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INFLUENCE OF COBALT COMPLEX ON THERMAL PROPERTIES OF POLY(ETHYLENE TEREPHTHALATE)/POLYCARBONATE BLEND

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The effects of processing time and concentration of cobalt acetylacetonate III complex in poly(ethylene terephthalate)/polycarbonate reactive blending were investigated. The blend was prepared in an internal mixer at 270°C, 60 rpm, at different processing times (5–20 min) and catalyst concentration (0.00625–0.075 mass%). The reaction product was evaluated by differential scanning calorimetry (DSC), thermogravimetry (TG) and wide angle X-rays scattering (WAXS).

In general, the DSC curves showed two glass transition temperatures (T_g's) close to each homopolymer, independent of the processing time and complex's concentration, suggesting the presence of two phases: one rich in PET and other one rich in PC. In all cases, melting temperature (T_m), cold crystallization temperature (T_{cc}) and crystallinity degree (X_c) were progressively reduced with blending conditions. The TG curves presented two decays. The first one represented the PET rich phase and the other one was related to the PC phase. The WAXS diffractograms showed that the Bragg's angle and interplanar spacing of PET remaining practically unchanged.

Keywords: *cobalt catalyst, PET/PC blend, reactive blending, transesterification reaction*

Introduction

Blends comprising poly(ethylene terephthalate) (PET) and polycarbonate (PC) have received special attention because of their potential industrial application. Both homopolymers are widely used as engineering plastics [1]. PC has excellent impact, thermal and tensile properties which makes it suitable to use in jet aircraft windows, compact discs (CD) and digital video discs (DVD), however, it has poor solvent and chemical resistances. On the contrary, PET is strong against several chemicals but it has low impact strength. Reactive blending is a most useful technique when used to produce new polymer blends. Advantages of this process are facile polymerization process, high flexibility and versatility, lower capital investment and reduced impact on the environment. PET/PC reactive blending has given rise to conflict results in the literature mainly due to differences in composition, type and amount of catalyst, and preparation [2–4]. During the melting process, several reactions can occur but an exchange/transesterification reaction plays the most important role in the final product. Its extent controls on the production of block and/or random copolymers, which affect the miscibility of the system. In general, the type and amount of catalyst and the processing time are responsible for the degree of transesterification reactions thus leading to a copolymer with a one or more T_g's [5–10]. Marchese *et al*. studied PET/PC blends in presence of titanium, samarium and erbium catalysts. It was noticed that titanium catalysts formed a system with a unique T_g over shorter processing times while the other catalyst systems required longer times to attain a miscible system [11]. The influence of lantanium acetylacetonate on the PET/PC reactive blending was investigated by Kong *et al*. Two T_g's were found which indicated that the system was partially miscible, showing one amorphous phase rich in PET and other one rich in PC [12]. Conversely, Hanrahan *et al.* pointed that blend of PET/PC formed a completely immiscible system and PC exerted a significant influence on PET's melting behavior and heat of fusion [13]. Nassar *et al*. have reported that PET/PC melt blending led to the formation of a homogeneous amorphous material for compositions over 70 mass% of PET but remained inhomogeneous at concentrations below 70 mass% [14].

In this paper we have investigated the effect of processing time and content of cobalt(III) acetylacetonate complex in PET/PC reactive blending. DSC, TG and WAXS analysis were carried out in order to evaluate the thermal properties and crystal parameters of the reaction products.

Experimental

Materials

PET and PC were supplied by Braskem and GE Plastics South America, respectively. The intrinsic viscosity (ASTM D 4603) [15] and density (ASTM D 792) [16]

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of PET were 0.80±0.02 dL g^{-1} and 1.39 g cm^{-3}, respectively. The PC MFI (ASTM D 1238) [17] and density (ASTM D 792) [16] were 2.5 g/10 min and 1.2 g cm^{-3}, respectively. The commercial cobalt(III) acetylacetonate was produced by J. T. Baker Chemical Co. All of them were used as received.

