



## Reactive blending as a tool for obtaining poly(ethylene terephthalate)-based engineering materials with tailored properties

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### ABSTRACT

The structure and properties of blends of poly(ethylene terephthalate) (PET) with poly(trimethylene terephthalate) (PTT) at PTT concentration  $\leq 30$  wt.%, obtained with three different methods: from solution, melt extrusion, and direct spinning, are investigated. Relationships between the method of preparation and properties of blends are established. All blends show glass transition temperature at values determined by composition, and crystallization properties also dependent on the preparation method. Blends obtained from solution show separated melting of components. For blends obtained from the melt only PET crystallizes. The melting temperature decreases with the residence time of the melt at high temperatures, due to occurrence of ester exchange reactions. It is shown that reactive blending of PET/PTT mixtures occurring during preparation is a versatile route for obtainment of engineering materials with good mechanical properties, high crystallinity, glass transition temperature lower than that of PET, and melting temperature that may be controlled by the processing conditions.

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### 1. Introduction

Poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), and poly(butylene terephthalate) (PBT) are thermoplastic engineering materials of large commercial importance, thanks to their outstanding physical and mechanical properties such as high strength, stiffness, toughness and heat resistance [1]. PET is the highest-volume polyester produced and is used in numerous applications such as films, fibers, and packaging [1,2]. PBT is namely used as an insulator in the electrical and electronics industries. Compared to PET, PBT has lower strength and rigidity, better impact resistance, and a lower glass transition temperature [1,2]. PTT is the youngest member of the series to reach industrial production because of the relatively high price of 1,3-propanediol monomer. Only after development of a low cost innovative synthetic process for production of 1,3-propanediol based on hydroformylation of ethylene oxide using a soluble catalyst in 1995 [3], the Shell Chemicals started PTT mass production. In PTT the properties of PET of high performance plastomer are

combined with those of PBT showing better processing characteristics, better elastic recovery and higher crystallization rate than PET. PTT, indeed, can be easily spun into fibers and yarns, and can be used in numerous applications such as carpeting, textiles and apparel, engineering thermoplastics, nonwovens, films and monofilaments [4–7].

The introduction of PTT into the market has greatly enhanced the research interest for this polymer also because of the possibility of obtaining binary blends of PTT with other polyesters, in particular with PET, showing combined useful properties of both components. Blending, indeed, is a simple, economical, and versatile route to produce new materials with tailored properties, without resorting to the synthesis of a totally new compound [8].

Binary blends of PET and PTT have been recently studied. It has been shown that the two components are completely miscible in the glassy state in the whole composition range, independent of preparation method, i.e. solution blending and melt-blending [9–12]. A single glass transition temperature is indeed observed, gradually decreasing with PTT content from the value of pure PET ( $\approx 89$  °C) to that of pure PTT ( $\approx 35$  °C). In the case of blends prepared by co-precipitation of the two components from solution, it has been shown that as precipitated samples show independent melting of the two components at temperatures close to the melting temperature of neat PET and PTT [12]. The two polyesters do not form co-crystals [9–12], even though, for short residence

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time of the melt at high temperature, they crystallize simultaneously, with formation of crystals within the same spherulites [9]. For blends obtained by melt processing of the two components, or by prolonged heat treatment of solution blends at high temperatures in the melt state, ester exchange reactions between the chains of the two components occur, leading to formation of copolymer chains with the potential to act as compatibilizer [9–12]. The extent to which transesterification reactions occur depends on the initial degree of compatibility, and on blending parameters such as maximum temperature achieved in the melt, duration of heat treatment and mixing parameters, viscosity match, etc. [9–12]. The most remarkable effect of transesterification reactions is in the emergence of a single melting temperature of the blends with a tendency of the melting endotherm to move toward lower temperatures with the residence time of the melt at high temperatures [9,12].

With the aim to exploit the lower glass transition temperature of PET/PTT blends and/or the intrinsic elastic properties of PTT fibers without impairing the good mechanical performance of PET, the possibility of production of fibers by blending PET with PTT has been also explored. It has been shown [13] that for fibers containing 10 wt.% PTT, an improvement of elastic recovery without drop of tenacity and modulus in comparison to pure PET fibers is achieved, and that the dyeing ability for PTT content of  $\approx 30$  wt.% is superior to that of PET and even better than that of pure PTT fibers. Therefore, the studies performed to date indicate that PTT is an excellent candidate for obtainment of PET-based materials with properties intermediate between those of the two components, or even with better performance.

