

Effects of composition and transesterification catalysts on the physico-chemical and dynamic properties of PC/PET blends rich in PC

A. Al-Jabareen · S. Illescas · M. LI. MasPOCH · O. O. Santana

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Abstract Melt blending of polycarbonate (PC)/poly(ethylene terephthalate) (PET) rich in PC at absence/present of different type of transesterification catalysts was carried out by using reactive extrusion method. The thermal, dynamic, and morphological properties were studied. It was found that all blends are formed by a PC matrix and a semicrystalline (12–20% of crystallinity) of PET dispersed phase. The addition of a catalyst in the mixing process promotes a refined and homogeneous dispersion of PET, as well as it enhances the dynamic mechanical behavior of PC/PET blends compared with PC. These effects are attributed to the emulsifying effect of the PC–PET copolymer generated by transesterification. Additionally, this copolymer contributes to the miscibility between phases as demonstrated by the glass transition (T_g) shift of PC phase and PET phase.

Introduction

Blends designed around polyethylene terephthalate (PET) are in great demand because of the tremendous versatility of this material and its inherent properties. Blends of PET and polycarbonate (PC) are one of the preferred for its overall balance of properties. These blends combine the solvent resistance advantages of PET with the high T_g and

toughness advantages of PC especially when miscibility of the blend components is achieved [1].

There were initial differences in opinion as to whether these blends were miscible. The miscibility of the PET/PC blends has been controversially discussed in literature, from completely miscible for all compositions [2], partially miscible [3, 4] to completely immiscible for all compositions [5–8]. Blends of PET/PC were reported to be miscible in the high polyester range, but blends below 70% polyester were seemed to be immiscible [3, 4]. These discrepancies were explained by the occurrence of transesterification reaction, which depends on the processing parameters, or to residues of catalysts used in synthesis of commercial PET.

Many researchers have carried out the transesterification reactions of PC/PET blends in the molten state. It is believed that the main reaction is the exchange reaction between PET ester and PC carbonate groups. Other subsequent reactions were degradation, pyrolysis, and gel formation, probably as a result of the instability of the ethylene carbonates produced by the exchange reaction [9]. Depending on the reaction, extension and unreacted PET and PC, a block or graft PET/PC copolymer will be the product. The chemical structure of the transesterification product was strongly dependent on both the melt blending time and on the kind of catalysts added. The products obtained after an extended time of transesterification reactions should be random copolymers [10–12].

In previous work [13, 14], our group has reported some results of the blending of PET/PC systems without using catalysts. The molecular weight of products was increased, the fluidity decreased, and crystallization of PET was restricted. This demonstrated that some extent of exchange reaction occurred. It was also found that at a lower PC content the fracture behavior is mainly controlled by

A. Al-Jabareen (✉)
Materials Engineering Department, AL-Quds University,
20002 East Jerusalem, Palestine
e-mail: ajabareen@science.alquds.edu

S. Illescas · M. LI. MasPOCH · O. O. Santana
Centre Català del Plàstic, Universitat Politècnica de Catalunya
(UPC), Colom 114, 08222 Terrassa, Spain

transesterification effects, while at a higher content the oriented and stratified morphology, which is developed, seems to control the fracture behavior.

Many articles investigated transesterification reactions occurring in PET/PC blends by using a transesterification catalyst to facilitate the process of reaction in PET/PC blends rich in PET [15–17]. Titanium tetrabutoxide and lead acetate hydrate were found to be the most active catalysts [10, 11, 15–18]. Recently lanthanum acetyl acetonate hydrate and cobalt acetyl acetonate were used in PET/PC blending [19, 20].

In this study, PC/PET blends rich in PC have been prepared with co-rotating twin-screw extruder to further optimize the effects of composition and types of transesterification catalysts on the physico-chemical and dynamic mechanical properties especially secondary relaxations, which has not been previously reported in the literature for these blends. The well-dispersed systems obtained and the effective compatibilized systems used in this research have led to better dynamic and mechanical properties than those previously reported. This work is a part of a complete study [21] where tensile and fracture behaviors of PC/PET blends were also evaluated.

Experimental

Materials and sample preparation

PET copolymer based on isophthalic acid ($\approx 2.3\%$), with intrinsic viscosity of 0.80 dL/g (in 1,1',2,2'-tetrachloroethane/phenol, 60/40 wt/wt, at 25 °C) and MFI of 19.1 g/10 min (at 260 °C, 1.2 kg, according to ASTM D 1238) and Lexan R123 PC with MFI of 9.6 g/10 min were used as the original materials. Samarium acetyl acetonate ($\text{Sm}(\text{acac})_3 \cdot x\text{H}_2\text{O}$ ($x = 3\text{--}4$)), calcium acetate hydrate ($\text{Ca}(\text{CH}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$), and zinc acetate hydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) purchased from Aldrich were used as a catalysts. IRGANOX 1425 [1:1-combination of calcium-bis(((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl)-ethylphosphonate) and polyethylene-wax] was also purchased from Aldrich and was used as stabilizer.

A COLLIN ZK-25 co-rotating twin-screw extruder with a $L/D = 36$ and a screw diameter of 25 mm was used for the melt mixture of PC/PET at temperature of 190–270 °C. A screw speed of 130 rpm for systems without catalysts was applied and 160 rpm in the presence of transesterification catalysts. The PET amounts added were 10, 20, and 30% w/w and the following code will be used: PC##, where ## is the nominal PC content (PC90, PC80, and PC70). Nitrogen and vacuum were applied to eliminate moisture and to reduce the possibility of secondary reactions or degradation. A catalyst (when used) is initially

dispersed mechanically on polymer pellets at (0.05 mass%) concentration with respect to the final product.

The extrudates were pelletized at die exit, dried, and extruded another time by a Collin Teach Line 20T-E single screw extruder with 20 mm diameter and length to a diameter ratio of 25:1 connected to large tube, die, and take-off post extrusion to produce extrudates of sheet shape of 0.7 mm under the same processing conditions of melt blending process. IRGANOX 1425 as a stabilizer was initially dispersed mechanically on polymer pellets at a concentration of 0.5% wt/wt with respect to the final product. It was used to prevent any additional modification/reaction (transesterification or degradation) of PC/PET blends containing catalyst to occur during sheet production. Before melt blending, the starting materials were dried. Polymers were held in a PIOVAN T30IX dehumidifying dryer hopper at 120 °C for 4 h.