Blending

PET/PC (50/50 mass%) blends were prepared in an Haake Reomix 600 internal mixer at 270°C, 60 rpm, at different processing time (5–20 min) and catalyst concentration (0.00625–0.05 mass%). Before their use, polymers were dried for 16 h at 120°C to remove water to prevent hydrolysis during melt processing.

After blending, the material was grounded to facilitate its handling.

Methods

Thermal analysis

Thermal analysis was carried out in a PerkinElmer differential scanning calorimeter (DSC-7), calibrated by high purity standards. The samples were initially heated from 40 to 280°C at a heating rate of 20°C min^{-1} under nitrogen atmosphere, kept for 2 min and then cooled up to 40°C at the same rate. A second heating procedure was then carried out until 280°C at 10°C min^{-1} and finally the sample was cooled up to 30°C at 10°C min^{-1}. After this thermal treatment, glass transition temperature (T_g), melting temperature (T_m) and enthalpy of fusion (ΔH_m) were measured during the second scan. The heating and cooling crystallization temperatures, T_c and T_{cc}, respectively, were determined when it was possible. The PET crystalline fraction (X_c) was calculated from the ratio of PET endothermic peak area (ΔH_m) taking into account the enthalpy of fusion of 100% crystalline PET (136 J g^{-1}) [18].

Thermogravimetric (TG) analysis was also carried out in a PerkinElmer TGA-7 between 30–700°C at a heating rate of 20°C min^{-1}, under nitrogen atmosphere. The starting/ending degradation temperatures and the curves profile were evaluated.

Wide angle X-ray scattering (WAXS)

The crystallographic parameters of PET were determined in Rigaku model DMAX 2200 X-ray equipment using a tension of 40 kV and current 30 mA. The Bragg's equation and equation were used to calculate the crystal parameters. The crystallite size (L_{hkl}) was calculated using the Scherrer equation, Eq. (1) [19]:

$$L_{hkl}=K\lambda/(\cos(\theta_{hkl})\Delta 2\theta_{hkl} \qquad (1)$$

where K=0.89; λ=wavelength; $2\theta_{hkl}$=Bragg's angle and $\Delta 2\theta_{hkl}$=width at half height.

L_{001} was calculated using the following Eq. (2) [20]:

$$L_{001}=L_{0-11}\cos\alpha_1 \qquad (2)$$

where α_1=67.7°; L_{0-11} is calculated through Eq. (1).

Results and discussion

TG analysis

The TG curves of PET, PC and blends are shown in Figs 1 and 2. The thermal curves of blends with 0.00625 and 0.05 mass% of catalyst were chosen as representative. The homopolymer curves showed a single decay. PET presented lower thermal resistance than PC. Both homopolymers left a carbonaceous ash. The blend without catalyst presented a degradation curve similar to those homopolymers and lay between them.

Considering the DTG curves (Figs 3 and 4), it was observed that the blends have degraded in two stages attributed to a PET rich phase and PC one, respectively. The starting and end temperatures, as well as the residue of thermal degradation of the samples are listed in Table 1. The onset temperatures have decreased with processing time and amount of catalyst. Similar behavior was observed for the end temperatures. Carbonaceous residue for all samples is around 14–25%. The blend prepared at 20 min presented lower thermal resistance than the other ones.

