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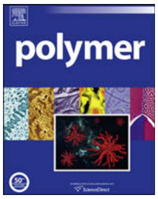

EVA/PBT nanostructured blends synthesized by in situ polymerization of cyclic cBT (cyclic butylene terephthalate) in molten EVA

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ABSTRACT

Poly(ethylene-co-vinyl acetate) (EVA)/poly(butylene terephthalate) copolymers were synthesized by the in situ polymerization of cyclic butylene terephthalate monomer (cBT) in the presence of molten EVA copolymer.

Titanium phenoxide $Ti(OPh)_4$ which leads to the highest degree of grafting compared to the more classical titanium system was used as the initiator for the ring-opening polymerization of the cBT monomer. The corresponding copolymer was characterized fully by ^1H NMR after selective extraction from the blend. As a result, a maximum of 11.3 wt% of EVA-g-PBT copolymer was synthesized by this method. Examination of morphology by transmission electronic microscopy (TEM) showed a fine dispersion of PBT phase with size ranging from 100 to 500 nm in diameter. This gave evidence for a crown structure of the PBT phase that is coated by EVA-g-PBT copolymer.

Finally, rheological and mechanical studies highlighted a specific behaviour of this material with improved mechanical properties at room temperature.

1. Introduction

Recently, several strategies have been developed to reach well structured polymer blends at the micro and nano-scale as described by Harrats et al. [1].

However, there remain a need for research into the synthesis of block or graft copolymers that would present ideally the ability to give nanostructures; this work is both scientifically challenging and industrially important. Reactive extrusion [2] in particular represents an attractive way to obtain such specific nanostructures. Generally, there are three main ways of synthesis of such copolymers:

a) Living copolymerization
b) Chemical modification by post polymerization
c) Coupling between two appropriately functionalized polymer chains

Methods a) and b) are associated with "the grafting from" approach and method c) belongs to the "grafting onto" route. Structures of copolymers obtained through methods b) and c) are specifically relevant to reactive extrusion since they are unattainable by classical copolymerization method. However, the main difficulty lies in the fact that the polymers/polymers or polymers/monomers systems are generally not miscible. The chemical reaction occurs at the interface and thus a large quantity of copolymer is difficult to obtain. This interfacial reaction leads to compatibilization of the blends by reactive mixing [3]. Thus, when synthesis of nanostructured copolymers or blends is required, other parameters have to be optimized in order to increase the concentration of the copolymers synthesized. In this case, the copolymers would arrange themselves at a nanometric scale but would also be organized at a larger scale, forming ultimately a fully nanostructured material. The formation of such a nanostructured material has to be related to the architecture of the copolymers based in particular on the size and the molar masses of the sequences or the grafts and also on the grafting ratio (copolymer concentration) and the type of reactive chains (position of the functional reactive group). For example, based on the coupling between two appropriately functionalized polymer chains, relevant results were reported by Leibler and his group [4–7]. They succeeded in the self-organization of grafted copolymers of poly (methylmethacrylate)/polyamide 6 and polyolefin/polyamide obtained by reactive mixing in the molten state. On the other hand, Flat [8] reviewed the synthesis by reactive extrusion and the characterization of new materials based on

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comb-like nanostructured copolymers. According to this concept, a nearly pure graft copolymer was obtained by Steurer et al. [9] through reactive blending of equal amounts of poly(styrene-co-maleic anhydride) and short polyamide 12. Orr et al. [10] employed a very fast cyclic anhydride-aliphatic amine reaction between polystyrene and polyisoprene end-capped with anhydride and amine functions, respectively, to create a uniform morphology with molecular scale self-assembly into cylindrical micelles over the entire sample. More recently, Robin et al. [11] investigated the reaction of PMMA functional oligomers onto maleic anhydride grafted polypropylene (PP-*g*-MAH) and poly(ethylene-*ter*-maleic anhydride-*ter*-methyl acrylate) (P(E-*ter*-MAH-*ter*-MeA)) and obtained PP-*g*-PMMA and P(E-*ter*-MAH-*ter*-MeA)-*g*-PMMA graft copolymers respectively. This work showed that this process allows the synthesis of PP-*g*-PMMA graft copolymers containing 6–45 wt% of PMMA side chains depending on PMMA chain length. The work also revealed that the speed of formation of the copolymer at a plane interface between two functionalized polymers is related to the reaction speed between both reactive groups of the corresponding chains. Furthermore this coupling reaction is strongly limited by the copolymer formed at the interface and a greater quantity of copolymer is formed more quickly in the case of short length chains. Therefore, to obtain high copolymer formation rates [5], it is important to use a very short functionalized compound with a fast reaction at the interface. An alternative way would be to prepare block or graft copolymers by polymerizing a monomer, in an extruder in presence of either end-group functionalized prepolymers or polymer that would act as the starter molecules [12]. In the case of polymer, the block copolymer structure will be obtained through a reaction between the polymer backbone and the growing species. Several parameters such as nature of the reaction, the monomer miscibility in the matrix melt, processing parameters, influence this method of copolymer synthesis. Focusing specifically on the ring-opening polymerization of cyclic monomers, Stevels et al. [13] reported the polymerization of L-lactide initiated by either a hydroxyl terminated poly-ε-caprolactone (PCL) or a polyethylene glycol. Three different prepolymers were used as potential initiators: a PCL diol with M_n of 1500 g mol^{-1}, a monofunctional PCL with a M_n of 6000 g mol^{-1} and a poly(ethyleneglycol) with a M_n of 2000 g mol^{-1}. Contrary to uncontrollable structures obtained through transesterification between both homopolymers, these authors have demonstrated that this co-extrusion is a very promising method to obtain such copolymers with high conversion of monomers and no residuals hydroxyl end groups. Lee et al. [14] used isocyanate-terminated telechelic PTMEG premixed with caprolactame to feed a twin-screw extruder to form the polyetheramide triblock copolymer. The conversion of caprolactame is typically around 95% and could be enhanced by devolatilization. The mechanical properties of the triblock copolymer indicated that depending on the polyether content, the formed copolymer would be either a good rubber reinforced polyamide or a polyamide thermoplastic elastomer. Zuniga-Matinez et al. [15] reported the polymerization of the ε-caprolactame monomer in the presence of a linear prepolymer of poly(ether-esteramide). Concerning the grafted copolymers, Hu et al. [12,16] synthesized copolymers with polyamide as graft by first preparing a polypropylene-g-isocyanate macroactivators. Madbouly et al. [17] studied the in situ polymerization of macrocyclic carbonates in the presence of PP-g-MA. The degree of polymerization was shown to decrease with increasing concentration of maleic anhydride which was consistent with the higher proportion of graft copolymer formed. Becquart et al. [18] related a method for the synthesis of polylactone-grafted EVOH from the in situ polymerization of ε-caprolactone. We also carried out the polymerization of ε-caprolactone from phenoxy titanium end-group created in situ in poly(bisphenol A carbonate) chains after an exchange reaction between carbonate function and titanium n-propoxide by reactive extrusion [19]. Depending on the processing parameters, block copolymers of PC and PCL can be obtained.