Characterization

Differential scanning calorimetry is performed using a Perkin Elmer Pyris 1 DSC equipped with Intercooler-IIP. The samples (10 mg) were heated from 30 to 270 °C at heating rate of 10 °C/min in a nitrogen atmosphere. The melting temperature (T_m) and cold crystallization temperature (T_{cc}) were determined by the maximum temperature endotherm peak and the minimum temperature exotherm peak, respectively. From each enthalpy and by making a correction according to the weight fraction of PET in the blends (x_{PET}), the degree of crystallinity (X_c) can be estimated to each thermal transition according to the following expression:

$$X_c = \frac{\Delta H_t}{\Delta H_f^\circ} \cdot 100\%, \quad (1)$$

where in this case ΔH_t is the area of the melting endotherm per gram of polymer PET (ΔH_f) subtracted from cold crystallization enthalpy (ΔH_{cc}) when the cold crystallization peak is appeared and ΔH_f° is the heat of fusion of a completely crystalline material sample which is $\Delta H_f^\circ = 135.8$ J/g [22].

Tan δ , storage modulus (E'), and their temperature dependence of the samples were determined by TA Q800 V7.4 build 127 dynamic mechanical analyzer (DMA). DMA test was conducted with the heating rate of 2 °C/min and frequency of 1 Hz in the temperature range of –140 to 280 °C using the single cantilever clamp and samples with the dimensions of 17.5 mm \times 12.5 mm.

A Joel JSM6400 scanning electron microscope (SEM) was used to study the morphology of the cryogenic fracture surfaces in the central zone of the sheet samples were parallel to the flow direction which was gold-coated with a thickness of 0.3 mm. A normal distribution was used to

obtain an estimate of the number average radius (R_n) and the volume average radius (R_v) according to Eqs. 2 and 3, respectively [23]:

$$R_n = \frac{\sum_i(N_v)_i R_i}{\sum_i(N_v)_i} \tag{2}$$

$$R_v = \frac{\sum_i(N_v)_i R_i^4}{\sum_i(N_v)_i R_i^3} \tag{3}$$

where $(N_v)_i$ is the number of particles with a radius R_i .

Attenuated total reflection (ATR) FTIR spectra were performed by using a Nicolet 6700 instrument in the range of 400–4000 cm^{-1} . The FTIR spectrum was obtained using 32 scans and 4 cm^{-1} resolution. The degree of transesterification was measured, using the characteristic band ratio of 1079 cm^{-1} /725 cm^{-1} .

Results and discussion

FTIR analysis

Figure 1 shows FTIR spectra for neat polymers and PC90 blends as an example of the results obtained. The first observation in blends without transesterification catalysts is that there was no shift of carbonyl band (1720 cm^{-1}) which corresponding to PET in the case of PC80 and PC70 while some shift occurred to high frequency for PC90 blends compared with neat PET. For blends with transesterification catalysts, there is a slight shift of carbonyl band to higher frequency as reported in Table 1. The same trend was noticed with the PC carbonyl bands of blends compared with PC homopolymer as shown in Fig. 1. According to Wang et al. [24] and Mendes et al. [25], these results can be explained by the production of long-chain segments of PC connected with PET by an ester exchange reaction. The resulting graft copolymer (main transesterification product) is mixed with the rest of the unreacted PET and PC polymers.

The second observation is the appearance of a new band at 1097 cm^{-1} as an indication of an aromatic–aromatic ester as shown in Fig. 2. These results agree with what was published by Wang et al. [24], Suzuki et al. [2], and Zheng et al. [26]. According to these authors, the appearance of this signal indicates that a high homogenization has been achieved as a result of a strong extension of transesterification reactions. In other words, at the initial stage of the blending process, the inherent immiscibility between the PET and the PC does not favor the kinetics transesterification reactions, but as the fraction of copolymer formed increases and intensifies its action as compatibilizer/emulsifier, it promotes the miscibility and/or the interaction between the phases of the system, which contributes to an increase in reaction speed.

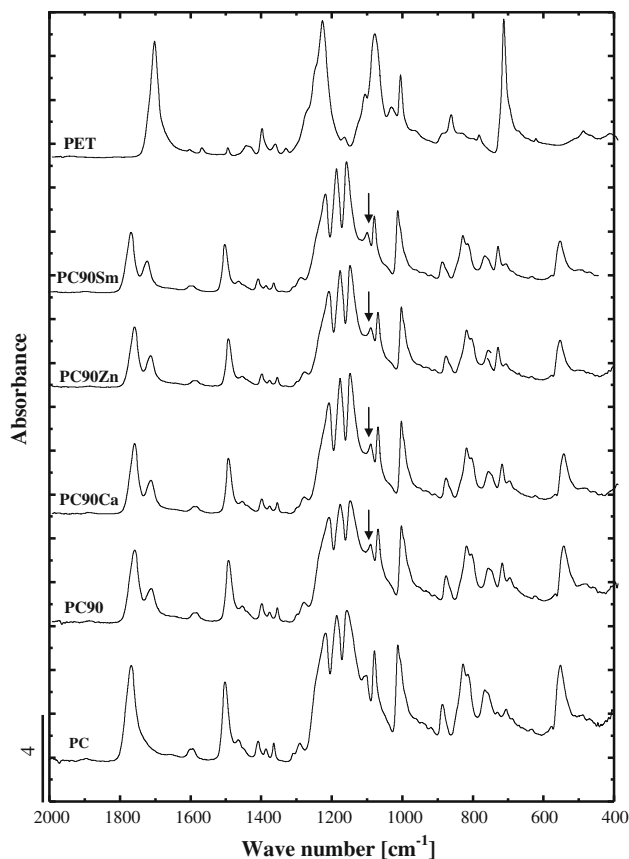


Fig. 1 The infrared spectrum of neat polymers and PC90 blends. The arrows indicate a character signal of new band

Table 1 Assignments of FTIR bands of PC/PET blends

Material	Wave number (cm^{-1})	Assignment
PET	1720	
PC90Ca	1723	
PC90Zn	1724	Carbonyl stretching of aromatic ester
PC90Sm	1723	
PC80Ca	1721	
PC80Zn	1722	
PC80Sm	1724	
PC70Zn	1721	

