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# Thermal characterization of reactive blending of 70PC/30PET mixtures prepared in the presence/absence of samarium acetylacetonate as a transesterification catalyst

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**Abstract:** Poly(ethylene terephthalate) (PET)/polycarbonate (PC) blends were prepared in the presence and absence of samarium (III) acetylacetonate hydrate [Sm(acac)<sub>3</sub>] used as an ester-ester exchange reaction catalyst. Differential scanning calorimetry (DSC) and thermogravimetric analysis/differential thermogravimetry (TGA/DTG) were used to study the variations in the thermal properties of blends before and after reactive blending. Solubility measurements in methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) and infrared spectroscopy were also employed to highlight the structural changes that occurred during mixing in the presence of Sm(acac)<sub>3</sub>. The DSC results showed two distinct transition temperatures ( $T_g$ ) for all the compositions. Also, the  $T_g$  values of components were shifted compared to the parent polymers in both the blends prepared with and without catalyst. Further, the  $T_g$  of the PET-rich phase was displaced to higher temperatures and that of the PC-rich phase showed a tendency to diminish as the catalyst's concentration increased. At the same time, the melting temperature ( $T_m$ ) of the PET-rich phase was shifted to lower temperatures. The evaluation of the compositions of the PC- and PET-rich phases using Wood's equation showed a strong dependence on the catalyst concentration. Furthermore, the thermogravimetric thermograms showed

that the thermal stability of the blends was between those of the homopolymers, and evidenced a net improvement relatively to the neat PET. The obtained results confirmed the aptitude of Sm(acac)<sub>3</sub> to promote exchange reactions between PC and PET, and to achieve their compatibilization through an interfacial copolymer synthesis process.

**Keywords:** PC/PET blends; reactive blending; transesterification; thermal properties.

## 1 Introduction

Polymer blending is a technique of interest that has captured the attention of numerous research groups since the 20th century to the present day. A polymer blend is a mixture of two or more polymers that have been blended together to create a new material with different physical properties [1, 2].

The important advantages of polymer blending can be summarized as the development of new properties or improvement of existing properties to meet specific needs, material cost reduction with little or no loss of properties, material processability improvement, and meeting the needs of emerging industries by surpassing the polymerization step. Polymer blends can broadly be classified into three categories: miscible, compatible, and immiscible polymer blends [2].

Polyesters/polycarbonate blends (PEST/PC) are of both scientific and commercial interests and were introduced in 1980. PC has been frequently used in blends with PEST, such as polyethylene terephthalate (PET), polybutylene terephthalate (PBT), and polyethylene naphthalate [3–5]. Typical applications of these blends are used in the automotive industry on exterior parts, such as bumper covers, for which good chemical resistance and impact resistance are required [5–7].

PC/PET blends have been extensively studied over the past two decades. Both PET and PC are important engineering plastics. Particularly, PC has exceptional impact and thermal and mechanical properties but presents poor resistance to solvents and chemical attacks. The blends

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**Correction note:** Correction added after online publication November 1, 2016: Mistakenly this article was already published ahead of print under the title “Thermal characterization of reactive blending of 70PC/30PET mixtures prepared in the presence/absence of samarium acetylacetonate as a transesterification catalyst”.

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intend to obtain the chemical resistance of PET without losing the good impact strength of PC [8–11].

In earliest studies, controversial results on the miscibility of blends were reported in the literature. Especially, the miscibility of PC/PET blends has been discussed, from completely miscible, partially miscible, to completely immiscible for all compositions [12–14]. Indeed, Nassar et al. [15] observed a single glass transition temperature ( $T_g$ ) for compositions containing >60–70 wt.% of PET, while the compositions below this range showed two glass transitions. From this, it was concluded that PC and PET are completely miscible in the amorphous phase for PET-rich compositions, whereas PC-rich blends separate into two amorphous phases that apparently contain both components. Moreover, it was suggested that very little if any interchange reactions occur between the ester and carbonate groups during melt mixing. In addition, Murff et al. [16] reported that PC-rich blends exhibited two glass transitions, while only one  $T_g$  could be found for PET-rich compositions. These results suggested miscibility over parts of the composition range, while others found that PC/PET blends were completely immiscible over all composition ranges [8, 14, 17, 18].

These contradictory results were explained by Porter and Wang [19], who attributed all the discrepancies to the occurrence of transesterification reactions between PC and PET due to the presence of residual synthesis catalysts. As well, Pilati et al. [20] reported that when PET and PC are melt mixed, they undergo chemical reactions that lead to changes in the chemical structure of the polymers. Moreover, Godard et al. [21] showed that the main reaction that occurs in PBT/PC mixtures is an exchange reaction between PBT ester groups and PC carbonate ones. Some other side reactions consecutive to the principal exchange process also take place, such as degradation, pyrolysis, and gel formation, resulting probably from the instability of the ethylene carbonates produced by transesterification. The copolymer deriving from transreactions influences strongly the homogeneity of the blends by acting as an interfacial agent, which complicates the determination of the real structural phase, resulting in the melt mixing of these homopolymers. According to Guessoum et al. [22], catalyzed exchange reactions between the carbonate groups of PC and the ester ones of PET initiate at the interface and cause the conversion of homopolymer chains to block copolymers, when the exchange rate is still weak. The block structure of the synthesized copolymer is, after more intense transreactions, converted to a random one, because exchanges concern also the copolymer chains for which the reactions could be faster and easier, due to the proximity of the reactive functional groups. However, without the deliberate incorporation of a transesterification catalyst,

ester-carbonate interchanges do not occur at all or produce practically unnoticeable effects on the final properties of the blend. In consequence, divergent conclusions on the miscibility of PC/PET blends and the chemical structure of the transesterification product arise mainly from the blending conditions, particularly, the blend composition, residual catalyst nature, and concentration and melt processing conditions such as time and temperature [23–25].