In the present study, our objective was to form a nanostructure based on EVA/PBT blends through the synthesis of EVA-g-PBT copolymers by in situ polymerization of cBT (cyclic butylene terephthalate) in the melt EVA. A main point of interest in this work was to characterize the structure and the amount of EVA-g-PBT copolymer in the blend and to examine the morphology and mechanical properties of such new nanostructures.

2. Experimental section

2.1. Characterization techniques

High resolution liquid NMR spectroscopy was used for characterizing the copolymer structure and its amount. The work was carried out on a Bruker AC 250 instrument working at 250 MHz for ^{1}H and 62.9 MHz for ^{13}C using CFCOOD/CDCl$_3$ or TCE/C$_6$D$_6$ as solvents. Chemical shift values (δ) are reported in ppm with reference to the internal standard tetramethylsilane (TMS).

Size exclusion chromatography (SEC) analyses were performed using a Waters gel permeation chromatograph equipped with 2 Styragel columns (HR1 and HR4) with a refractomer detector Waters R410. Measurements were made at 23 °C using THF as permeation solvent (1 mL/min) using standard polystyrene samples as references. The samples were analyzed in dynamic mode of shearing on a rheometer RMS800 (Rheometrics) using a parallel plate geometry with 25 mm diameter, the experiments were performed in the frequency range of 10^{-1}–10^2 rad/s. All experiments were performed in the domain of the linear viscoelasticty and under nitrogen atmosphere in order to prevent thermo-oxidative degradation. Furthermore, dynamic mechanical properties were studied using a DMA 2980 TA instrument in the rectangular tension mode. Samples with the following dimensions: length 15 mm, width 8 mm, and thickness around 0.70 mm were used. The temperature dependence of the complex Young modulus and loss angle (tan δ) was measured from −120 °C to 220 °C ($\dot{q} = 3$ °C min^{-1}) at the frequency of 10 Hz.

The microstructures of blends were determined by transmission electron microscopy (Philips CM 120). Ultrathin sections of 70 nm were obtained at low temperature (−100 °C) using an ultramicrotome LEICA equipped with a diamond knife, the sections were not stained. Tensile tests were carried out with an Instron tester (model 4206), on specimens at a strain rate equal to 10 mm min^{-1}.

2.2. Reagents

The ethylene and vinyl acetate (EVA 28 800) copolymer was supplied by ARKEMA. The amount of acetate groups is 28 wt%. The EVA 28 800 was selected for its low molar mass (M_n = 7900 g mol^{-1}) with a melt index of 800 (190 °C/2.16 Kg). Before use, EVA pellets was dried under vacuum at 60 °C.

The cyclic butylene terephthalate monomer (trade name: cBT100) is a product provided by the Cyclics company and is actually a mixture of five cyclic molecules of different sizes and thus of different molar mass. After ring-opening polymerization, the corresponding polymer and grafted copolymer will be named in the following text PBT$_{100}$ and EVA-g-PBT$_{100}$, respectively.

The structure of cBT100 monomer was confirmed by size exclusion chromatography (SEC) analysis using THF as solvent. Indeed, Fig. 1 shows that the first peak corresponds to cyclic monomer with the highest molar mass, whereas the last

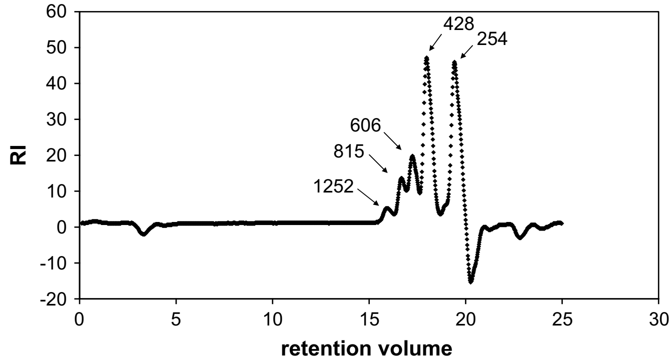

Fig. 1. SEC of the cBT100 and molar masses (g mol^{-1}) of the corresponding components.

corresponds to the lowest one. By numerical integration of the various peaks shown in Fig. 1 and by allocating to each molecule a given percentage, we find an average value of the molar mass of cBT100 monomer close to 442 g mol^{-1}.

The ring-opening polymerization of cBT100 will be carried out with the titanium phenoxide ($Ti(OPh)_4$) as initiator. This initiator was synthesized in our laboratory according to our previous work [19,20] and selected for its specificity in the grafting reaction.

Another cyclic butylene terephthalate monomer precatalysed (trade name: cBT160), also provided by the Cyclics company was used as a reference. The polymer obtained from the ring-opening polymerization of the cBT160 will be named in the following text PBT_{160}.

2.3. Reactive blending

12.5 g of cBT100 (0.0282 mol) and 36.25 g of EVA 28 800 (0.876 mol) were mixed with 1.25 g of titanium phenoxide (3×10^{-3} mol) in the chamber of an internal mixer (Rheocord Mixer). The temperature of the mixer chamber was set at 220 °C and the stirring speed of the rotors was 50 rpm. The molten medium was mixed for eighteen minutes. The material was then compression moulded using a laboratory press at 200 °C for 2 min into 1 mm thick sheets and then cooled to room temperature for characterization. The PBT_{100} molar mass targeted was $M_n \sim 4154$ g mol^{-1}. As the PBT_{100} chain growth is controlled by the cBT100 monomer/initiator ratio (polymerization degree: $DP_n = n(cBT)/n(Ti(OR))_4$ and the expected PBT_{100} concentration is 25 wt%, the concentration of titanium phenoxide used was 2.5 wt% (i.e. DPn = 9.4).