The third observation is that the degree of transesterification depends on the amount of PET and presence/type of catalyst as shown in Fig. 3. All blends without transesterification catalysts exhibits a degree of transesterification that decreased by increasing the amount of PET in the blend. The occurrence of interchange reaction in these blends may be due to the residues of catalysts used in PET synthesis. The ratio is the highest for blends containing Sm-based catalyst. The Zn-based catalyst promotes a high

Fig. 2 Structure of aromatic–aromatic ester compound formed during the interchange reaction between PET and PC components

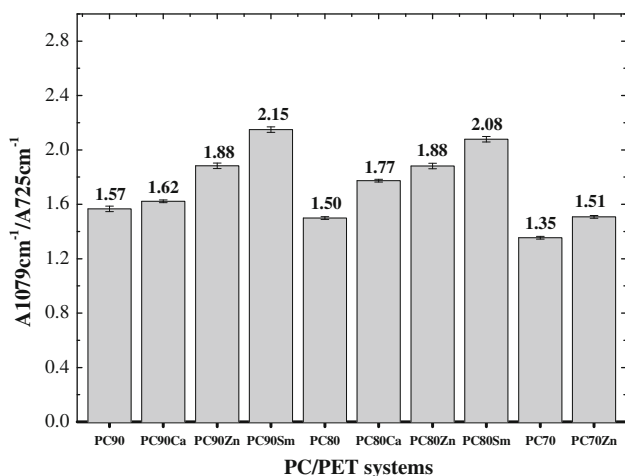
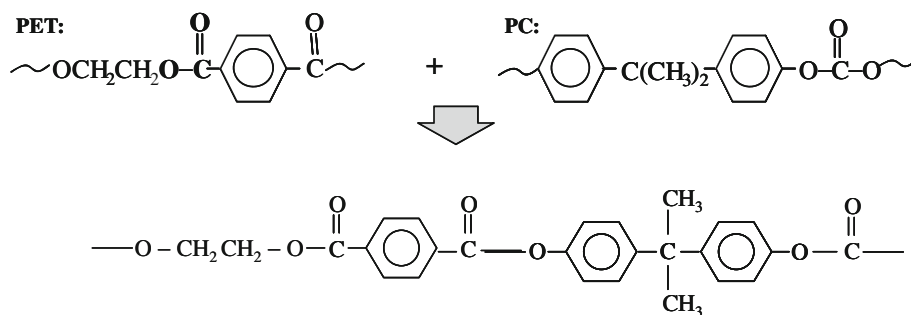


Fig. 3 Degree of transesterification of PC/PET systems which is calculated from the FTIR spectrum

ratio for both PC90Zn and PC80Zn, while PC/PET blends that have Ca-based catalyst show the lowest degree of transesterification among the systems even it increased by increasing the amount of PET. These results may reflect the capacity of the transesterification catalyst to produce or enhance the occurrence of interchange reaction between PC and PET phases. On the other hand, the variation of the ratio of degree of transesterification ($A_{1079} \text{ cm}^{-1}/A_{725} \text{ cm}^{-1}$) among the systems contain transesterification catalysts indicate its dependence on the type of catalyst. This does not agree with what Mendes et al. [25] said in his work that the degree of transesterification is constant and independent of type/amount of catalyst.

SEM analysis

Figure 4 gives an example of SEM microphotographs of the central region of the fractured surfaces of the PC/PET blends. Average particle size histograms were obtained from image analysis of the micrographs as shown in Fig. 5. A normal distribution was used to obtain estimate values of R_n , R_v , and d for blends as shown in Table 2.

For blends without transesterification catalysts, the presence of phases (binary structure) can be clearly

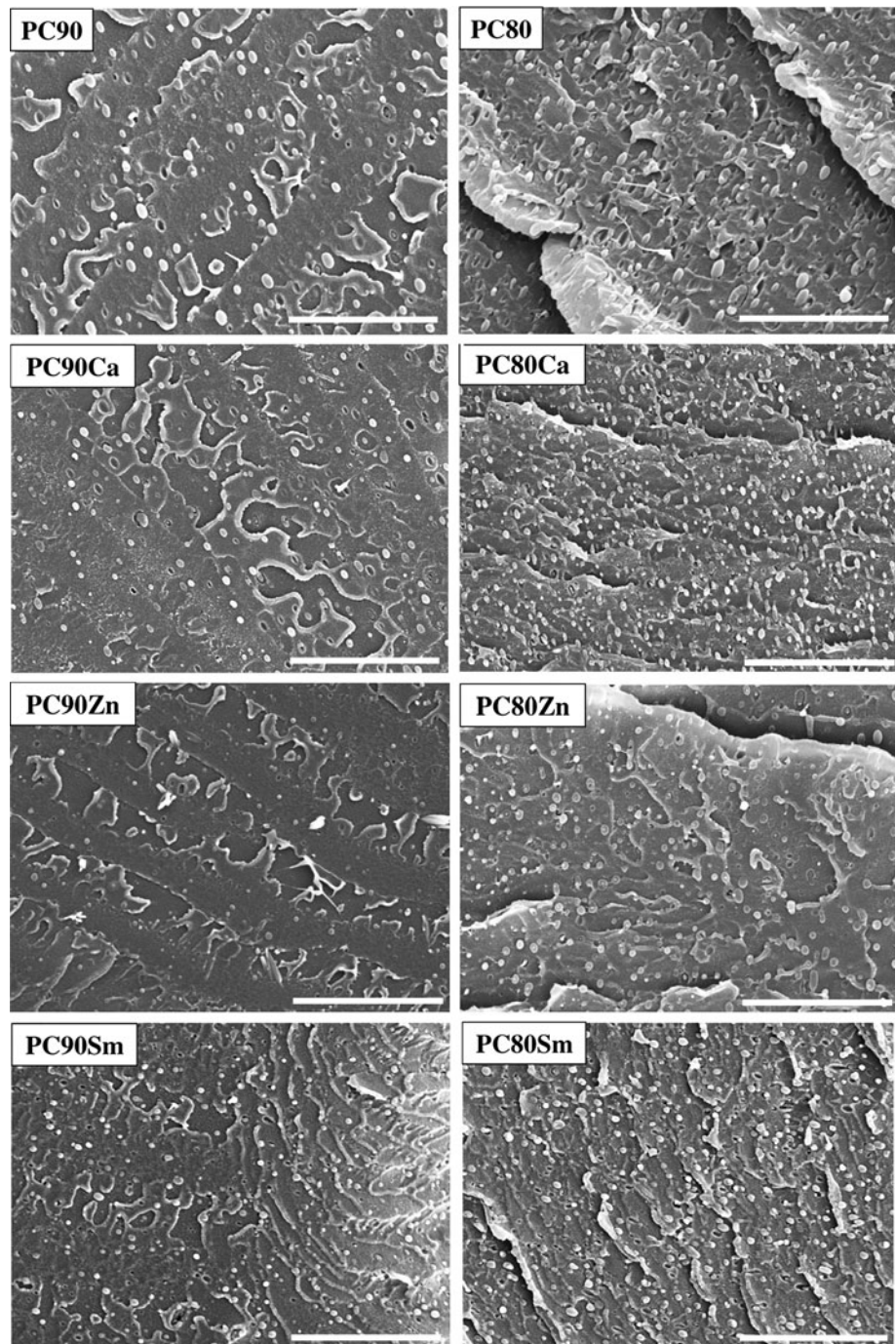
observed in all blends. PC90 blend has the finest dispersed phase compared with PC80 or PC70 that have a less uniform dispersion with a higher number average particle size. Significantly, the number average particle size of dispersed phases that are mentioned here are in the same range that has been cited by other works for blends containing equal or more than 10% by weight of PET [27–30].

