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Reactive compatibilization of blends of poly(2,6-dimethyl-1,4-phenylene ether) and poly(butylene terephthalate)

H.A.M van Aert[a,1], G.J.M. van Steenpaal[a], L. Nelissen[a,*], P.J. Lemstra[a], J. Liska[b], C. Bailly[c]

[a]*Eindhoven Polymer Laboratories, Eindhoven University of Technology, Den Dolech 2, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b]*General Electric Plastics BV, Plasticslaan 1, P.O. Box 117, 4600 AC, Bergen op Zoom, The Netherlands*
[c]*Université Catholique de Louvain, Croix du Sud 1, 1348, Louvain-la-Neuve, Belgium*

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Abstract

This paper deals with the development of a compatibilized polymer blend based on poly(2,6-dimethyl-1,4-phenylene ether) (PPE) and poly(butylene terephtalate) (PBT). Blending of PBT with PPE, with PBT as the continuous phase, could yield materials which are mutually incompatible, and the phase morphologies obtained during blending of these polymers are generally unstable. When PPE is functionalized selectively, in situ compatibilization during processing is feasible. Due to the formation of segmented copolymers, which act as compatibilizing agents, stabilization of the morphology obtained during blending is feasible. Different types of reactive PPE polymers were investigated, e.g. PPE with hydroxyalkyl, carboxylic acid, methyl ester, amino and *t*-BOC protected amino endgroups. These groups are positioned either in the middle of the chain or as the endgroup. All these reactive PPE polymers result in better compatibilization after mixing with PBT versus unfunctionalized PPE. PPEs with carboxylic acid endgroups proved to be the most efficiently compatibilized with PBT, for the PBT type employed in this study. Promoters, which catalyze or take part in the coupling between PBT and/or functionalized PPEs, such as triphenyl phosphite (TPP), sodium stearate, titanium (IV) isopropoxide and epoxy resins, were used in order to improve compatibilization of the PPE/PBT blends. The use of these promoters proved to give synergetic compatibilization in combination with functionalized PPEs.

Keywords: Poly(2,6-dimethyl-1,4-phenylene ether); Poly(butylene terephtalate); Triphenyl phosphite

1. Introduction

This paper deals with the development of a compatibilized polymer blend based on poly(2,6-dimethyl-1,4-phenylene ether) (PPE) and poly(butylene terephtalate) (PBT). PPE/PBT blends can combine advantageous/complementary properties of both polymers for structural applications. PPE is a commercially produced polymer which has good thermal, electrical and mechanical properties, dimensional stability as well as solvent resistance towards solutions of acids and hydroxides. A disadvantage of PPE is a required high processing temperature (at/above 300°C) and solvent resistance towards hydrocarbons, oils and fluids used in automotive industry.

Since these polymers are immiscible, an appropriate compatibilization is necessary to obtain suitable combination of the properties [1]. Compatibilization is based on copolymer formation during melt processing via reaction of functionalities of both polymers. This can be provided via two steps: PPE functionalization and reactive extrusion with PBT. PPE has to bear a functionality, capable to react with the endgroups of PBT (COOH, hydroxyalkyl). This can be done, e.g. by redistribution reaction of PPE with functional phenols (carboxylic, hydroxyalkyl, amino, ester) [2,3].

Generally, in situ reactive compatibilization is technologically preferred rather than the addition of a specially tailored, usually expensive copolymer. Compatibilization using added surface-active agents or the in situ generation of surface-active species is generally considered to be the determining factor to make compatible polymer blends. However, next to the chemistry involved in (reactive) compatibilization, rheological parameters are of importance in the process of dispersing polymer A into polymer B [4]. Generally, mixing of immiscible (polymer) liquids involves the deformation of a dispersed phase A in a flow field,

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[*] Corresponding author. Tel.: +31-040-2473093; fax: +31-040-2436999.

E-mail address: l.n.i.h.nelissen@tue.nl (L. Nelissen).