The present work consists in a contribution that aims essentially to highlight the thermal properties of PC/PET blends before and after blending with a transesterification catalyst, which is samarium (III) acetylacetonate [ $\text{Sm}(\text{acac})_3$ ]. The effects of exchange reactions between PC and PET have also been quantified by evaluating the fractions of PC and PET in both PC- and PET-rich phases as a function of samarium concentration, by using differential scanning calorimetry (DSC) results and Wood's equation.

## 2 Materials and methods

### 2.1 Materials

A PET resin with an intrinsic viscosity of 0.8 g/dl was obtained from Tongkook (Seoul; South Korea; TexPet 874-C80). The commercial PC (Makrolon 2807) was supplied by Bayer Company (Leverkusen, Germany). The melt flow index of PC was 10 g/10 min.  $\text{Sm}(\text{acac})_3$  was purchased from Sigma Aldrich (Taufkirchen, Germany).

### 2.2 Preparation of PC/PET blends with and without catalyst

At first, the polymers PC and PET were vacuum dried in an oven for 24 h at 100°C. Then, uncatalyzed and  $\text{Sm}(\text{acac})_3$ -catalyzed PC/PET blends were prepared according to a weight ratio of 70 : 30 in a Brabender internal mixer at a temperature of 270°C and a mixing speed of 30 rpm for 20 min. After the melting of homopolymers, the  $\text{Sm}(\text{acac})_3$  catalyst was introduced at concentrations of 0.01, 0.15, and 0.020 phr. Then, the obtained catalyzed and uncatalyzed mixtures were pelletized to obtain samples for characterization.

### 2.3 Measurements

#### 2.3.1 Solubility

In order to obtain information on the solubility changes due to the structural evolution during melt blending,

PC/PET blend samples weighing 0.10 g ( $m_0$ ) were extracted for 24 h in a volume of 30 ml methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) (PET is soluble in  $\text{CH}_2\text{Cl}_2$ , contrary to PC, which is totally insoluble in this solvent) according to ASTM D 297 [25]. The suspension was filtered, and the soluble and insoluble fractions were recovered. A film of the soluble fraction was obtained after  $\text{CH}_2\text{Cl}_2$  evaporation. The insoluble fraction was dried at 100°C, and then weighed ( $m$ ) to evaluate the solubility using the following equation:

$$\text{Solubility (\%)} = \left( \frac{m_0 - m}{m_0} \right) \cdot 100 \quad (1)$$

### 2.3.2 Fourier transform infrared spectroscopy (FTIR) analysis

FTIR analysis was employed to point out structural variations after exchange reactions between PC and PET. FTIR spectra were obtained between 400 and 4000  $\text{cm}^{-1}$  using a Perkin Elmer infrared spectrometer.

### 2.3.3 DSC

Calorimetric analysis was performed using a Setarame differential scanning calorimeter (DSC131 EVO), by heating the samples from room temperature up to 300°C, at a heating rate of 10°C/min, under nitrogen. The values of  $T_g$  and melting enthalpy ( $\Delta H_m$ ) and temperature ( $T_m$ ) were evaluated from the thermograms obtained at the second heating scans.  $T_m$  was taken at the maximum of the endothermic melting peak.  $T_g$  values were also estimated using the Fox equation [26] for predicting miscibility:

$$\frac{1}{T_g} = \frac{\omega_{\text{PET}}}{T_{g\text{PET}}} + \frac{\omega_{\text{PC}}}{T_{g\text{PC}}} \quad (2)$$

where  $\omega_{\text{PET}}$  and  $\omega_{\text{PC}}$  are, respectively, the PET and PC weight fractions and  $T_{g\text{PC}}$  and  $T_{g\text{PET}}$  are the glass transition temperatures of PC and PET, respectively.

### 2.3.4 Thermogravimetric analysis (TGA)

The thermal stability of the blends was assessed on studying the thermogravimetric thermograms obtained from a Perkin Elmer TGA-4000 instrument, by heating the samples from 30°C to 700°C at a heating rate of 10°C/min under nitrogen atmosphere. The onset, maximum, and end degradation temperatures ( $T_{\text{onset}}$ ,  $T_{\text{max}}$ ,  $T_{\text{end}}$ ), and the residue contents were evaluated.