Therefore, as the PET content on the blend decreases, the sample exhibits more thin and fine spherical shaped particles distributed uniformly throughout a continuous matrix. Though for these blends, no catalyst was added, there is clear evidence of some interaction of PET with PC. Since such fine morphologies and interfacial adhesion can be only obtained by the action of some emulsifier at the interface, particularly at low PET content, which agreed with FTIR results [2, 30]. Another explanation is related to the decrease of coalescence phenomena in the case of PC90 due to the increased of the concentration of dispersed phase.

For PC90, the achieved balance between the extension of the transesterification reaction and the low amount of PET makes the PET finely dispersed. Additionally, PC is a more viscous material than PET; and in these conditions, the dispersion capability is higher when PC phase is the matrix, leading to small droplets. These results are in agreement with the conclusion of Nassar et al. [3]. In contrary, PC70 blend exhibits elliptically shaped particles as a consequence of the orientation that produced by the flow direction as shown in Fig. 6.

When the blends are prepared in the presence of transesterification catalysts, it can be seen from Figs. 4 and 5 that the blends show a finer morphology with smaller spherical particles in comparison with their homologues without catalysts. Adding Ca-based catalyst to PC90 and PC80 blends refined their morphologies and reduced the number average particle sizes to 0.51–0.55 μm . By the same way, the addition of Sm-based catalyst to PC90 or PC80 decreased the average size of their particles to about 0.39–0.49 μm and refined more their dispersion. It seems that Zn-based catalyst is the more active among the catalysts used, so it reduced the mean particle sizes to 0.29–0.47 μm for PC90Zn and

Fig. 4 Scanning electron micrographs of the fracture surfaces parallel to the flow direction of the blend specimens. Scale bars: 10 μm



PC80Zn and to 0.54 μm for PC70Zn. It is clearly that the presence of Zn-based system exhibits the finest morphology and the higher dispersion uniform among all blends studied here.

PC70Zn is worth special attention. Since it has a large amount of PET, some of the particles have an elliptical shapes oriented on the flow direction, while others have a spherical shapes without orientation. Moreover, the number average particle size is small compared to PC70 blend as shown in Fig. 6.

The finer morphology of PC/PET blends with transesterification catalysts in comparison with the blends prepared in the absence of these catalysts is the consequence of the transesterification products. A decrease of the interfacial tension is provided by the copolymer molecules generated at the interface through in situ transesterification reactions, which is called the emulsifying effect. It was well known that blends based on immiscible polymer pairs were characterized by great interfacial tension, which made the dispersion during the blending operation difficult, and

Fig. 5 Particle size histograms obtained from image analysis of the micrograph of **a** PC70 and **b** PC70Zn

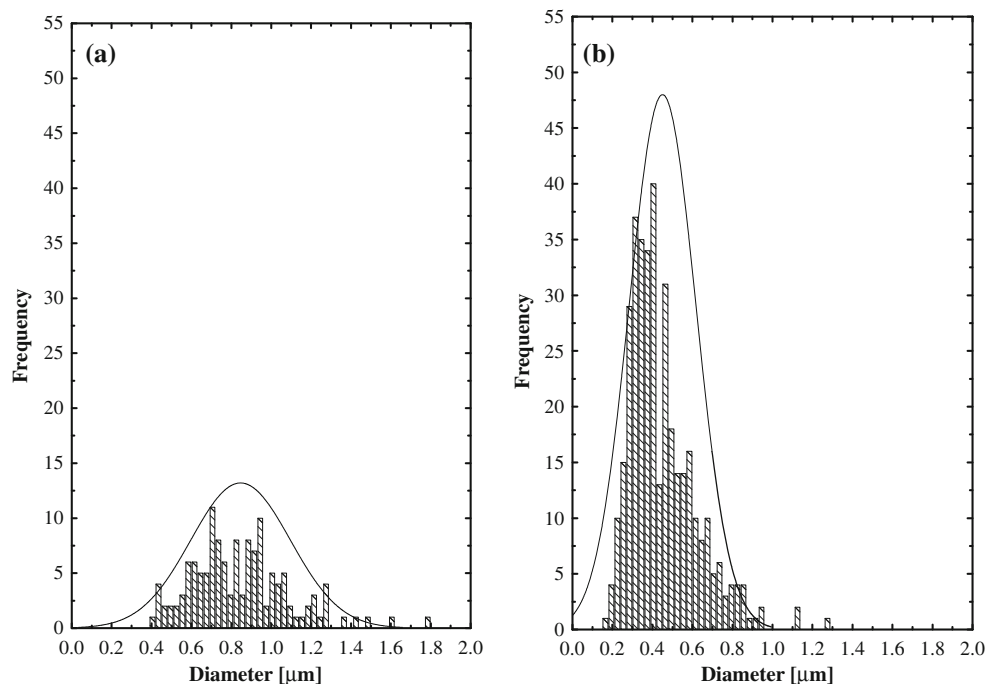


Table 2 Characteristic parameters of PC/PET blends obtained from analysis of their SEM micrographs