SEC results (Fig. 2), using a common solvent (THF) for EVA 28 800, cBT100 and the present reactional medium noted EVA/cBT100/$TiO(Ph)_4$ revealed an almost complete disappearance of the five peaks initially associated with the different cyclic monomer species in the cBT100. From the area ratio, we can estimate the conversion under these processing conditions to be 96% (Evaluation carried out by preserving the same cBT100 concentration for both initial and final solutions (5 mg/mL)). On these chromatograms, one can also notice a complex form for the retention peak corresponding to the highest molar mass in this medium. Additional to the peak attributed to the pure EVA 28 800, two others components can be detected in the same range of retention volume. This indicates that other polymeric species have been formed during in situ polymerization of the cBT100 in the presence of EVA 28 800 melt.

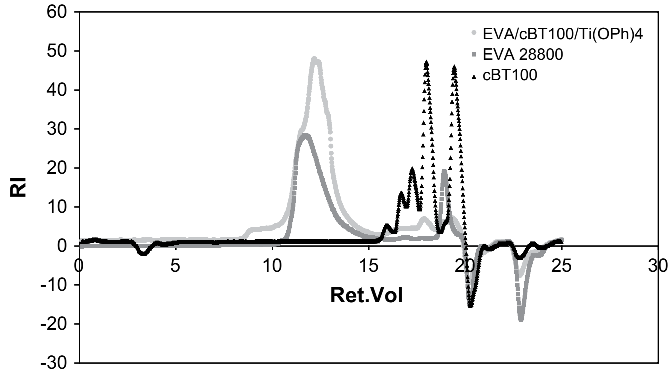

Fig. 2. SEC analysis of EVA/cBT100/$Ti(OPh)_4$, EVA 28 800 and cBT100.

A reference blend noted EVA/PBT_{160} was also obtained in the same mixing conditions by the polymerization of 12.5 g of cBT160 (precatalyzed) in presence of 37.5 g of EVA 28 800.

2.4. Extraction of the copolymer EVA-g-PBT_{100}

The EVA-g-PBT_{100} copolymer was isolated from the blend and purified according to the method provided by Pilati [21] (Fig. 3). First of all, solubility tests showed that EVA 28 800 was soluble in hot toluene and hot 1,1,2,2-tetrachloroethane (TCE), but was insoluble in dichloroacetic acid (DCAA). PBT_{100}, on the other hand, was soluble in DCAA at room temperature and in hot TCE, but insoluble in toluene [22,23].

5 g of EVA/cBT100/$Ti(OPh)_4$ sample was added to 100 mL DCAA and stirred at room temperature for 24 h. Following this, the suspension was filtered. The clear solution was precipitated in water and the resulting precipitate was washed with water and dried until constant weight. This product is referred to as fraction 1. The insoluble fraction of the first filtration was extracted with hot toluene in a Soxhlet apparatus for 3 days. This solution was then precipitated with methanol and the precipitate, after being washed with methanol and dried, is referred to as fraction 2. The residue of this second extraction was further extracted with hot TCE in a Soxhlet apparatus for 3 days. The solution obtained was precipitated with methanol, washed and dried. It constituted fraction 3. The residue of this third extraction is referred to as fraction 4. Nevertheless, it was not possible to characterize these last both fractions.

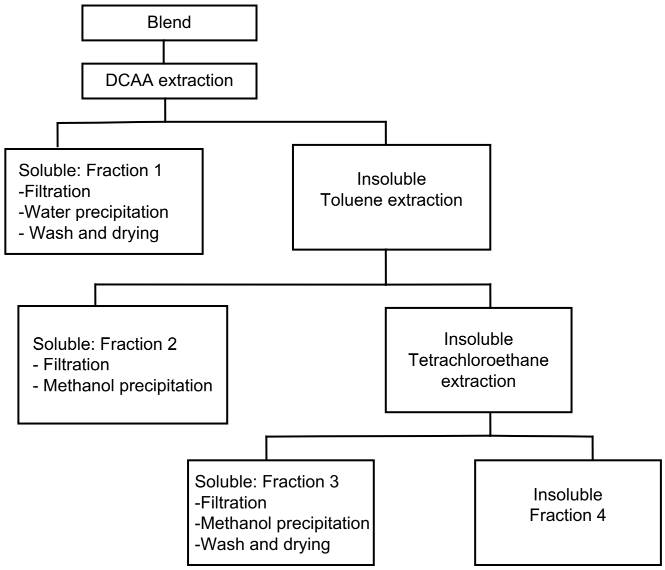

Fig. 3. Scheme of the extraction steps of the EVA-g-PBT_{100} copolymer.

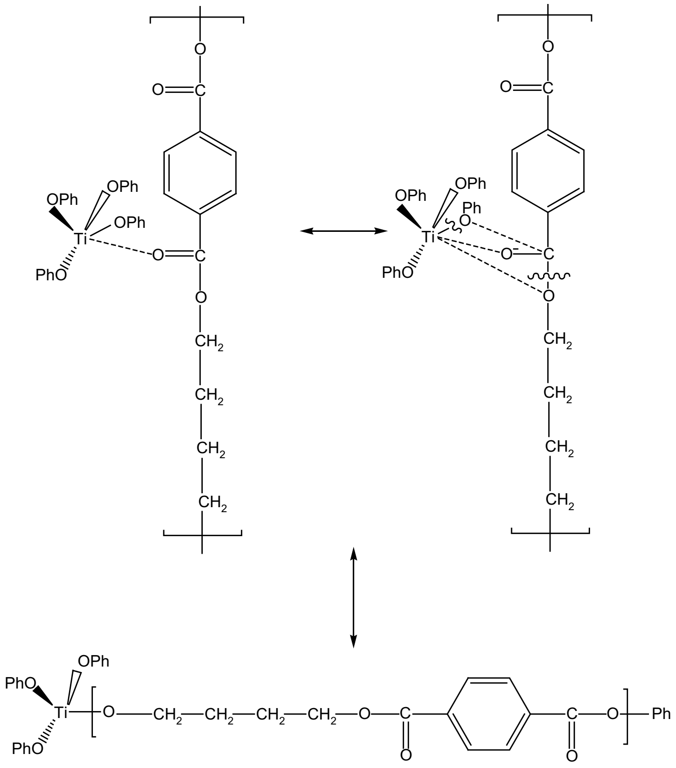

Fig. 4. Coordination-insertion mechanism of the cBT100 polymerization.