## 3 Results and discussion

### 3.1 Solubility measurements

The first evidence for the occurrence of exchange reactions between PC and PET during melt mixing was provided by the results of the solubility test. Table 1 reports the solubility values obtained from the  $\text{CH}_2\text{Cl}_2$ -insoluble fractions for PC and PET homopolymers and 70PC/30PET blends prepared with and without an added catalyst. It shows that PC is completely soluble, whereas PET is practically insoluble in  $\text{CH}_2\text{Cl}_2$ . After extraction, the 70PC/30PET blend prepared without added catalyst left about 26% of insoluble PET, indicating that PC was completely removed from the blend by this treatment. The solubility value for the uncatalyzed blend indicates, approximately, the total absence of exchange reactions between the two homopolymers during melt mixing.

For the 70PC/30PET-catalyzed blends, the solubility decreases for the blend with 0.1 phr of  $\text{Sm}(\text{acac})_3$  compared to the initial value of the soluble fraction (74%). According to Pilati et al. [20], Mendes et al. [25], and Ignatov et al. [27], the variations in solubility are attributed to exchange reactions between PC and PET. Indeed, the solubility value suggests that a certain amount of PET fragments has been transferred to the PC-rich phase, resulting in the possible formation of block copolymers. After the addition of 0.15 and 0.20 phr of catalyst, the solubility increases to about 80% and 92%, respectively, indicating that an extensive exchange process has occurred between PC and PET. Indeed, the solubility enhancement could be ascribed to the fact that as the catalyst concentration increases, further PET chains move toward the PC-rich phase and that the long insoluble PET copolymer segments are shortened due the occurrence of transreactions within the copolymer chains. This result confirms that the produced copolymer is formed from shorter PET blocks linked to PC segments, which promote their solubility into  $\text{CH}_2\text{Cl}_2$ . Correspondingly, Guessoum et al. [28] noticed

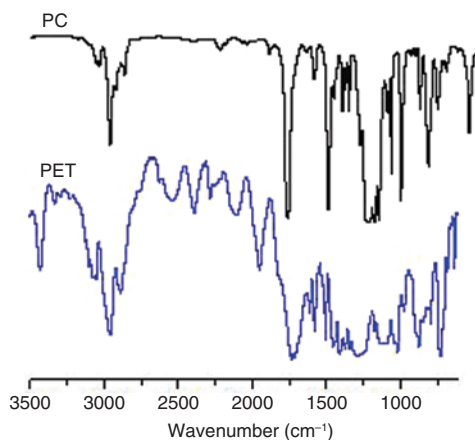
**Table 1:** Solubility values for PC, PET, and uncatalyzed and catalyzed 70PC/30PET blends.

Samples	Solubility (%)
PET	–
PC	100
70PC/30PET	74
70PC/30PET/0.10 Sm	67
70PC/30PET/0.15 Sm	80
70PC/30PET/0.20 Sm	92.5

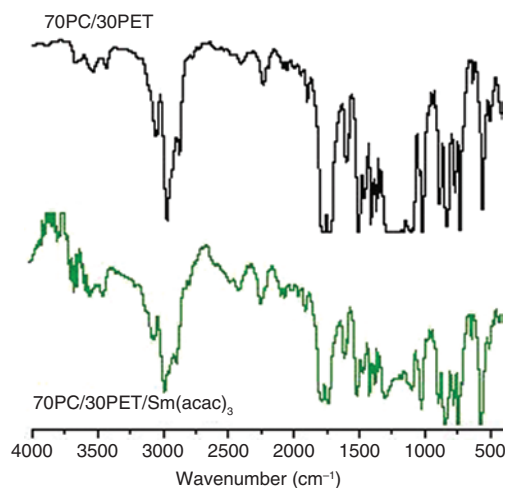
that the melt mixing of PC/PET blends with 0.25 phr of tetrabutyl orthotitanate for 30 min resulted in a totally amorphous structure as the consequence of the complete randomization of the copolymer structure. Also, Maurizio Fiorini et al. [29] suggested that the decrease in solubility is due to the formation of a block copolymer, whereas a solubility increase results from an alternating one. These findings are supported by Ignatov et al. [30], who studied the influence of the  $\text{Sm}(\text{acac})_3$  catalyst concentration on the solubility of PC/PET blends in methylene chloride. They found that the soluble fraction decreased initially with the increase of catalyst concentration and showed that the formation of PC/PET block copolymers results in a lower solubility of the blend. Accordingly, Maurizio Fiorini et al. [29] observed that when no exchange reaction occurs, the weights of the soluble and insoluble fractions remain constant, as they contain only PC and PET, respectively. In contrast, when exchange reactions take place, a progressive shift toward larger amounts of the soluble or insoluble fractions is expected because the resulting block copolymers have a different solubility due to the dominance of PC or PET blocks. In other words, this means that PET blocks are present in the soluble fraction when the solubility of PC blocks prevails, and that PC blocks are present in the insoluble fraction when the prevailing effect is the insolubility of PET blocks.