Material	R_n (μm)	R_v (μm)	Polydispersity (d)
PC90	0.68	0.84	1.23
PC90Ca	0.55	0.70	1.27
PC90Zn	0.29	0.36	1.24
PC90Sm	0.39	0.46	1.20
PC80	0.75	0.95	1.26
PC80Ca	0.51	0.64	1.26
PC80Zn	0.47	0.63	1.30
PC80Sm	0.49	0.61	1.23
PC70	0.85	1.10	1.29
PC70Zn	0.54	0.81	1.49

contributed to unstable morphology and poor adhesion. In addition to the emulsifying effect, it is also recognized that the presence of a copolymer layer covering the particles hinders coalescence during melt blending and might even have a larger effect than interfacial tension reduction [31].

The reduction on the average particle sizes and the increasing of the number of particles of catalyzed blends reveal that the addition of transesterification catalysts is sufficient to hamper particle–particle coalescence and so to generate a co-continuous morphology. This clear difference of dispersibility from blend prepared on the absence of catalysts is attributed to the transesterification reaction and demonstrates that the two PET and PC phases appear to be more compatible as a result of the treatment with the transesterification catalysts, which emphasizes the results of FTIR analysis.

By analyzing PC/PET blends with transesterification catalysts at a high magnification (8000 \times), reveals that the dispersed phase shows white spots or very fine particles called “microinclusions” (Fig. 7, identified by circles) dispersed in isolated manner in the matrix but near the interface matrix–large particles. Winey et al. [32] reported that the random copolymers can form an encapsulating layer around the dispersed phase domains, as shown in the case of (PS/PMMA/SMMA) blend system. These very fine particles can be observed only in the presence of transesterification catalysts where the possibility of interchange reaction to occur is more as proved by FTIR analysis. One explanation could be that the copolymer generated by transesterification reactions has the ability to encapsulate the dispersed layer, which is the PET in this case. Therefore, these microinclusions may be PET particles encapsulated inside the copolymers formed during the blending process through transesterification reactions. Another observation that some particles showed more adhesion to the matrix than others. This may indicate that the reactions are not uniform which reflects the graft-block nature of the PET–PC copolymer generated.

Thermal and dynamic mechanical analysis

Table 3 shows the thermal properties of neat polymers and PC/PET blends. For all PC90 blend samples, two glass transitions appeared: the lower ones correspond to PET phase, while the higher ones correspond to PC phase as shown in Fig. 8a. Therefore, two amorphous phases are present, one containing prevalently PC (PC-rich phase) and

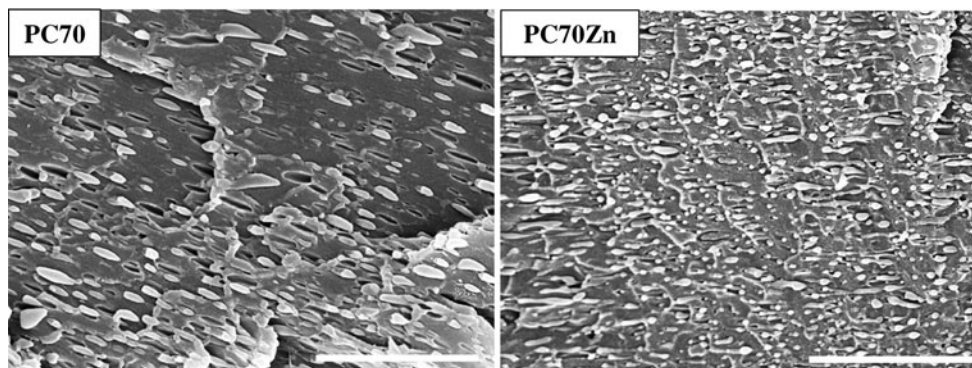


Fig. 6 Scanning electron micrographs of the fracture surfaces parallel to the flow direction of the blend specimens. Scale bars: 10 μm

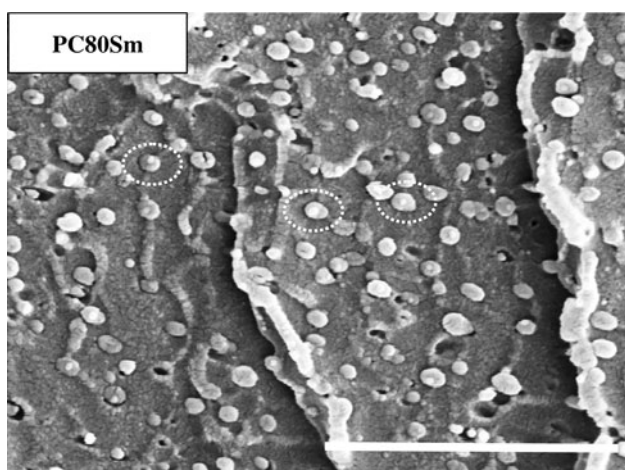


Fig. 7 Scanning electron micrographs of the fracture surfaces parallel to the flow direction of the blend specimens. Scale bars: 7 μm

the other one containing prevalently PET. These observations agree with results obtained by SEM analysis. As common thermal behavior for all PC90 blends, they are not able to crystallize (cold crystallization) during heating.

T_g values of PC90 without transesterification catalysts are similar to the corresponding T_g values of neat polymers. On the other hand, when the catalyst based systems were used, there is a shift to higher temperature for the T_g 's of PET phases and to lower temperature for the T_g 's of PC phases compared with neat polymers. This variation of T_g temperature could be a consequence of the interchange reaction that occurred between the different phases of the blend during melt blending process and so partial miscible blends were obtained [17].

The change of T_g values depends on the type of catalyst used, that is, the higher shift can be noticed in PC90Zn followed by PC90Sm and PC90Ca, which may reflect the activity of these catalyst which confirmed the FTIR analysis.