3. Results and discussion

3.1. Identification of the EVA-g-PBT$_{100}$ copolymer

The objective of the present work was to take advantage of the living character of the PBT$_{100}$ chains growing from cBT100 ring-opening polymerization to increase, through the specific exchange reaction between the living PBT$_{100}$ end-chain and the EVA acetate groups, the probability of grafting and consequently the concentration of the copolymer formed in the blend. The cBT ring-opening polymerization mechanism proceeds with both initiation and propagation steps [24]. The conditions of cBT polymerization and research on suitable initiators have been recently studied [25]. Classically for these living ring-opening polymerization, the length of the polymer chains depends directly on the ratio $DP_n = [M]/[I_0]$ where [M] and $[I_0]$ are the monomer and initiator concentrations, respectively. As shown in Fig. 4, the polymerization proceeds via an acyl-oxygen cleavage of the cBT100 with insertion of the monomer into the metal-oxygen bond of the initiator. First, the monomer forms a complex with the initiator through interactions between the carbonyl group of the cBT100 and the metal atom, followed by ring opening of the cBT100 which occurs via cleavage of the acyl-oxygen bond.

Thus, when the polymerization of the cBT100 initiated by the titanium phenoxide takes place in the presence of the EVA 28 800 melt, two kinds of reactions occurs leading to the grafting process as shown in Fig. 5. First, a transfer reaction between the acetate group of the EVA and the living Ti-O-PBT$_{100}$ end bond results in EVA chain functionalized by $Ti(OPh)_3$ and PBT$_{100}$ functionalized by an

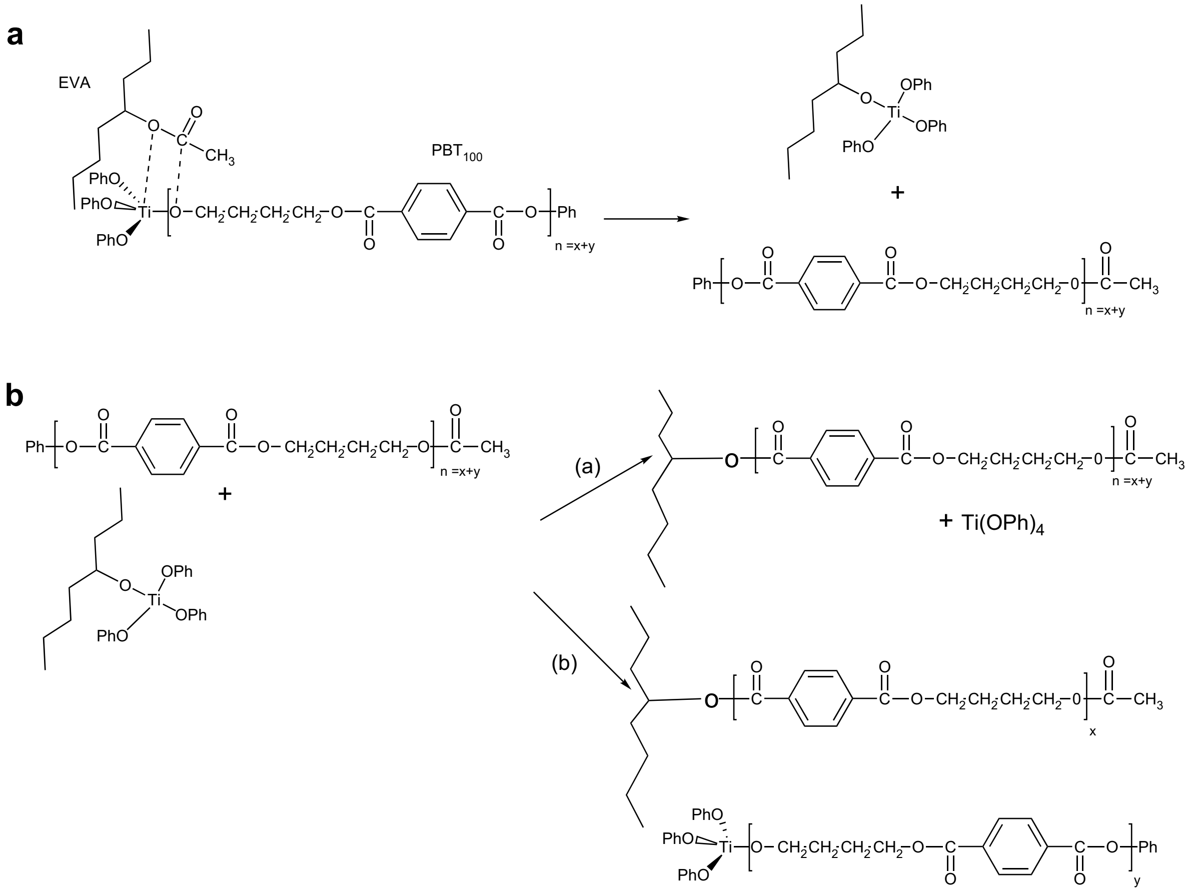

Fig. 5. Reaction of PBT$_{100}$ grafting resulting in the EVA-g-PBT$_{100}$ copolymer synthesis.