[1] Current address: Agfa-Gevaert N.V., Septestraat 27, B-2640 Mortsel, Belgium.

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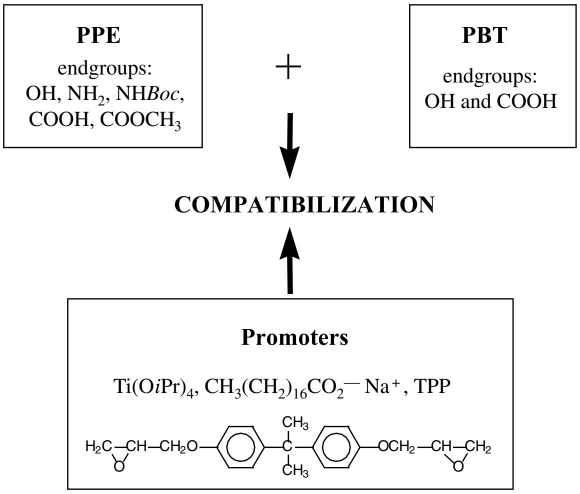


Scheme 1.

resulting in an increased interfacial surface area. In the case of polymer melts, the viscosities are relatively large (small Reynolds numbers) and the deformation of the dispersed phase A is mainly governed by the capillary number (Ca) [4], the ratio of the (deforming) shear stress τ exerted on the dispersed phase by the external flow field and the (shape conserving) interfacial stress σ/R where σ is the interfacial tension and R the local radius of the dispersed phase: $Ca = \tau R/\sigma$. Above a critical value, Ca_{crit}, the viscous shear stress overrules the interfacial stress and the dispersed phase will break up into smaller droplets. The critical capillary number depends both on the viscosity ratio, p, between dispersed and continuous phase ($p = \eta_d/\eta_c$), and the type of flow. In simple shear flow, break up of the dispersed phase is rather easy at viscosities ratios close to unity, at least for Newtonian liquids as shown by Grace [5]. In the case of viscoelastic liquids, i.e. polymer melts, the situation is more complex but, in general, to disperse a polymer A into B (the continuous phase), the viscosity of A should be preferably lower than the viscosity of B. At typical melt blending temperatures, the viscosity of PPE is much higher than that of PBT. The exact viscosity ratio is difficult to measure in this case. In this paper rheological parameters were not taken into account but the emphasis is laid upon in situ reactive compatibilization. The preliminary test for morphology stabilization via in situ compatibilization was annealing at elevated temperatures and then using electron-microscopy to study the particle size distribution. Although these annealing tests are not conclusive for phase morphology upon the further processing of the compatibilized blends, they serve the purpose of a first screening on in situ compatibilization.

Often, formation of copolymers during reactive compatibilization is reflected in a shift of the glass transition temperatures of both polymers and can be detected by techniques like differential scanning calorimetry (DSC) and dynamical mechanical thermal analysis (DMTA) [7]. DMTA is more powerful to detect glass transition temperatures especially in blends of PPE and PBT, in which the glass transition temperature (T_g) of PPE and melting point (T_m) of PBT are close together. The compatibilization can be visualized by a decrease in the T_g of the PPE phase. The use of PPEs with a higher functionality content (e.g. carboxylic acid), which have in most cases a lower molecular weight, generally yield a shift of the tan δ peak to lower temperatures. However, it is very difficult to differentiate between a shift of the T_g caused by a higher copolymer content or caused by a lower molecular weight of the functional PPE [6]. Therefore, DMTA is only indicative but not conclusive to determine the extent of compatibilization and in this report conclusions are based on electron microscopy.