### 3.2 Infrared spectroscopy

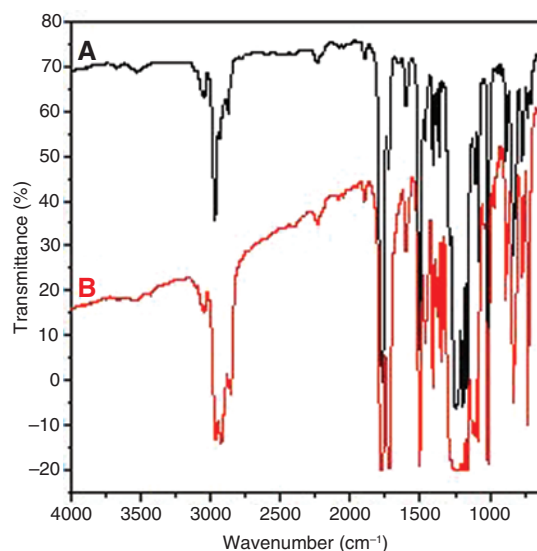
Transesterification is a chemical reaction that may change the composition of blend components. Infrared spectroscopy is used to ascertain whether transesterification had occurred in the examined blends. The infrared spectra of neat polymers and PC/PET mixtures melt blended without and with  $\text{Sm}(\text{acac})_3$  catalyst are shown in Figures 1–3.



**Figure 1:** Infrared spectra of PC and PET homopolymers.



**Figure 2:** Infrared spectra of 70PC/30PET melt blended with and without  $\text{Sm}(\text{acac})_3$  catalyst.



**Figure 3:** Infrared spectra of  $\text{CH}_2\text{Cl}_2$  soluble (A) and insoluble (B) fractions of 70PC/30PET blend catalyzed with 0.15 phr  $\text{Sm}(\text{acac})_3$ .

The carbonyl group bands of PC and PET appear at 1776 and 1721  $\text{cm}^{-1}$ , respectively. The changes in those two bands have been commonly used to identify the transesterification reactions between PET and PC [31]. For both uncatalyzed and catalyzed blends, infrared spectra combine the absorption bands of the homopolymers. The characteristic region of PC and PET carbonyl groups does not reveal the presence of carbonyl stretching bands of aromatic/aliphatic and aliphatic/aliphatic carbonate groups expected at 1763 and 1745  $\text{cm}^{-1}$ , respectively. This is probably due to the overlapping of several bands in this region according to Berti et al. [32]. However, it is also possible that, due to their low thermal stability, some of these

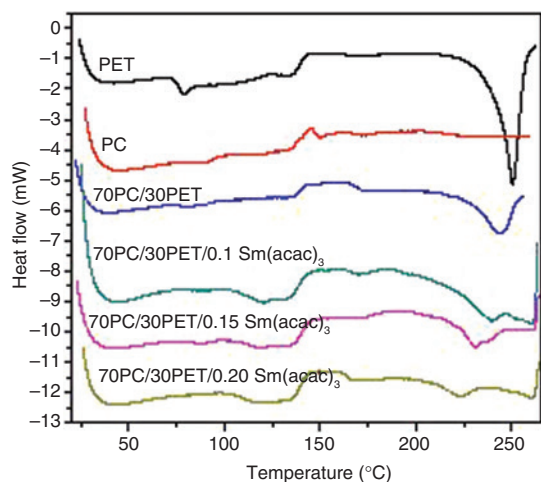
carbonate groups are never present at a high concentration because their rate of disappearance through side reactions is very fast. In this context, it has been reported that aliphatic-aliphatic carbonate groups are not thermally stable even at relatively low temperatures [32].

Thus, in our study, FTIR analysis does not give clear information about the occurrence of transesterifications during the melt mixing of PET and PC with  $\text{Sm}(\text{acac})_3$ . For this reason, an FTIR study of soluble and insoluble fractions collected from solubility measurements for the blend catalyzed with 0.15 phr of  $\text{Sm}(\text{acac})_3$  has been performed and represented in Figure 3. A PC carbonyl group band is detected in the spectra of the insoluble fraction, which should contain only PET if no transesterification reaction occurs. In addition, a PET ester carbonyl group band is observed in the infrared spectra of the soluble fraction, which is expected to contain only PC if exchanges between PC and PET are not allowed. These results support the fact that PET sequences have been transferred into the PC-rich phase and made soluble in  $\text{CH}_2\text{Cl}_2$  by the reaction between PC and PET via a transesterification process. In contrast, PC units have moved toward the PET-rich phase, which is insoluble in  $\text{CH}_2\text{Cl}_2$ . Similar results have been reported by several authors [29, 33].

### 3.3 Thermal behaviors of PC/PET blends

#### 3.3.1 Glass transition

Figure 4 shows the DSC thermograms of the PC and PET homopolymers and the 70PC/30PET mixture melt blended with and without the  $\text{Sm}(\text{acac})_3$  interchange catalyst.



**Figure 4:** DSC thermograms of neat polymers and 70PC/30PET mixtures melt blended with and without  $\text{Sm}(\text{acac})_3$ .

The PET thermogram reveals essentially the glass transition temperature at approximately  $76^\circ\text{C}$ , and a melting endotherm between  $200^\circ\text{C}$  and  $270^\circ\text{C}$  and presenting a maximum around  $250^\circ\text{C}$ . However, the PC thermogram shows only the glass transition at about  $147^\circ\text{C}$ . The thermograms of the PC/PET blends combine the thermal characteristics of PC and PET, and reveal variations that depend on the catalyst concentration. The thermal characteristics of the homopolymers and blends are summarized in Table 2.