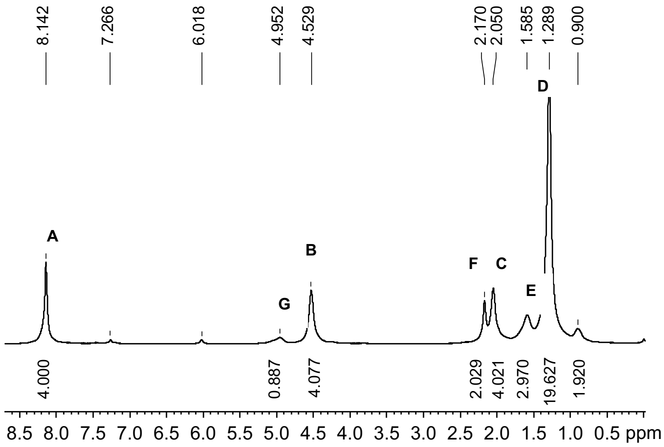

Fig. 6. ^{1}H NMR spectrum (250 MHz) of fraction 1 in $CF_3COOD/CDCl_3$ (1/1 by volume) at ambient temperature.

acetate group (Fig. 5a). This observation was already confirmed in a Phd study dedicated to the grafting of poly-ε-caprolactone on EVA backbone [26]. Based on model compounds (heptyle acetate instead of EVA) approach and mainly NMR analysis, around 90 mol% of acetate end groups is obtained after 1 h at 160 °C of in situ polymerization of ε-caprolactone by $Ti(OPh)_4$ in presence of heptyle acetate (molar ratio 45/5/1 ε-caprolactone, heptyle acetate, initiator).

Then, either this new titanate species would react on an ester function of PBT_{100} chain (Fig. 5b), or on the phenoxyl ester end group (Fig. 5b), this latter reaction being favoured for the following reasons. Indeed in our previous results dedicated to the ring-opening polymerization of the ε-caprolactone [20] initiated by the titanium phenoxide, we evidenced first that on average, one phenoxide ligand initiates the ring-opening polymerization. When after complete monomer conversion, an increase of the polymer molar mass was observed with a diminution of the concentration of phenoxyl ester end groups. Actually, this phenomenon is due to transesterification reactions favoured with end groups in case of polymerization with $Ti(OPh)_4$. Indeed the C–O bond of phenoxyl ester terminal is more prone to nucleophilic substitution than the C–O bond in repetitive unit due to the influence of phenyl group on electronic delocalisation. This leads to more selective transfer reactions and consequently is more efficient for grafting reactions.

After extraction, the mass distribution of the fractions was as follows: fraction 1: 20.2%, fraction 2: 64.6% and fraction 3 and 4: 15.2%. Fractions 3 and 4 were not analyzed because of experimental difficulties.

Fraction 1: The ^{1}H NMR spectrum of this fraction is depicted in Fig. 6 and analyzed according to the chemical structure of EVA and PBT depicted in Fig. 7. The main resonance corresponding to the chemical shifts of the PBT protons A,B and C. A,B and C are associated with the aromatic proton, and with the protons of $–CH_2–$ in α and β position of –O–CO– groups (Fig. 7), respectively. The relative proportions of each peak intensity are consistent with the number of protons.

Others peaks appeared in the spectrum which after comparison with the ^{1}H NMR spectrum of the EVA 28 800 were found to correspond to the methylenic protons D of the ethylene sequence, methylic protons E in α position of the CH groups, methyl protons F of the acetate groups and protons G in α position of the acetate groups, respectively. However, the proton resonance F, according to the previously described mechanism can be attributed also to some PBT_{100} end-chains due to the exchange reaction between the living PBT_{100} end-chain and the EVA 28 800. Nevertheless, the intensity of signals D, E, F and G are in agreement with the expected ratio. This observation associated with the fact the no new signals attributable to grafted species were detected give a clear evidence that fraction 1 is composed of EVA 28 800 and PBT. The ratio of each polymer can be evaluated based on the proton intensity G and B/4. We obtained 53.2 mol% of PBT_{100} and thus 46.8 mol% of EVA 28 800, respectively, and these would certainly correspond to low molar mass chains.

Fraction 2: This fraction corresponds to compounds insoluble in DCAA but soluble in hot toluene. The ^{1}H NMR analyses (Fig. 8) was realized in a mixture of TCE/C6D6 in which a small quantity of the sample was not soluble. As previously mentioned, we recognized first the protons resonance of both polymers within that case a predominance of the resonance of EVA 28 800. In the spectrum of the soluble part we found the peaks characteristic of EVA 28 800 and also of PBT_{100}.

However, by zooming on the region 4.0–6.0 ppm, which is associated with the –CH– protons resonance, a new peak at 5.36 ppm can be detected. This signal, according to a paper dedicated to transesterification study between EVA 2803 and PBT (Orgater TMNO from Atochem) can be associated with the CHα′ carrying grafted polybutyleneterephthalate [27].

From these spectra, we can estimate the presence of EVA-g-PBT_{100} copolymer in this fraction. However, the exact proportion of the copolymer will only be roughly given due to the incomplete solubility of this fraction in TCE/C_6D_6. Table 1 gives the amount and composition of the different fractions.

This synthesis of EVA-g-PBT_{100} copolymer by in situ polymerization of the cyclic butylene terephthalate monomer (cBT100) in the presence of molten EVA 28 800 leads to a minimum amount of copolymer of 11.3 wt% in fraction 2. This value may be minimized because of the non-analysis of the fractions 3 and 4. These results may represent an enhancement when compared to previous work from the literature focalised on transesterification reactions. For example, in a previous study dedicated to the transesterification reaction between PBT and EVA polymers which are immiscible polymers, the synthesis of the EVA-g-PBT copolymer was shown to be located at the interface leading to the stabilisation of the interface [22,27]. Consequently, the quantity of the copolymer created is insufficient for the formation of a nanostructured blend material, at least at a sub-microscale level. Indeed Flat [5] concluded that a nanostructured morphology can be obtained if the amount of grafted copolymer is higher than a threshold value, between 20 and 50 wt%. Under these conditions, it would be then expected that

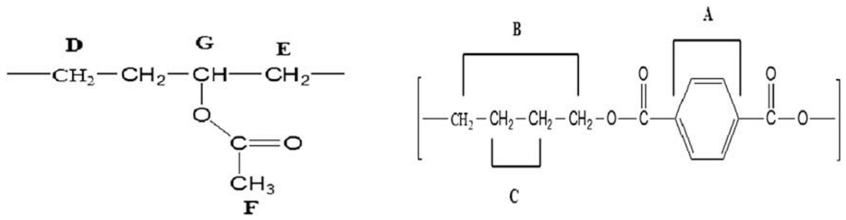

Fig. 7. Chemical structure of EVA and PBT.