Extensive studies concerning the development of compatibilizing immiscible blends of PPE and polyesters have been reported, either via addition of an interfacially-active bock copolymer [7–9] or using in situ reactive compatibilization [10–40]. However, no detailed information is published on the influence of the type of reactive group attached to the PPE chain on the in situ compatibilization of PPE/PBT blends. Because of the facile synthesis of various types of reactive PPEs as described previously [2,41,42], this study is focused on the chemistry in the reactive compatibilization. In situ compatibilization during reactive processing requires modified PPEs that show reactivity towards either the ester functionality or the carboxylic acid and hydroxyalkyl endgroups of PBT. Applying the redistribution method, as described previously [2], and the phenolic endgroups modification, PPEs with various types of endgroups can be prepared, like carboxylic acid, hydroxyalkyl, amine and methyl ester functionalities. The effectiveness of these different endgroups in reacting with PBT can then be easily investigated.

Besides the addition or formation of interfacially-active copolymers, the addition of some low molecular weight promoters, such as transesterification catalysts and chain extenders, can influence the morphology of immiscible blends [43,44]. Various transesterification catalysts [45–48] and chain extenders [49–61] are reported for polyesters. Transesterification catalysts like titanium(IV) isopropoxide (tetra-isopropyl titanate) and sodium stearate (sodium octadecanoate), and chain extenders like triphenyl phosphite (TPP) [62–68] and epoxy resins that mainly consist of the bisglycidyl ether of bisphenol acetone (DGEBA) are known as compatibilization promoters. In combinations with reactive PPE these promoters could possibly yield a synergetic compatibilization of the immiscible PPE/PBT blends (Scheme 1: (Reactive compatibilization of PPE/PBT blends)).

In this paper, we emphasize the chemistry in the reactive compatibilization of PPE/PBT blends. Therefore, this investigation may be considered as a preliminary study to obtain information on the effectiveness of various reactive PPEs and low molecular weight promoters to form interfacially-active compounds during the reactive processing (Scheme 1).

Table 1
Endgroup concentrations of PBT used

Polymer	[COOH] (μeq/g)	[OH] (μeq/g)	$\bar{M}_w$ (kg/mol) (GPC, PS equivalent)
PBT	40	20	108.5

Modified PPEs were blended with PBT in a laboratory-scale mini-extruder and the morphology of the blend obtained was mainly investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The size of dispersed phase, adhesion and stability of the blend morphology are investigated.

2. Experimental

2.1. Materials

Samples of PPE and PBT were obtained from General Electric Plastics: unmodified PPE (IV = 0.40 dl/g, $\bar{M}_w =$ 30.2 kg/mol) and PBT ($\bar{M}_w =$ 108.5 kg/mol).

Epoxy resin, Epikote 828, was obtained from Shell. TTP and titanium isopropoxide were obtained 97% pure from Aldrich. Sodium octadecanoate (sodium stearate) was obtained >98% pure from Fluka.

Hydroxypropyl-modified PPEs were prepared by endgroup modification. A hydroboration/oxidation reaction of bis(allyl)-terminated PPE telechelics yields bis(hydroxypropyl)-terminated PPE. Allyl-terminated PPE was prepared by reaction of allyl bromide with 2,6-(dimethylphenol)-terminated PPE.

All other PPEs with functional endgroups were prepared by redistribution of PPE with a functional phenol, as described previously [2]. Hydroxyethyl-modified PPE was obtained by redistribution of PPE with hydroxyethylphenol (HEP). Amino-terminated PPE was prepared by redistribution of PPE with 4-hydroxyphenylethylamine (tyramine). PPE with *t*-BOC protected amino groups was prepared by redistribution with *t*-BOC-protected tyramine. Carboxylic-acid-modified PPE was prepared by redistribution of PPE with either (4-hydroxyphenyl)propionic acid (HPPA), 4,4′-bis(4-hydroxyphenyl)pentanoic acid (BHPPA) or 4,4′-bis(3,5-dimethyl-4-hydroxyphenyl)pentanoic acid. Methyl-ester-functionalized PPE was prepared from redistribution of PPE with (4-hydroxyphenyl)propionic acid methyl ester or 4,4′-bis(3,5-dimethyl-4-hydroxyphenyl)-pentanoic acid methyl ester.

All molecular weights stated in this paper are uncorrected molecular weights related to polystyrene standard samples as determined by GPC.