For the blends melt mixed without the  $\text{Sm}(\text{acac})_3$  catalyst, Figure 4 reveals that the  $T_g$  of the PET-rich phase is slightly higher than that of neat PET. It increases from  $76^\circ\text{C}$  to  $79^\circ\text{C}$  for the 70PC/30PET mixture. In opposite, the PC-rich phase  $T_g$  is lower than that of the neat PC and is situated around  $142^\circ\text{C}$ . Fraisse et al. [34] reported a similar result that they assigned to the occurrence of transesterification reactions in the absence of a catalyst. The occurrence of interchange reactions between PC and PET melt mixed without a catalyst was also reported by several authors [12, 23, 35]. Also, Frounchi et al. [36] suggested that, due to their higher mobility, the PET molecules diffuse into the PC-rich regions and cause a plasticizing effect, which reduces the  $T_g$  of the PC-rich phase.

On the other hand, the thermal behavior of the 70PC/30PET blend was investigated in the presence of the  $\text{Sm}(\text{acac})_3$  catalyst when the concentration has been varied from 0.10 to 0.15 and 0.20 wt.%. Figure 4 shows clearly that after blending with the  $\text{Sm}(\text{acac})_3$  interchange catalyst, the two transition temperatures related to the PC- and PET-rich phases are still observed for all the compositions. This implies that two amorphous phases are still present in the catalyzed blends. However, it has been noticed that the  $T_g$  of the PET-rich phase was higher than that for pure PET, while the  $T_g$  of the PC-rich phase was lower than that observed for the neat PC. It seems that the addition of the  $\text{Sm}(\text{acac})_3$  catalyst promotes transesterification reactions by favoring the mutual diffusion of both homopolymer molecules, which encourages compatibility [13].

**Table 2:** Analysis of DSC thermograms for PC and PET homopolymers, and PC/PET blends melt mixed without and with  $\text{Sm}(\text{acac})_3$  catalyst.

Samples	$T_{g\text{PET}} (^\circ\text{C})$	$T_{g\text{PC}} (^\circ\text{C})$	$T_m (^\circ\text{C})$	$X_c (\%)$
PET	76	–	250	33.37
PC	–	147	–	–
70PC/30PET	79	142	244	14.92
70PC/30PET/0.10 Sm	84	138	239	14.66
70PC/30PET/0.15 Sm	83	139	231	13.82
70PC/30PET/0.20 Sm	85	139	224	12.85

Moreover, on comparing the  $T_g$  measured values for catalyzed blends with those characteristics of the uncatalyzed one, we noticed that on increasing the  $\text{Sm}(\text{acac})_3$  concentration, the  $T_g$  of the PET-rich phase shifts to a higher temperature and attains  $85^\circ\text{C}$  for the catalyst concentration of 0.20%. At the same time, the increase in the  $\text{Sm}(\text{acac})_3$  catalyst concentration does not seem to affect the PC-rich-phase  $T_g$ , which is significantly lower than that of the PC homopolymer but invariable relatively to the uncatalyzed blend, as it is reported in Figure 5. According to Reinsch and Rebenfeld [23], the shifts in the component  $T_g$ s could be attributed to the fact that the glass transition of PET takes place in the presence of the glassy PC phase. Thus, the rigid PC “matrix” could contribute in increasing the  $T_g$  of the PET-rich phase. The presence of the rigid glassy PC matrix domains may act to raise  $T_g$  through a friction process at the interface between the two phases. On the other hand, the glass transition of PC in the blend takes place in the presence of rubbery PET, which may effectively plasticize the PC at the interface and cause the depression of its  $T_g$  in the blends [23].

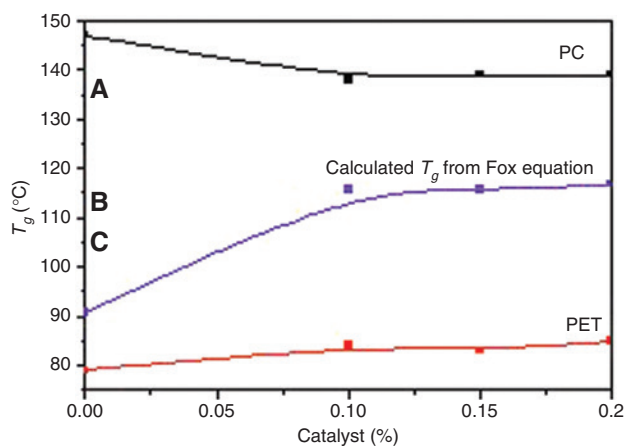
In summary, the variations detected on the glass transition behavior of PC- and PET-rich phases into PC/PET blends are probably the consequence of an induced compatibilization, promoted by the occurrence of transesterification reactions. In this context, it has been reported that glass transition shifts in polymer blends are most generally observed due to physical interactions at the interface between the components [37]. Thus, the occurrence of interchange reactions into the PC/PET mixtures provides the opportunity for PC units to pass into the PET phase and for PET ones to enter the PC domains. These exchanges contribute to the creation of copolymers that

act as interfacial agents and improve the compatibility between the two phases [22].