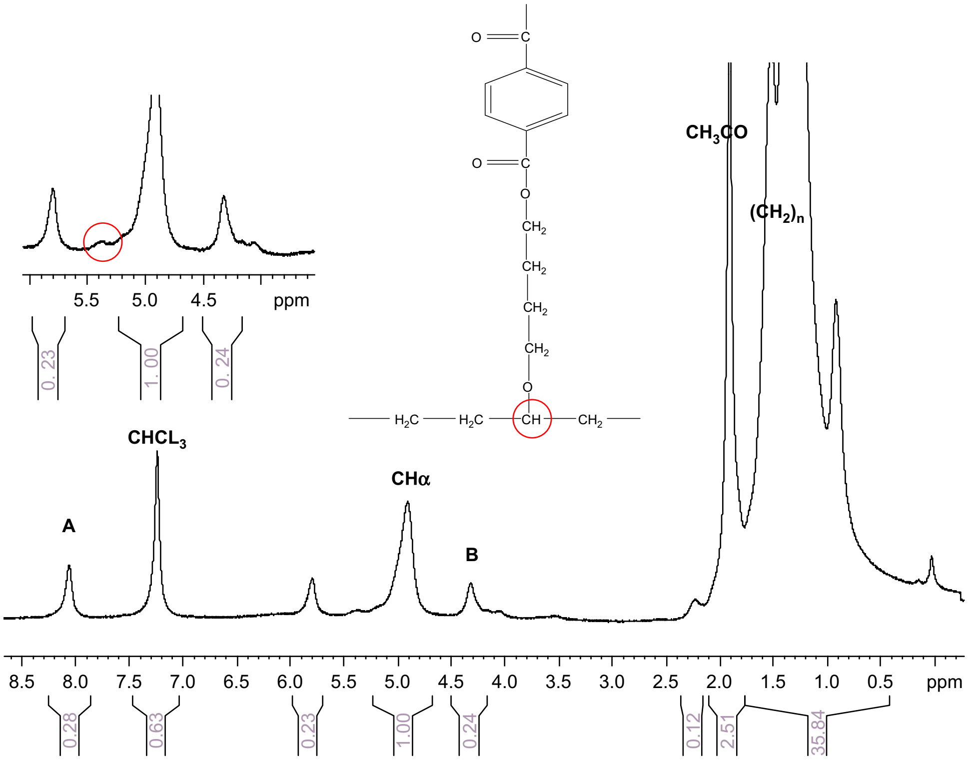

Fig. 8. ^{1}H NMR spectrum (250 MHz) of fraction 2 in TCE/C_6D_6 at ambient temperature.

a macro-phase separation of the blend can be avoided since the copolymer should be able to accommodate the corresponding non-grafted polymers. The amount of grafted copolymer synthesized during mixing is then a crucial parameter. In our case, the threshold value of the copolymer was not achieved. Nevertheless, the evaluation of the morphology and the properties of such blends represent a further point of interest.

3.2. Morphology and properties

First of all, the morphology of the reactional medium EVA/cBT100/Ti(OPh)$_4$ was characterized by TEM analysis. Fig. 9 shows a fine dispersion at a sub-micron scale of PBT$_{100}$ droplets dispersed in the EVA 28 800 matrix.

Scaffaro et al. [28] have previously demonstrated that a binary blend of PBT(Arnite TO8 200 from DSM, 80 wt%)/EVA (Greenflex FC 45 from Polimeri Europa, 20 wt%) with a vinyl acetate content of 14% by weight gave particle dimensions of PBT of about 5 μm with a poor dispersion in the matrix and a low interfacial addition between EVA and PBT. In fact without the formation of in situ copolymer, PBT droplets are submitted to coalescence under flow. Indeed, Cassagnau [29] has shown in previous work, that the diameters d_v of PBT particles in virgin EVA 28 03(Atochem)/PBT(Crastin S600 DuPont) blend increases from $d_v = 0.8$ μm to $d_v = 1.5$ μm with increasing the PBT concentrations from 20 to 30 wt%, respectively. Consequently, the in situ formation of EVA-g-PBT$_{100}$ copolymers lead to a stable sub-microscale structure of the blend for a relatively high concentration of PBT$_{100}$ phase (25 wt%) in the present blend system. However, it is interesting to note that a crown type nano-structure can be observed within the EVA 28 800/cBT100/Ti(OPh)$_4$ interphase which is rich in EVA-g-PBT$_{100}$ copolymer. It is important to emphasize that copolymers tend to segregate to the interface where they screen contacts between PBT$_{100}$ and EVA 28 800 and promote the formation of small and fine spherical nodule of PBT$_{100}$ with a size ranging from 100 to 500 nm (Fig. 9a) by reducing interfacial tension and suppressing coalescence events.

Table 1
Analysis and results for different fractions.

	Fraction 1	Fraction 2	Fractions 3 and 4
% weight of the various fractions	20.2	64.6	15.2
% molar of the PBT$_{100}$	53.2	17.52	—
% weight of the PBT$_{100}$	10.74	11.3	—

Note, that the use of core-shell or vesicular terminology seems not to be appropriate to describe this particular morphology. A micelles structure [30–32] of copolymers at the interface of PBT$_{100}$ droplets/EVA 28 800 matrix as reported in the literature is presented in Fig. 9b. The average size of these micelles copolymers is 50 nm. This structure was also described by Leibler [5] as spherical and worm-like micelles.

Nevertheless, according to work of Flat [8], the synthesis of 11.3 wt% of EVA-g-PBT$_{100}$ (without considering the nature of the fractions 3 and 4) copolymer is not enough to reach the nano-scale structure. As a result, the copolymer is not able to accommodate the two non-grafted homopolymers allowing then a sub-micron phase separation. The final blend can be then imagined as a complex ternary blend of the expected grafted copolymer with the two non-reacted polymers forming crown type morphology at nano-micro scale.