In the studies performed to date a direct relationship between the effect of reactive blending on the structure, physical and mechanical properties of PET/PTT blends obtained via different methods has not been yet performed. In this paper a detailed structural investigation is performed on PET rich blends with PTT aimed at establishing direct relationships between the method of preparation of the blends, their structure, thermal and physical properties. To this aim, PET/PTT blends in the composition range 5–30 wt.% of PTT have been prepared according to three different methods, i.e. by precipitation from solution (solution blends, SB) melt extrusion (MB) and direct melt spinning of mechanical mixtures of the two components to obtain fibers (FB). The use of the direct spinning method for the preparation of blend fibers relies on the miscibility of PET and PTT in the melt state without any need of adding a third component as compatibilizer. It allows obtaining fibers from the two polyesters without the need to prepare blend chips prior spinning, as a necessary step generally used to achieve an effective dispersion of the components [8,14].

The structure and properties of all blends are analyzed and compared also with those of samples of the pure components prepared following the same procedure. This is the first comparative and systematic investigation of the effect of the preparation method on the structure and properties of PET/PTT blends. This study is aimed not only at clarifying basic aspects related to the unavoidable occurrence of reactive blending of PET and PTT chains during the preparation step and successive heat treatments, but also to highlight the beneficial effect of ester exchange reactions on the final properties of this class of new materials, especially suited for applications in fiber technology.

## 2. Experimental section

### 2.1. Materials

PET and PTT chips used in this study are commercial grades from Tondgooyan petrochemical company, Iran, and Shell chemical

company, USA, respectively. Shapes of PET and PTT chips are cylindrical and spherical with approximate number of chips per gram of 36–40 and 39–44, respectively. Solvents of analytical grade have been purchased from Aldrich and used as received. The commercial grade of PET sample contains 0.34 wt.%  $\text{TiO}_2$  as de-lustering agent [15a] and corresponds to 1.01 wt.% diethylene glycol content [15b] and 21 meq/kg carboxyl end groups concentration [15c]. Intrinsic viscosity (IV) has been measured at 25 °C for PET and 30 °C for PTT using an Ubbelohde viscometer in a 60/40 wt.% mixture of phenol/1,1,2,2 tetrachloroethane [16]. For PET and PTT, intrinsic viscosity values of 0.65 and 0.92 dL/g have been calculated, respectively. For PET, the number average molecular mass  $M_n$  of 24 kDa has been obtained from the intrinsic viscosity value using the relationship  $[\eta] = K M_n^\alpha$ , with  $K = 7.61 \cdot 10^{-4}$  and  $\alpha = 0.67$  for PET [16a], whereas for PTT the relationship  $[\eta] = K' M_w^\alpha$  with  $K' = 5.36 \cdot 10^{-4}$  and  $\alpha = 0.69$  has been used, giving a mass average molecular mass  $M_w$  of 48 kDa ( $M_w/M_n \approx 2$  in both cases) [16b].

### 2.2. Preparation of blends

Chips of the two polyesters have been first dried in a vacuum oven at 140 °C for 24 h prior their usage. Successively, weighted amounts of the dried samples have been mechanically mixed to obtain PET/PTT mixtures at weight percent ratio 95/5, 90/10, 80/20 and 70/30 to be used for the preparation of blends. Three different methods have been used to prepare the samples: precipitation from solution, extrusion from the melt and direct spinning of mechanical mixtures of the components from the melt to obtain fibers. The direct spinning of the mixtures of the two components from the melt implies that no additional step for the preparation of blend chips is used to obtain the fibers. Pure PET and pure PTT samples have been also obtained using the same procedures of the blends, in order to have a more direct comparison of the properties of the blends with those of pure components. Here in the following the samples obtained according to three different methods will be indicated with symbols SB for the systems obtained from solution, MB for those obtained by melt extrusion and FB for the fibers.

#### 2.2.1. Solution blends

Pure components as well as their mechanical mixtures have been dissolved at 60 °C in chloroform/trifluoroacetic 80/20 v/v solutions, precipitated by addition of methanol and then dried in a vacuum oven at 80 °C for 24 h.

#### 2.2.2. Melt extruded blends

Melt extrusion has been conducted under nitrogen atmosphere using a single-screw extruder ( $L/D = 25$ ,  $D = 35$  mm with  $L$  and  $D$  the length and diameter of screw) equipped with static mixer and a die section. Four different zone temperatures of 250, 270, 280, and 290 °C (230, 240, 250 and 260 °C for pure PTT) have been used corresponding to the feeding, metering, melt-blending, and die units, respectively for a total residence time of the melt in the extruder of  $\approx 15$  min.

#### 2.2.3. Preparation of fibers

Melt spinning has been conducted in nitrogen atmosphere using the same screw extruder apparatus as before, but coupled to a spinneret unit having 36 circular holes, each of 0.25 mm diameter. Five different zone temperatures of 250, 270, 280, 290, and 290 °C have been employed corresponding to the feeding, metering, melt-blending, die, and spinneret block, respectively. For pure PTT the five temperature zone were at 230, 240, 250, 260 and 260 °C. Also in this case the processing conditions have been controlled in such a way that the total residence time of the melt in the spinning

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