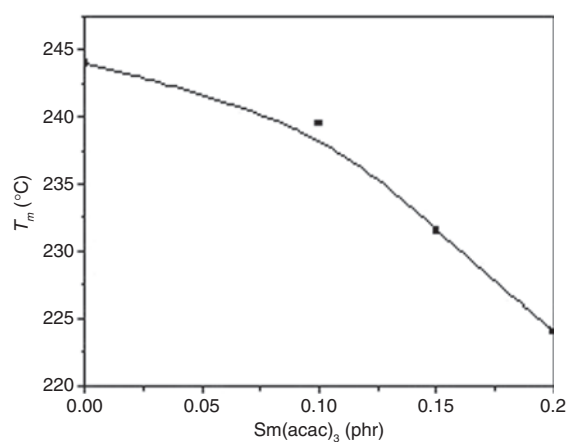
### 3.3.2 Melting behavior

Figure 6, depicting the melting behavior of the PET-rich phase in uncatalyzed and catalyzed blends, provides additional pieces of evidence on the occurrence of exchanges between PC and PET, and points out the effects of PC transferred units on the melting process of the PET-rich phase. Indeed, this figure reveals that when PET and PC are melt mixed without a catalyst, the melting endotherm is slightly displaced toward lower temperatures and the temperature at the maximum of the melting peak decreases from  $250^\circ\text{C}$  to  $244^\circ\text{C}$ . This suggests that only small or no exchanges were possible during melt blending. Also, the shift in the melting endotherm indicates that the fusion of PET crystallites occurs for lower temperatures because they are not as perfect as those formed in the neat PET.

For catalyzed 70PC/30PET systems, Figure 6 shows a more pronounced shifting of the melting endotherm toward lower temperatures. A significant decrease in the  $T_m$  of the PET-rich phase is noticed as the  $\text{Sm}(\text{acac})_3$  catalyst concentration is increased.  $T_m$  passes from  $250^\circ\text{C}$  for neat PET to  $224^\circ\text{C}$  for the PET-rich phase into the blend melt mixed with 0.20% of  $\text{Sm}(\text{acac})_3$ . The depression of the PET melting temperature results from defects in PET crystallites assigned to the formation of PC/PET copolymer chains and other by-products of the interchange reactions [13]. Hanrahan et al. [38] also reported that transesterification reactions affect the melting behavior of a crystallizable polymer through their effect on nucleation or spherulitic growth rates. These results agree with those reported by



**Figure 5:** Variations of PC- and PET-rich phases  $T_g$  as a function of  $\text{Sm}(\text{acac})_3$  concentration.



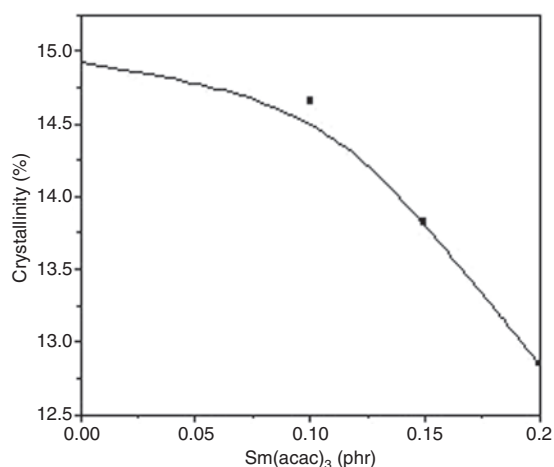
**Figure 6:** Effects of  $\text{Sm}(\text{acac})_3$  concentration the melting temperature of PET in 70PC/30PET blends.

Mendes and Pereira [39], who associated the changes of  $T_g$  and  $T_m$  of the parent polymers to the esterification and transesterification reactions inside the phases and at the interfacial region. Thus, it seems that during blending, bulky PC units are transferred into PET chains, which disturb the PET crystallization and produce less perfect crystals that melt for lower temperatures.

### 3.3.3 Crystallinity

Figure 7 shows the crystallinity ( $X_c$ ) variations for 70PC/30PET blends prepared without and with the  $\text{Sm}(\text{acac})_3$  catalyst. The crystallinity for neat PET was approximately 33.37%. After blending with PC, the PET crystallinity decreased in both uncatalyzed and catalyzed blends, irrespective of the added catalyst concentration. The effects of blending and transesterification on the crystallization behavior of PET within PC/PET blends have been subjected to extensive studies [12, 40–43], where authors pointed out hindering effects induced particularly for high PC and catalyzed interchange reactions. The alteration in PET crystallization is associated to an increase in the cold crystallization temperature and a reduction of the melting temperature.

Indeed, the crystallization of PET seems to be physically restricted in the presence of PC domains. Mendes et al. [40] found that in the presence of PC, the crystallinity of PET decreases by about 50%. Also, it recognized that in polymer blends composed of an amorphous polymer and a crystallizable one, the crystallinity of the crystallizable polymer is greatly hindered by the amorphous component [28]. Accordingly, Nassar et al. [15] showed that the



**Figure 7:** Effect of  $\text{Sm}(\text{acac})_3$  concentration on the crystallinity of PET in 70PC/30PET blends.

presence of PC greatly alters the crystallization behavior of PET but does not completely prevent its development.