Although the formation of the nanostructure remains that of the crown type, a dramatic change of the macroscopic properties of the blend can be expected. The viscoelastic behaviour ($G^*(\omega) = G'(\omega) + jG''(\omega)$) of the material EVA 28 800/cBT100/Ti(OPh)$_4$ is shown in Fig. 10. More precisely, Fig. 10a shows the frequency dependence of the complex shear modulus at two temperatures,

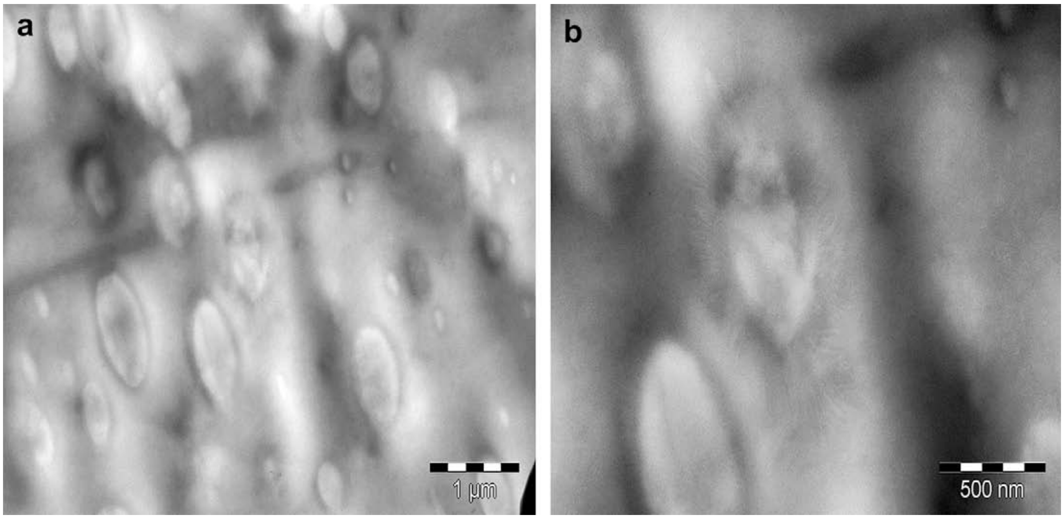

Fig. 9. Morphology by TEM of EVA/cBT100/Ti(OPh)$_4$ reactional medium synthesized from in situ cBT100 polymerization.

below (T = 120 °C) and above (T = 240 °C) the melting temperature of the PBT$_{100}$ phase (Tm = 225 °C).

At these two temperatures, the viscoelastic properties of the material is quite different as a strong increase of the storage modulus is observed at T = 120 °C compared with the modulus at T = 240 °C. The order of magnitude of this change when the PBT$_{100}$ phase is crystalline is close to 100 whereas it was observed that for virgin polymer blends [22] a slight change, exactly 1.84, according to the equation $G^*(\omega) = G^*m(\omega)((1+3/2\phi)/(1-\phi))$derived from the equation law, ($G^*{}_m(\omega)$ is the complex shear modulus on the matrix and ϕ the volume concentration of the solid phase). Actually, at temperature below the melting temperature of the PBT$_{100}$ phase, the storage modulus reaches permanent elastic properties with an equilibrium modulus close to 10^4 Pa. Above the melting temperature of the PBT$_{100}$, the material flows and one can even see a complex shear behaviour related to a branched system close to

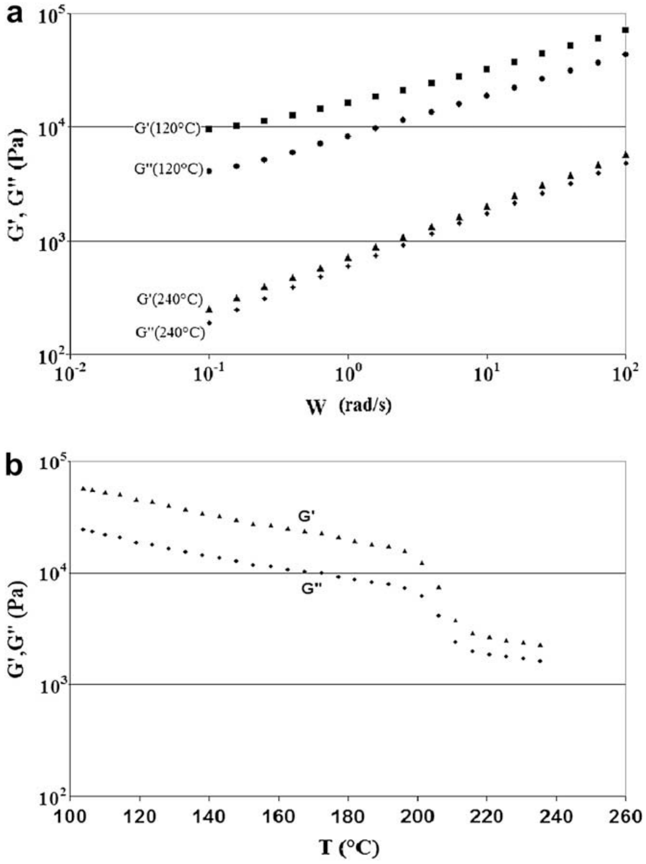

Fig. 10. Viscoelastic behaviour of the in situ EVA/cBT100/Ti(OPh)$_4$ blend. (a) Frequency dependence of the complex shear modulus at two characteristic temperatures, below (T = 120 °C) and above (T = 240 °C) the PBT$_{100}$ melting temperature (b) Temperature dependence.