By comparing the measured T_m values of PC90 samples with that of neat PET sample, it is possible to observe the

shifting of T_m values to lowering temperatures as shown in Table 4 and Fig. 9a. This shift is higher in blends containing transesterification catalysts and depending on the type of catalyst employed. That is, PC90Zn exhibits the highest T_m shift to lower temperature followed by PC90Sm and PC90Ca.

This variation on T_m values of the blends compared with neat PET and the absence of cold crystallization temperature phenomena may be due to the dispersion and droplet size of PET in the PC bulk as suggested by Molinuevo et al. [33]. The PET droplet size is higher in PC90 compared with PC90 systems in the presence of transesterification catalysts. Zn-based catalyst enhances the best dispersion and the lowest PET droplet size among the PC90 systems as shown in the morphology analysis. Another reason is the lost structural regularity of the interchange reaction product, which leads to a shorter crystallizable sequence which in turn will produce thinner lamellar crystals that melt at lower T_m . In addition, there is not only a change in the melting temperature depending on the presence/absence of catalyst and the type of catalyst but also, a slight change in the ΔH_f values by the same trend as the T_m .

In general, PC90 blends are partially miscible due to the big difference between their T_g values and corresponding theoretical T_g values according to Fox's equation for totally miscible blends as shown in Table 3. The $T_{g\text{Fox}}$ values were calculated by the empirical Fox equation [34],

$$\frac{1}{T_g} = \frac{x_{\text{PET}}}{T_{g\text{PET}}} + \frac{x_{\text{PC}}}{T_{g\text{PC}}}, \quad (4)$$

where x_{PET} and x_{PC} are the weight fractions of PET and PC, respectively.

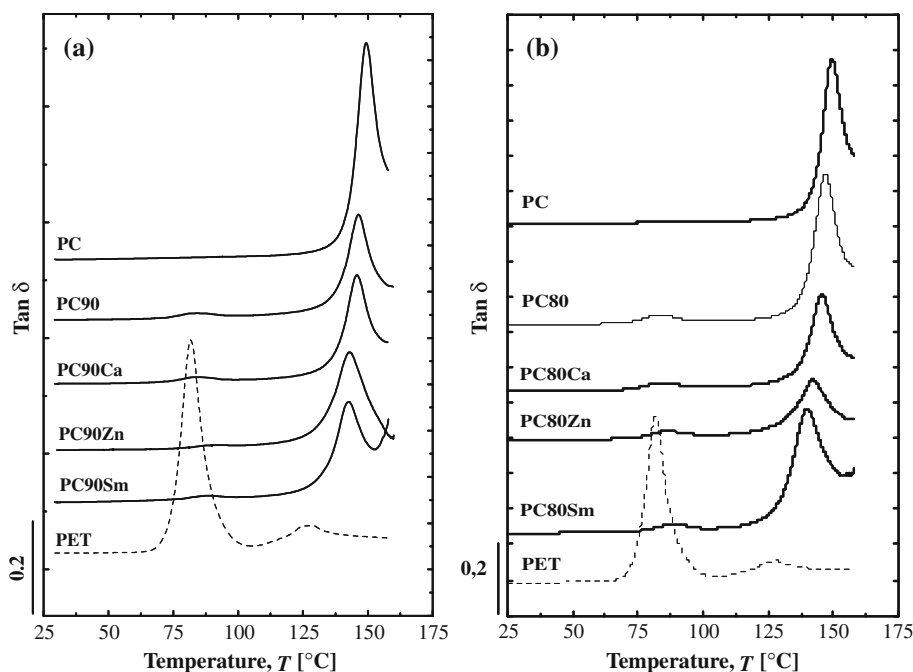
PC80 blends with transesterification catalysts exhibit the same thermal behavior as PC90 blends except, that the variation of T_g values compared with neat polymer is very slight and less than that found in PC90 systems as shown in Fig. 8b. This could be related to the increase in the amount of PET in PC80 blends compared with PC90 blends,

Table 3 DMA characterizations, interphase composition, and “PET and PC participation effectiveness degrees on the PC and PET rich phases” of the PC/PET blends

Material	$T_{g(\text{PET})}$ (°C)	$T_{g(\text{PC})}$ (°C)	$T_{g\text{Foxa}}^a$ (°C)	T_{β} (°C)	w_{PET}'	w_{PC}''	e_{PET} (%)	e_{PC} (%)
PC	–	149	–	–92	–	–	–	–
PC90	84	146	132	–65	0.001375	0.001899	1.22	0.02
PC90Ca	85	145	132	–89	0.001375	0.013268	1.24	0.15
PC90Zn	91	143	132	–89	0.090746	0.062092	46.55	0.75
PC90Sm	89	143	132	–87	0.068141	0.032131	38.79	0.38
PC80	83	147	123	–87	0.002872	0.002053	10.50	0.03
PC80Ca	84	145	123	–86	0.002750	0.007588	1.10	0.19
PC80Zn	87	142	123	–86	0.031783	0.017049	11.45	0.44
PC80Sm	89	140	123	–85	0.129297	0.060228	35.50	1.70
PC70	84	147	115	–84	0.020464	0.041461	5.55	0.58
PC70Zn	86	146	115	–84	0.024843	0.013268	5.84	1.79
PET	82	–	–	–83	–	–	–	–

^a Calculated from Fox's equation

Fig. 8 The effect of temperature on $\tan \delta$ of neat polymers and **a** PC90 blends and **b** PC80 blends. There is a shift in curves to make space between them and so the maximum and width peak of the peaks appear clearer



meanwhile, the amount of catalyst is constant, i.e., dilution effect. Despite this slight variation on T_g 's values, it is evident that interchange reaction may occur between different phases, even at small amounts as shown by FTIR analysis.

T_m values of PET crystalline region of PC80 blends in the presence/absence of catalyst based systems are less than that of corresponding T_m value of neat PET sample as shown in Table 4 and Fig. 9b. Adding catalyst to PC80 slightly lowered T_m and ΔH_f values especially in PC80Sm and PC80Zn, and prevent the appearance of cold crystallization peak during heating scans. These effects could be related to the droplet size/dispersion of PET phase in the

bulk as mentioned before [33]. Catalyst based systems make the morphological dispersion of particles more fine and reduce the particle size of dispersed phase that contributes or facilitates the formation of droplet size phenomena and increases the solubility of PET phase in PC major phase.