In the case of catalyzed blends, the crystallization hindrance is due to the insertion of bulky PC units into PET chains [12, 41]. Indeed, Marchese et al. [42] reported that if the crystallization process is hindered, this could be due either to the formation of a more homogeneous blend or to the decrease in the lengths of PET blocks in the formed copolymer. Similarly, Aravind et al. [43] found that the crystallinity of poly(trimethylene terephthalate) (PTT) in PTT/PC blends decreases while the PC content in the mixtures increases. The authors suggested that the loss of crystallinity is due to the formation of random copolyesters resulting from transreactions between PTT and PC.

### 3.3.4 Weight fractions of PC and PET into PET- and PC-rich phases

From the  $T_g$  values of PC and PET phases into the PC/PET blends, the apparent weight fractions of PC and PET dissolved into the PC- and PET-rich phases, respectively, can be evaluated. The apparent weight fractions of PC are determined in the PC-rich phase and the PET-rich phase by using Wood's equation, which is often used to describe the dependence of  $T_g$  on the composition in random copolymers. Wood's equation is given as follows [44]:

$$T_g = \omega_1 T_{g1} + \omega_2 T_{g2} \quad (3)$$

where  $T_g$  is the observed  $T_g$  for the copolymer,  $\omega_1$  is the weight fraction of homopolymer 1 having  $T_{g1}$ , and  $\omega_2$  is the weight fraction of homopolymer 2 having  $T_{g2}$ . Kim and Burns [45] rearranged Eq. (3) to the following form:

$$\omega'_1 = \frac{Tg_{1,b} - T_{g2}}{T_{g1} - T_{g2}} \quad (4)$$

where  $\omega'_1$  is the apparent weight fraction of polymer 1 in the polymer 1-rich phase and  $T_{g1,b}$  is the observed  $T_g$  of polymer 1 in the blends. Table 3 reports the apparent weight fractions of PC and PET into PC- and PET-rich phases for the uncatalyzed and catalyzed blends, and as a function of the  $\text{Sm}(\text{acac})_3$  catalyst concentration. As it appears, the weight fractions of PET dissolved into the PC-rich phase ( $\omega'_2$ ) are higher than those of the PC component units into the PET-rich phase ( $\omega'_1$ ). This implies that the PET units are more transferable to the PC-rich phase than the PC ones due to their lower viscosity.

Also, the blend fractions vary trivially with the catalyst concentration. Similar results have been reported by several other authors [22, 46], who explained that during

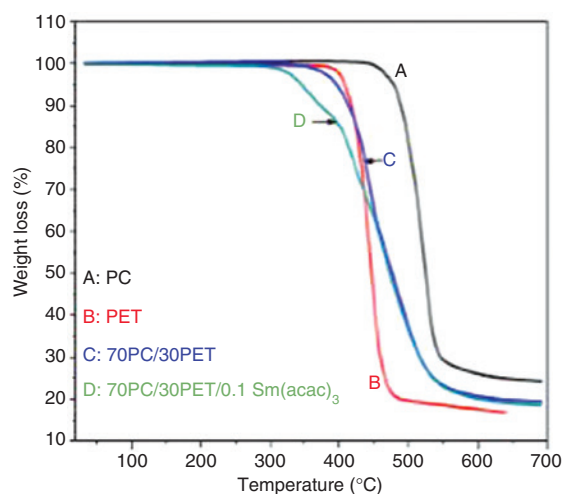
**Table 3:** PC and PET apparent weight fractions into PC- and PET-rich phases for 70PC/30PET blends melt mixed with and without  $\text{Sm}(\text{acac})_3$ , evaluated by using Wood's equation.

Samples	PC-rich		PET-rich	
	$\omega'_1$ (PC)	$\omega'_2$ (PET)	$\omega''_2$ (PET)	$\omega''_1$ (PC)
PC	1.00	–	–	1.00
70PC/30PET	0.9295	0.0705	0.9577	0.0423
70PC/30PET/0.10 Sm	0.8732	0.1268	0.8873	0.1127
70PC/30PET/0.15 Sm	0.8873	0.1127	0.9014	0.0986
70PC/30PET/0.20 Sm	0.8873	0.1127	0.8732	0.1268
PET	–	1.00	1.00	–

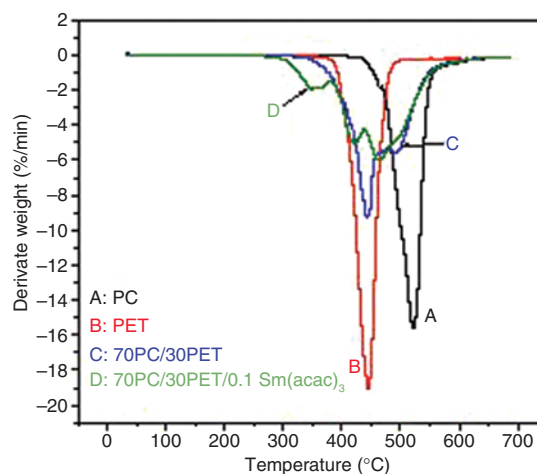
the first period of mixing, transreactions are limited to the interfacial regions where only the PET and PC chains involved in this area are concerned by interchanges. Thereafter, transesterification reactions continue probably between the blocks contained into these same copolymer chains without further or a little transfer of additional PET and/or PC units. Thus, it appears that due to the vicinity of reactive functional groups, transreactions seem to be particularly faster between the copolymer segments than at the interface between homopolymer chains, where the mixing conditions (shear and mixing time) are required to permit the reactive groups to come into contact and interact.