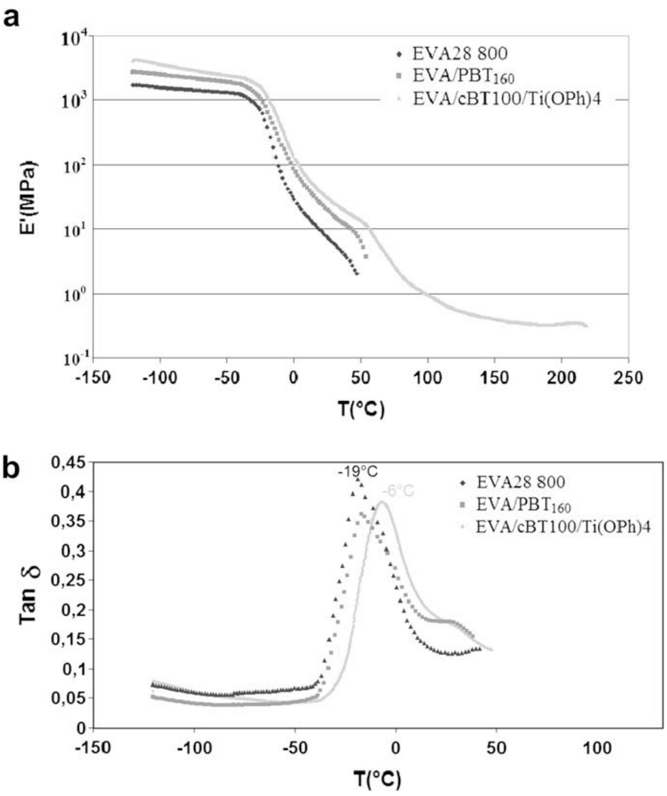

Fig. 11. DMA analysis. Samples: EVA 28 800, EVA/PBT$_{160}$ and EVA/cBT100/Ti(OPh)$_4$ a) Temperature dependence of the storage Young modulus and b) tan δ at the frequency f = 10 s^{-1}.

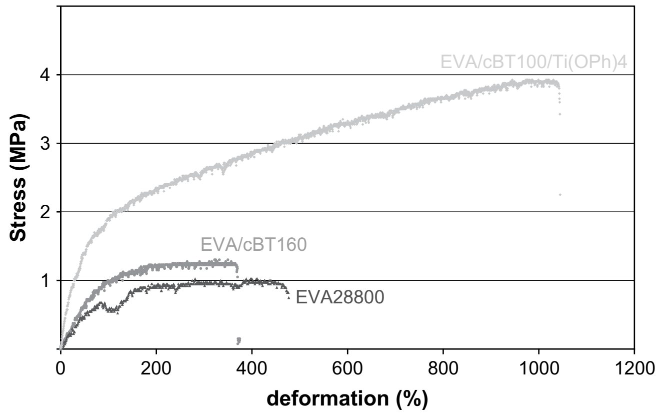

Fig. 12. Tensile properties at room temperature of EVA 28 800, EVA/PBT$_{160}$ and EVA/cBT100/Ti(OPh)$_4$ blends.

the crosslinking percolation threshold. Actually, branched and connected microstructure of EVA-g-PBT$_{100}$ copolymer can be expected from a chemistry point of view.

Furthermore, the thermomechanical properties of the different medium are depicted in Fig. 11. More precisely, Fig. 11a,b shows the temperature dependence of the storage Young modulus and tan δ, respectively. As expected from Fig. 10, storage modulus exhibits an elastic plateau modulus up the melting temperature of EVA 28 800 phase (Tm ~ 55 °C) and until the melting of the PBT$_{100}$ dispersed phase for the EVA 28 800/cBT100/Ti(OPh)$_4$ reactional medium. Note that the modulus of a typical EVA 28 800/PBT$_{160}$ reference blend cannot be assessed in such conditions as the viscoelastic behaviour is controlled by the melting behaviour of the matrix (viscoelastic behaviour of a filled system with spherical droplets). To sum up, this sub-micron phase separated blend exhibits a plateau modulus up to the melting point of the PBT$_{100}$ phase. This phenomenon, in the absence of the formation of a total nanostructured blend, can be found in the crown morphology of this kind of material due to the amount of EVA-g-PBT$_{100}$ copolymer. Furthermore, tan δ variation shows that the mechanical transition temperature associated with the glass temperature of EVA 28 800 increases from −19 °C for EVA 28 800 to −6 °C for in situ synthesized EVA 28 800/cBT100/Ti(OPh)$_4$ blend. Actually, the blend can be described as a complex ternary blend of the expected grafted copolymer forming a nano-structure interphase with the two parent non-reacted polymers.

Finally, Fig. 12 shows the tensile properties of the samples. As rigid polymer, PBT should play an important role in mechanical properties of the EVA based blends. Regarding EVA/PBT$_{160}$ reference blend, Young's modulus and tensile strength increase only slightly, compared with pure EVA 28 800. The decrease in the elongation at break is explained by the formation of two macrophases with poor cohesion in this non-compatibilized blend. On the other hand, a clear and strong improvement of the tensile properties (Young's modulus, tensile strength and elongation at break) can be observed for PBT$_{100}$ polymerized in situ in EVA 28 800/cBT100/Ti(OPh)$_4$ reactional medium (See data in Table 2). This feature can be attributed to the formation of EVA-g-PBT$_{100}$ copolymer and the formation of a nanostructure at the interphase.

Table 2
Tensile properties of different samples.

	EVA 28 800	EVA/PBT$_{160}$	EVA/cBT100/Ti(OPh)4
Young's modulus E (MPa)	0.81	1.13	3.47
Tensile strength σT (MPa)	0.95	1.25	3.92
Elongation at break A (%)	470	365	1030

4. Conclusion

The objective of the present work was to prepare EVA/PBT nanostructured blends. For that purpose, a new approach for the synthesis of EVA-g-PBT grafted copolymers was investigated by in situ polymerization of cyclic butylene terephthalate monomer cBT100 in the presence of molten EVA 28 800 and Ti(OPh)$_4$. The ring-opening polymerization of the cBT100 was initiated by titanium phenoxide Ti(OPh)$_4$. Due to the aromatic character of this titanium derivative, the transfer reaction of the living PBT chain onto the EVA 28 800 backbone is enhanced. The copolymer structure and amount was carefully accessed and then precisely characterized by NMR study. A proportion of around 11 wt% of EVA-g-PBT$_{100}$ copolymer was obtained thanks to a judicious choice of the initiator and of the component polymers.

Furthermore, the corresponding EVA 28 800/cBT100/Ti(OPh)$_4$ blend has then been characterized by a variety of complementary techniques. Results from all these techniques indicate that the mechanical and rheological properties are promising. For instance, the improvement of tensile strength properties is clearly due to copolymer formation and its tendency to segregate at the interface. The formation of such a nanostructure at the interface (crown type morphology) promotes the formation of fine and stable spherical droplet of PBT$_{100}$ with sizes ranging from 100 to 500 nm.

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