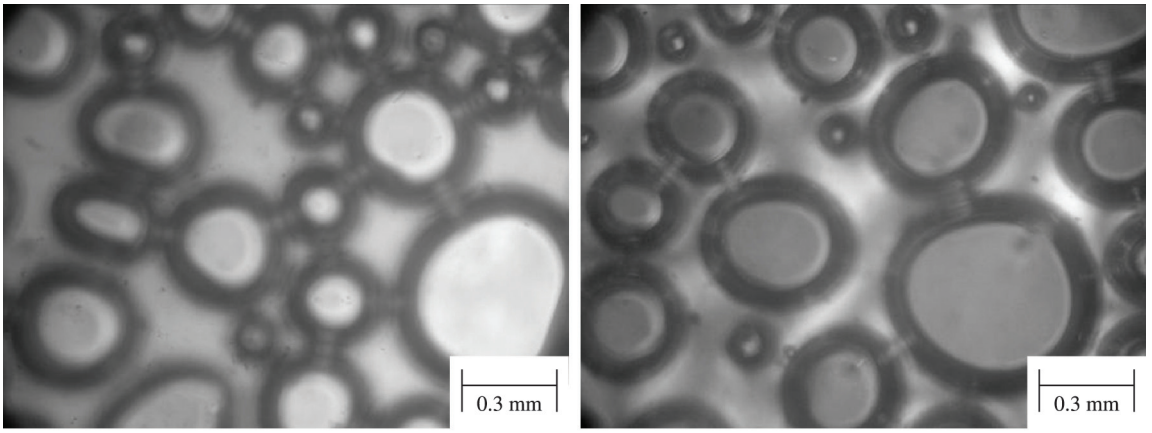

Figure 4. OM image of the blend before SSP: a) molten mass at 280°C; b) after cooling.

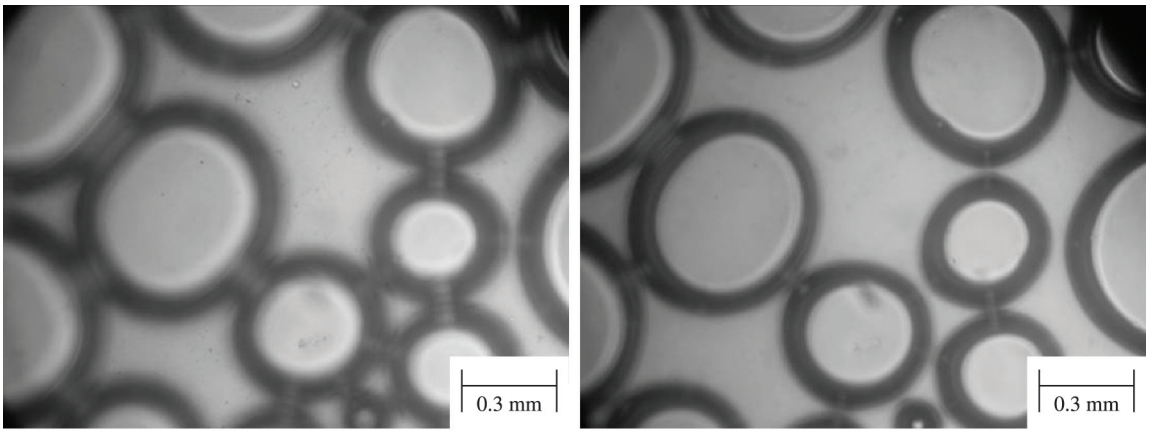

Figure 5. OM image of the blend after SSP(185°C): a) molten mass at 280°C; b) after cooling.

Table 3. Intrinsic viscosity of the materials, before and after SSP.

Sample	SSP Temperature (°C)	Before SSP Intrinsic viscosity (η)	After SSP Intrinsic viscosity (η)
PET		0.81	0.96
PC		1.58	1.57
A0	----	0.653±0.001	----
A1	180.0	----	0.654±0.001
A2	182.5	----	0.867±0.002
A3	185.0	----	0.831±0.003
A4	187.5	----	0.840±0.002
A5	190.0	----	0.889±0.001

Conclusion

A systematic study of SSP concerning the PET/PC (80/20) melting extruded blend as function of temperature was presented. The blend's composition and viscosity of the precursor polymers determined the blend morphology – PET and PC were matrix and dispersed domains, respectively. Compatibility was evidenced as bridges – block copolymers produced in the blending process – connecting the PET and PC phases. Considering that PC did not undergo on post-condensation reaction, and PET-PC transesterification, acidolysis and alcoholysis reactions could be neglected during the SSP, the changes in thermal properties and the increase of intrinsic viscosity of the blend were ascribed to the PET esterification and transesterification reactions. According to the IV values, the material could be useful for using in PET-carbonated soft drink bottles.

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