2.2. Techniques

The PPE/PBT samples were microtomed on a Utrotomo Nova at room temperature, yielding coupes of approximately 100 nm. The coupes were etched 11 min in OsO_4 vapor and afterwards 11 min in RuO_4 vapor. Transmission Electron Microscopy was performed on a Philips TEM CM12. Further morphology studies were done on Au/Pd sputtered fracture surfaces using a Cambridge Stereoscan 200 SEM. Molecular weight determination of all functional PPEs was performed using a chloroform/ethanol mixture (98/2 (v/v)) as eluent at 40°C. Equipment used for the analysis was: a Waters 150-CV ALC/GPC apparatus; PL gel columns 10^3 and 10^5 Å; and a Waters 490E programmable multiwavelength detector (PPE detected at 280 nm, polystyrene standards detected at 254 nm).

2.3. Preparation of PPE/PBT blends

All blending experiments have been carried out under similar experimental conditions. PPE/PBT blends are prepared using a laboratory-scale mini-extruder, which operates continuously or batch wise. The device consists of two co-rotating, closely intermeshing, self-wiping, conical screws and is equipped with a recurrent loop and valve system. The device allows processing of small quantities of material (volume = 6 cm^3) at temperatures up to ca. 400°C in a way equivalent to large scale industrial co-rotating twin screw extruders. Consequently, this is suitable for initial experiments in blending chemically modified PPE with PBT in order to perform a reactive compatibilization. All extrusion experiments were performed at 260°C, mixing time ca. 3 min, after complete filling during 5 min.

2.4. Annealing of PPE/PBT blends

Blended PPE/PBT strands were annealed during 10 min at 260°C in a Linn Elektronik VMK39 oven, equipped with a precise temperature controller (±1°C).

3. Results and discussion

3.1. Materials selection and PPE/PBT blending

The characteristics of the PBT used are reported in Table 1. In our research, we aimed to obtain an improved crystalline-polymer-based material, combining properties of the continuous PBT phase and dispersed PPE particles. Therefore, we based our fundamental work on blends with PPE/PBT weight ratio of 40:60, which proved to yield dispersed PPE particles in a continuous PBT matrix for the PBT investigated.

The blending experiments were performed on small-scale extrusion under the same experimental conditions. To obtain a stable compatibilized morphology, even after annealing, a blending time of at least a few minutes is required. Longer blending times do not cause a large change in morphology. The presence and type of reactive endgroup as has much larger influence on the morphology, as compared to the extrusion conditions. When the extrusion experiments are performed reproducible morphologies are obtained. Of course, when extrusion experiments are performed on a larger scale the minimal blending time should be optimized again and are not equivalent with industrial experiments, but this was not the aim of our fundamental work. Nevertheless, the small scale blending experiments give already an indication which tools can be used to control the morphology in PPE/PBT blends.

The annealing process has significant influence on the morphology, in particular when unmodified polyphenylene ethers are used. In case of reactive PPEs, blockcopolymer structures are in situ formed during blending with the PBT. These blockcopolymer structures stabilize the morphology in an annealing process.

The molecular weights of all employed PPEs were measured by GPC. The molar masses are relevant in particular for the reactive PPEs, while the concentration of the reactive endgroups is directly linked to the polymer molecular weight. Furthermore, in this study we did not use large deviations in molecular weight while this influences the miscibility of the blend obtained.

3.2. Blends of PBT and carboxylic-acid-modified PPE

It should be noted that PPEs are modified by reacting a functional phenol in a redistribution reaction using tetramethyldiphenoquinone (TMDPQ) as oxidant, consist of a mixture of functionalized and unfunctionalized homopolymer [2,41,42]. This is a direct result of incorporation of both the functional phenol and 3,3′,5,5′-tetramethylbiphenyl-4,4′-diol, which is formed from TMDPQ. Therefore, when we describe a redistribution-modified PPE we always will encounter the functionality content, expressed in wt% functional phenol attached to the PPE [2,42]. The functionality content can be adjusted by varying the amount of the reacting phenol and reaction conditions. These modified PPEs can be obtained on a large lab-scale using a fast redistribution reaction catalyzed by TMDPQ.