There is a shift of T_{cc} value of PC80 by 5 °C compared with neat PET sheet sample, while it disappeared in all PC80 blends with transesterification catalysts as shown in Table 4. This demonstrates that the PET crystallization rate during cold crystallization is reduced by the presence of PC. This could be attributed also to the effect of PET–PC copolymer that was generated through reaction between the

Table 4 DSC characterization of sheet samples calculated from the first heating scans and storage modulus, E' of neat polymers and PC/PET blends

Material	T_{cc} (°C)	T_m (°C)	T_{β} (°C)	ΔH_f^a (J/g)	X_c (%)	E' (GPa)
PC	–	–	–92	–	–	2.31 ± 0.01
PC90	–	240	–65	22.1	16.3	2.25 ± 0.09
PC90Ca	–	239	–89	20.2	14.9	2.68 ± 0.09
PC90Zn	–	237	–89	15.7	11.6	2.64 ± 0.08
PC90Sm	–	238	–87	16.7	12.3	2.52 ± 0.08
PC80	137	242	–87	28.8	20.2	2.48 ± 0.12
PC80Ca	–	242	–86	27.1	19.9	2.34 ± 0.07
PC80Zn	–	242	–86	16.5	12.1	2.23 ± 0.10
PC80Sm	–	238	–85	26.7	19.6	2.15 ± 0.09
PC70	147	243	–84	22.6	18.6	2.27 ± 0.11
PC70Zn	–	241	–84	27.1	19.9	2.17 ± 0.08
PET	133	246	–83	5.4	4.0	2.48 ± 0.07

^a ΔH_f is corrected according to the PET phase content in the blend

components especially in the presence of catalysts. This copolymer may reduce the mobility of the PET chains on the crystal surface because of the constraints from the high T_g PC domains and the copolymer chains will also act as defects during chain folding [27]. In addition, the reduced particle size and the well distribution of these particles could play an important rule in the T_{cc} shifting.

The thermal behavior of PC70 blends is very similar to that of PC80 blends. There is a glass transition temperature

for each phase and T_m value of PC70 lowered compared with corresponding T_m of pure PET sheet sample. Similarly, the addition of Zn-based catalyst to PC70 systems lowered T_m value of PET crystalline phase compared with neat PET or PC70 without catalysts as shown in Table 4.

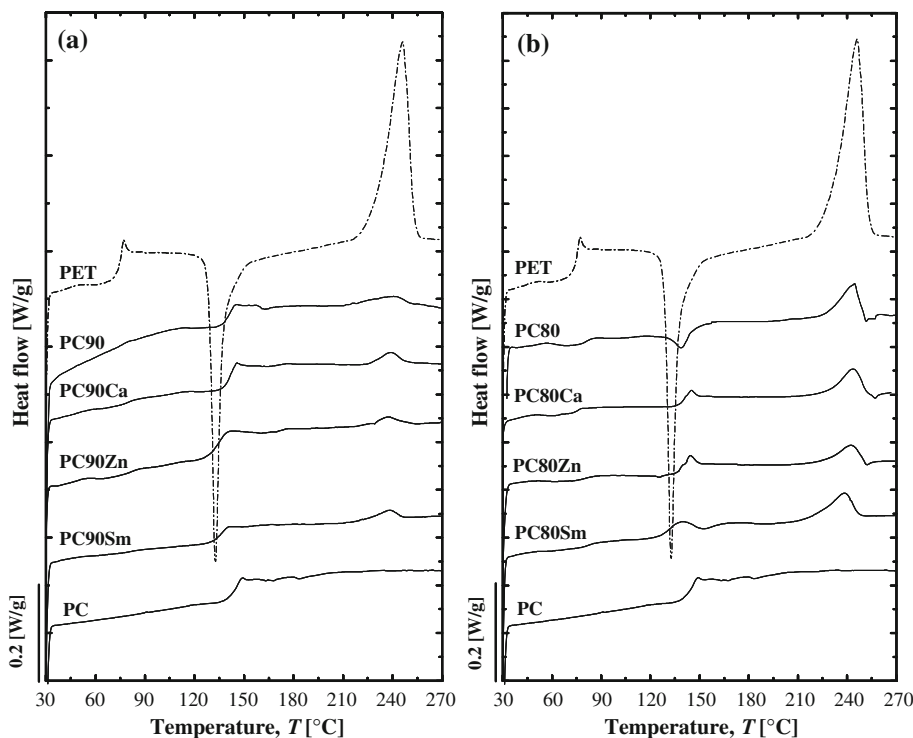
It can be observed that the PET phase generated in the blends has a higher degree of crystallinity (X_c) than neat PET where both cooled under the same conditions of processing as shown in Table 4. Here, the transfer of heating and cooling rate of the PET phase of the blends may be slower. The PC phase surrounding the PET phase would act as thermal insulation, which makes its cooling speed lower than neat PET extruded and so may increase its crystallinity. Also, there is the possibility of degradation process (decrease in length of chains) that would be highly feasible in blends with a catalyst. However, the proportion of the crystalline phase in total mass of blend is very low and hopefully will not have any further effect on mechanical properties.

From T_g values, the composition of the PC and PET phases in the blend can be evaluated assuming that the Fox equation [35] reproduces the T_g composition relationship for these blends. Thus, the Fox equation can be rearranged as:

$$w'_{PET} = \frac{T_{gPET}(T_{gPC} - T'_{gPC})}{T'_{gPC}(T_{gPC} - T_{gPET})}; \tag{5}$$

$$w''_{PC} = \frac{T_{gPC}(T''_{gPET} - T_{gPET})}{T''_{gPET}(T_{gPC} - T_{gPET})}$$

Fig. 9 First heating scans of neat polymers: **a** PC90 blends and **b** PC80 blends



where T_{gPET} , T_{gPC} , $T_{gPET''}$, and $T_{gPC'}$, are the measured glass transition temperatures (in Kelvin degree) of neat PET, neat PC, PET-rich phase, and PC-rich phase, respectively. $w_{PET'}$ and $w_{PC''}$ are the estimated apparent weight fraction of PET in the PC-rich phase and the estimated apparent weight fraction of PC in the PET-rich phase, respectively.