### 3.4 Thermal stability of PC/PET blends before and after transreactions

The thermogravimetric and differential thermogravimetry (DTG) curves of PC, PET, and PC/PET blends are represented in Figures 8 and 9, respectively. The thermal characteristics, namely,  $T_{\text{onset}}$ ,  $T_{\text{max}}$ , and  $T_{\text{end}}$  and residue content are reported in Table 4. The PC/PET blend melt mixed with 0.1 phr  $\text{Sm}(\text{acac})_3$  catalyst is chosen as representative for all studied blends. The homopolymers degrade according to a single-step process. According to the DTG traces, the onset of the thermal degradation



**Figure 8:** TG thermograms of neat polymers and their blends.



**Figure 9:** DTG thermograms of neat polymers and their blend.

of PET and PC appears at 444°C and 523°C, respectively. PET exhibits a lower thermal resistance than PC as evidenced by the lower values of the starting and final degradation temperatures. At the end of decomposition, PET and PC left around 16% and 24% of carbonaceous ash, respectively.

**Table 4:** TGA parameters for PC, PET, and 70PC/30PET blends.

Samples	Degradation temperatures (°C)		Residue content (%)	$T_{\text{max}}$	
	$T_{\text{onset}}$	$T_{\text{end}}$		PC-rich phase	PET-rich phase
PC	445	593	24.18	523	–
PET	375	498	16.74	–	444
70PC/30PET	348	582	19.34	494	448
70PC/30PET/0.1 Sm	279	600	18.41s	420	465



For the (70 : 30) PC/PET blend melt mixed without catalyst, the thermogravimetric and DTG thermograms (Figures 8 and 9) show that decomposition occurs in two steps: the first step represents the PET-rich phase degradation while the second step is related to the PC-rich phase. The uncatalyzed blend exhibits an intermediate thermal resistance. The decomposition of the PC-rich phase occurs at relatively lower temperatures relatively to the homopolymer. A similar result has been reported in a study on PC/PLA blends by Phuong et al. [47], who proposed that the thermal decomposition of PLA accelerates the degradation of the PC phase. The DTG thermograms (Figure 9) show two peaks of degradation that confirm that the blend decomposes in two steps: the first one is correlated with the PET-rich phase and the second one with the PC-rich one. After melt blending with 0.1 phr of the  $\text{Sm}(\text{acac})_3$  catalyst, the thermal decomposition of the PC/PET blend is carried out in three steps, which emphasizes that a third phase is present in the catalyzed mixture. This additional stage appears before the two initial degradation steps related to the homopolymers, which suggests that the phase responsible for this degradation step possesses an intermediate chemical structure between those of PC and PET because it resulted from catalyzed interchanges at the interface. Swoboda et al. [48] also observed an additional weight loss peak located before the two initial degradation steps and concluded that in blends, an additional thermal degradation mechanism leading to the formation of volatile species occurs, and a possible assumption is that it is due to the transesterification reaction at the interface between PET and PC, which leads to chain breaking as a side effect. The copolymer phase presents a lower stability relatively to the uncatalyzed system and the PC- and PET-rich phases. This is an indication that the occurrence of transesterification reactions in the PC/PET system blended in the presence of the  $\text{Sm}(\text{acac})_3$  catalyst produces a less stable material than the uncatalyzed blend and the forming components. Similar results were observed by Swoboda et al. [49], when they assumed that transesterification reactions lead to the blend compatibilization by copolymer formation at the interface; however, it decreases the thermal stability.

## 4 Conclusion

In this work, the influence of the  $\text{Sm}(\text{acac})_3$  catalyst on thermal properties has been investigated. The variations detected on the glass transition behavior of PC- and PET-rich phases into PC/PET blends were the consequence of

an induced compatibilization, promoted by the occurrence of transesterification reactions. Also, the decrease in the PET melting temperature resulted from the formation of PC/PET copolymer chains after the insertion of bulky PC units into PET chains, which also caused its crystallinity reduction. The occurrence of transreactions during melt blending in the presence of the  $\text{Sm}(\text{acac})_3$  catalyst has been evidenced by the solubility measurements of the catalyzed blend in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). The infrared analysis of soluble and insoluble fractions proved the presence of PC into the insoluble fraction, which should contain only PET if no transesterification reaction occurs. Additionally, PET carbonyl groups were observed in the infrared spectra of the soluble fraction, which is expected to contain only PC. Wood's equation was employed to evaluate PC and PET apparent weight fractions in 70PC/30PET blends prepared with and without added  $\text{Sm}(\text{acac})_3$ .

Despite the effectiveness of  $\text{Sm}(\text{acac})_3$  in the promotion of interchanges between PC and PET, it contributes to the conception of less stable PC/PET blends than the uncatalyzed blend and the forming homopolymers, as it was concluded from the TGA.

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