Several types of carboxylic acid endgroups, capable of reacting with polyesters, are incorporated as a tail-end as illustrated in Scheme 2 (Carboxylic-acid-modified PPEs prepared by redistribution using: A — (4-hydroxyphenyl)-propionic acid (HPPA); B — bis(4-hydroxyphenyl)pentanoic acid (BHPPA); and C — bis(3,5-dimethyl-4-hydroxyphenyl)pentanoic acid (BDMHPPA)). We employed three different carboxylic-acid-modified PPEs in the reactive compatibilization experiments. All types were prepared using the PPE-redistribution method [2] by reacting the following phenols: (4-hydroxyphenyl)propionic acid (HPPA), 4,4′-bis(4-hydroxyphenyl)pentanoic acid (BHPPA) and 4,4′-bis(3,5-dimethyl-4-hydroxyphenyl)pentanoic acid (BDMHPPA). The first two phenols are incorporated as endgroup, while the last *ortho*-methyl substituted bisphenol is predominantly incorporated in the center of the PPE chain. In general, when *ortho*-methyl substituted functional bisphenols are reacted, a redistribution reaction occurs at both sides of the bisphenol-yielding telechelics with the functional group in the middle of the polymer chain. These functional tetramethylbisphenol-modified PPEs yield graft copolymers upon reaction with PBT. The carboxylic acid functionalities are proposed to react with the hydroxyalkyl endgroups of the PBT in an esterification and/or with the main-chain ester units of the PBT in a transesterification reaction.

Differences between compatibilized (stabilized blend morphologies) with non-compatibilized (unstabilized) morphologies using electron microscopy are shown in Figs. 1 and 2. In these figures the SEM and TEM pictures of PPE/PBT-1 samples with unmodified PPE (Figs. 1A, 2A and B) and bis(hydroxyphenyl)pentanoic acid (BHPPA)-modified PPEs (Scheme 2B; Fig. 2C and D) are compared.

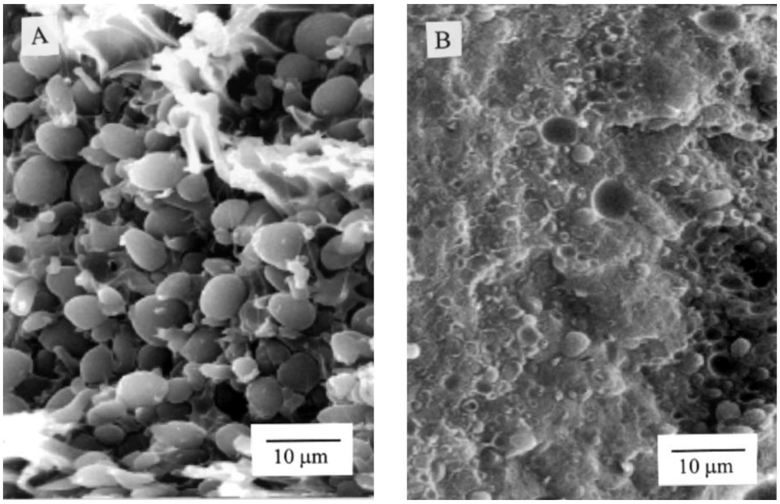


Fig. 1. Scanning Electron Microscopy (SEM) pictures of PPE/PBT-1 blends in a 40/60 weight ratio. (A) SEM picture of blend with unmodified PPE (IV = 0.4 dl/g, $\bar{M}_w = 46.3$ kg/mol). (B) SEM picture of blend with bis(hydroxyphenyl)pentanoic acid (BHPPA)-modified PPE (functionality content 1.09 wt% BHPPA, $\bar{M}_w = 12.95$ kg/mol).