Santana et al. [36] calculated the degree of participation of each component of (PC/ABS) blends in the conjugated phase by a factor called the efficiency factor (e) considering the weight fractions of each component according to the following equation:

$$e_{PET} = \frac{w'_{PET} \cdot x_{PC}}{(w'_{PET} \cdot x_{PC}) + ((1 - w'_{PC}) \cdot x_{PET})} \cdot 100 \quad (6)$$

and,

$$e_{PC} = \frac{w''_{PC} \cdot x_{PET}}{(w''_{PC} \cdot x_{PET}) + ((1 - w''_{PET}) \cdot x_{PC})} \cdot 100. \quad (7)$$

Applying Eqs. 5, 6, and 7, the apparent weight fraction of PET in the PC-rich phase ($w_{PET'}$) and apparent weight fraction of PC in the PET-rich phase ($w_{PC''}$) have been calculated. By using the apparent weight fractions, the PET participation effectiveness degree on the PC rich phase and the PC participation effectiveness degree on the PET rich phase were determined and presented in Table 3.

In general, PET dissolves more in the PC-rich phase than does the PC in the PET-rich phase for all PC/PET blends despite the composition of the blends, or the presence/absence of the catalyst, or its type which agree with the other thermal properties. The apparent solubility of PET in PC-rich phase, or PC in rich PET phase decreases when increasing the weight fraction of PC in the blends as predicted by PC/PET blends that have Zn-based catalyst. The maximum solubility of PET in PC-rich phase has been achieved by using Zn-based catalyzed system ($e_{PET} = 46.5\%$) followed by Sm-based catalyst ($e_{PET} = 38.8\%$), which reflects the activity of these transesterification catalysts as shown in Table 3. In contrary, the solubility of PET phase of blends that have Ca-based catalyst is the lowest one, which agrees with other thermal analysis obtained. It is worth mentioning that the efficiency factor of PC phase (e_{PC}) has the same trend of e_{PET} values. That is, the maximum solubility of PC in PET-rich phase has been obtained by using Sm- and Zn-based catalyst systems, while Ca-based catalyst caused the minimum solubility.

Table 3 also reports the secondary relaxation (T_{β}) values of neat polymers and PC/PET blends according to the peak maximums of $\tan \delta$ curves. The T_{β} values of PC/PET blends are higher compared with neat PC and decreased compared with the neat PET. These shifts of T_{β} to higher values compared with neat PC are very clear in the blends with

transesterification catalysts, which is another indication of the possibility of the occurrence of interchange reaction. That is, the coupled motion of carbonate and phenylene units, which is responsible for the β relaxation [37], is partially hindered because of the restriction of the carbonate unit motion by ester groups. This may also explain that the level of disorder in a transient network is decreased.

The decreasing of β transition of PC/PET blends compared with neat PET sample can be interpreted by two ways. (1) The hindered motion of the methylene sequences of the chain, in both the noncrystalline and crystalline regions of the polymer, which may be produced due to interchange reaction (2) The increasing of the sequence length of $[CH_2]$ units in the copolymer that occurred during the transesterification reaction between PC and PET [38].

It is possible to observe that most of PC/PET blend systems exhibit a dynamic mechanical behavior in between the neat polymers; that is, below neat PET and above neat PC sheet samples. This means that the dynamic properties, storage modulus at room temperature, of the blends affected by the amount of PET used in addition to the presence of transesterification catalysts as shown in Table 4.

Among the PC/PET blends without transesterification catalysts, PC80 exhibits the better storage modulus value, which defines a significant positive deviation from the rule of mixtures followed by PC90 and PC70.

The storage modulus of PC/PET blends in the presence of transesterification catalysts is more or less similar to neat PC despite the slight increase when the Ca- and Zn-based catalysts were presented especially at low amounts of PET. In the case of PC90Zn and PC90Ca, it is found that the storage modules were enhanced or increased by 14 and 16%, respectively. The enhancement of storage modulus values can be explained in term of strong interactions occurred between the PC and PET components. This indicates that an important paper plays the balance between interface adhesion, morphology of the mixtures, and extension of the transesterification. By this form, it would be reasonable to think that the copolymer formation, preferably located in the interface of the phases, would promote a mechanical compatibility at least to low strains for the type of imposed blends.

It must be taken into account that due to relative slow cooling rate applied during calendaring processing stage, PET phase (dispersed one) developed higher crystallinity degrees than neat PET sheet (12–20 vs. 4%, see Table 3). As it is well known, an increase in crystallinity promotes an increase in E' . In this case, it is expected that dispersed phase acts like rigid particle reinforcement if good adhesion is assured. This adhesion between phases is enhanced in the blends when pro-transesterification catalyst is used, due to the generation of PC–PET copolymers.

Conclusion

The physico-chemical and morphological characterization of PC/PET blends prepared by melt blending in the absence and presence of three transesterification catalysts have been investigated on the PC-rich composition range.

According to the evidence obtained through FTIR under the blending conditions employed, it can be concluded that all PC/PET blend systems are capable to induce chemical exchange reactions especially at the presence of catalysts.

Through the DSC and DMTA techniques, it is found that all PC/PET blends are partially miscible and the degree of miscibility depends on the amount of PET, presence/absence of catalyst, and type of catalyst used. In general, as the amount of PET increases, the degree of transesterification decreases. Additionally, the presence of catalyst promotes more interchange reactions between PC and PET components especially Zn- and Sm-based catalyst in agreement with FTIR results.

SEM analysis confirms the binary phase feature of all blends studied. PC/PET blends showed a morphological transition from “spherical texture” (PC90 and PC80 systems) to “elliptical” for PC70 and “texture filament” for PC70Zn. These morphological features reflect the influence of PET amount from one hand and the interchange reactions that may occurred on the other hand. It has been observed that transesterification catalysts reduced the particle sizes of blends and make their dispersion finer and uniform in comparison with blends without catalysts.

The addition of transesterification catalysts to the blends promotes an increase on storage modulus (E') of the blends considering the values obtained by the parent polymers. This trend should be attributed to the higher adhesion between phases and the higher crystallinity of PET droplets (compared with neat PET).

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