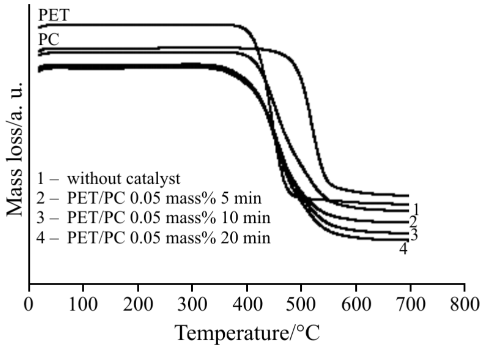

Fig. 1 TG curves of samples

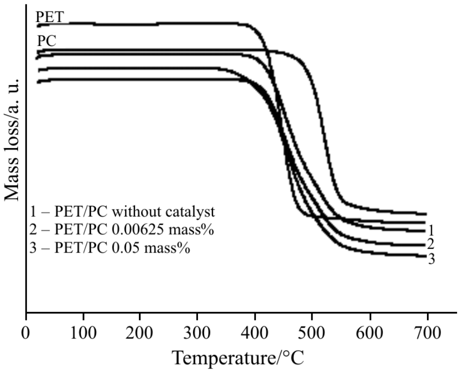

Fig. 2 TG curves of samples

Table 1 Data taken from the TG curves for PET, PC and PET/PC blends

Sample	Reaction time/min	Catalyst/mass%	Degradation temperature/°C		Residue/%
			start	end	
PET	10	–	395	480	14
PC	10	–	450	552	25
PET/PC	10	–	398	544	20
PET/PC	10	0.00625	395	538	20
PET/PC	10	0.0125	392	535	19
PET/PC	10	0.025	386	526	19
PET/PC	10	0.05	362	515	19
PET/PC	10	0.075	352	509	20
PET/PC	5	0.05	362	515	19
PET/PC	10	0.05	380	517	19
PET/PC	20	0.05	342	518	19

Table 2 DSC parameters for PET, PC and PET/PC blends

Sample	Reaction time/min	Catalyst/mass%	T_g PET/°C	T_g PC/°C	T_c/°C	T_m/°C	X_c/%
PET	10	–	76	–	132	248	30.2
PC	10	–	–	140	–	–	–
PET/PC	10	–	77	–	143	245	25.9
PET/PC	10	0.00625	77	–	144	246	26.8
PET/PC	10	0.0125	77	–	146	244	24.1
PET/PC	10	0.025	77	–	153	241	21.1
PET/PC	10	0.05	84	–	–	235	25.3
PET/PC	10	0.075	96	–	–	231	–
PET/PC	5	0.05	80	–	171	236	32.0
PET/PC	10	0.05	84	–	–	235	25.3
PET/PC	20	0.05	89	–	181	234	19.6

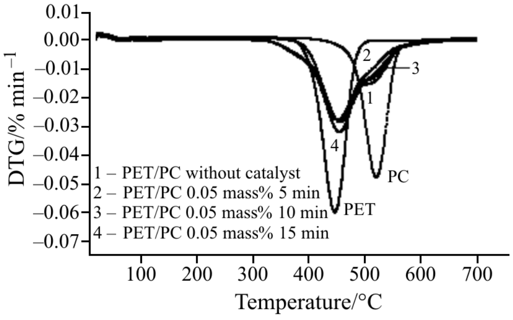

Fig. 3 DTG curves of samples

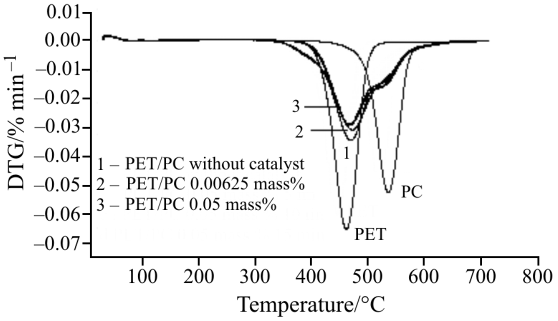

Fig. 4 DTG curves of samples

In most of cases a partially miscible system was formed due to the transesterification reactions that have occurred during the processing of the blends.

DSC investigations

In Figs 5 and 6 the DSC curves of the samples are shown. As expected, the PET curve showed glass transition, heating crystallization and melting temperatures while the PC curve showed only its T_g for all blends. The DSC curves were similar to PET, however, the T_c shifted to higher temperature and overlapped the glass transition of PC.

Table 2 summarizes data of the homopolymer and blends taken from the DSC curves. The thermal parameters of PET and PC are in agreement in the literature sources [21]. Considering the processing time, it was noticed that T_g of PET glass increased slightly in the blends, T_c was displaced from 132 to 181°C and T_m also reduced strongly. With respect to catalyst concentration, until 0.025 mass% there was no observable change on the T_g of PET but the T_c shifted to higher temperature (153°C) and T_m has decreased.

Table 3 WAXS parameters for PET, PC and PET/PC blends

Sample	Reaction time/min	Catalyst/mass%	Plane								
			(100)			(010)			(001)		
			2θ/degree	*D*/Å	L_{100}	2θ/degree	*D*/Å	L_{010}	2θ/degree	*D*/Å	L_{001}
PET	10	–	25.9	3.44	101.8	17.2	5.16	118.2	14.3	6.2	52.4
PC	10	–	–	–	–		–	–	–	–	–
PET/PC	10	–	25.3	3.52	67.38	16.7	5.31	119.9	13.8	6.4	53.3
PET/PC	5	0.05	–	–	–	16.9	5.25	82.0	14.0	6.33	34.1
PET/PC	10	0.05	–	–	–	17.0	5.22	67.4	14.2	6.24	24.3
PET/PC	10	0.00625	–	–	–	16.9	5.25	104.5	14.1	6.28	41.6
PET/PC	10	0.0125	–	–	–	16.8	5.31	104.4	13.9	6.37	39.9
PET/PC	10	0.025	–	–	–	16.9	5.24	120.0	14	6.33	44.2
PET/PC	10	0.075	–	–	–	16.9	5.25	125.6	14.0	6.33	48.2

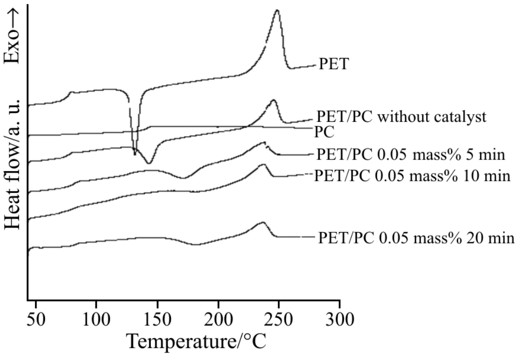

Fig. 5 DSC traces for PET, PC and PET/PC blends

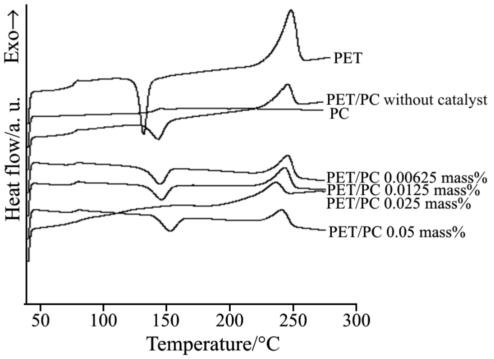

Fig. 6 DSC traces for PET, PC and PET/PC blends

Above that concentration the glass transition of the blend increased and attained a unique value around 96°C, indicating that an amorphous material was formed. The T_c and T_m have disappeared. In all cases the degree of crystallinity was reduced.

During the mixing process, several reactions, mainly exchange/transesterification reactions occur which play an important role in the final product. This extent controls the production of copolymers and affects the miscibility of the system. The DSC results clearly corroborate the TG ones.

WAXS analysis

With regard to the processing time the reduction of the crystallite size was observed with a lower degree of perfection. The same behaviour was found with respect to catalyst content. Variation in the crystallite size was obtained by Sherrer's equation are listed in Table 3. The *d* spacing and Bragg's angle did not show any significant changes and were independent of reaction time and catalyst content. Most of blends did not present crystallite size in the L_{100} direction. The level of transesterification reaction predominantly affected the crystallization of PET.

Conclusions

Reactive blending of PET/PC in the molten state at different processing times and cobalt complex concentrations was carried out and subsequently analysed using DSC, TG and WAXS techniques. The results indicate that the addition of varying amounts of catalyst promoted changes in the thermal properties and crystallographic parameters of PET. The materials obtained varied from crystalline to amorphous due to the level of the exchange reactions occurred during processing. These changes indicated that copolymers were formed.

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