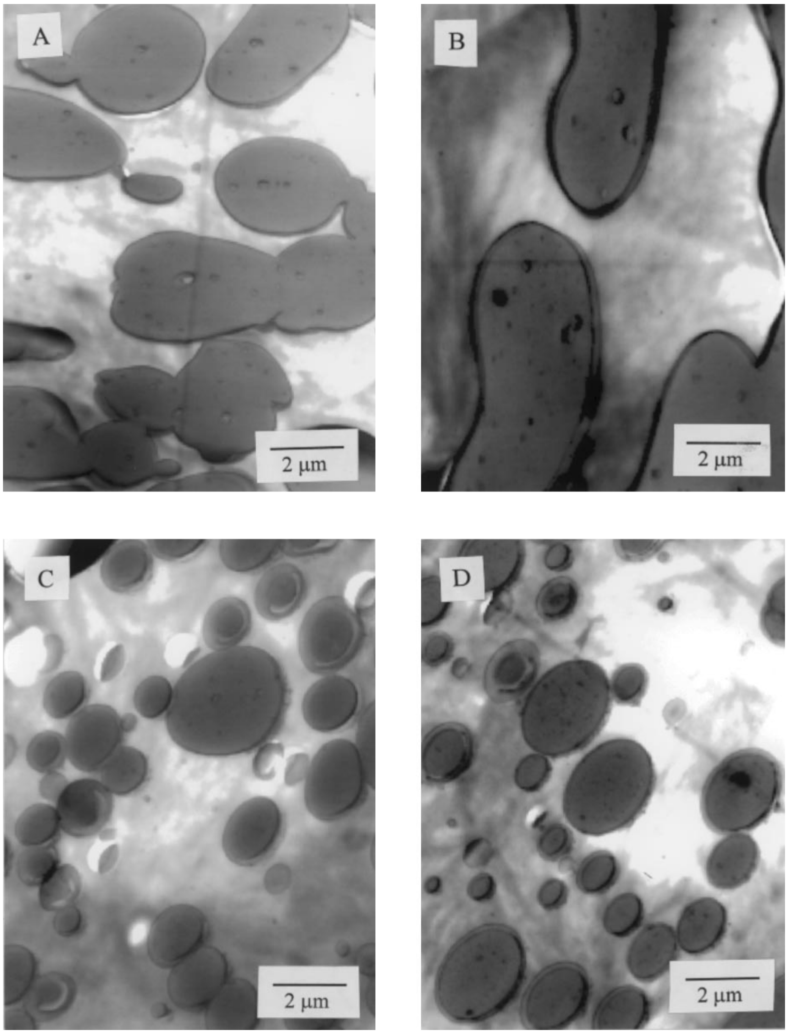


Fig. 2. Transmission Electron microscopy pictures of blends with PPE/PBT-1 weight ratio 40/60 with unmodified PPE (IV = 0.4 dl/g, $\bar{M}_w = 46.3$ kg/mol) or bis(hydroxyphenyl)pentanoic acid (BHPPA)-modified PPE (functionality content 1.09 wt% BHPPA, $\bar{M}_w = 12.95$ kg/mol). (A) TEM picture of blend with unmodified PPE before annealing. (B) TEM picture of blend with unmodified PPE after annealing. (C) TEM picture of blend with modified PPE before annealing. (D) TEM picture of blend with modified PPE after annealing.

Adhesion of the dispersed PPE particles with the continuous PBT phase can be indicated by means of using SEM. The authors are aware of the fact that with SEM no quantitative level of adhesion can be determined. The PPE/PBT blend with unmodified PPE shows large PPE particles in a continuous PBT matrix and no significant adhesion is observed, while the PPE/PBT blend with BHPPA-modified PPE (Scheme 2B) shows a better adhesion.

The SEM picture of the blend with modified PPE shows a more compatible phase morphology (Fig. 1B). SEM pictures of cryogenic fracture surfaces give a qualitative indication of the compatibilization. We will consider different regimes of compatibilization: (a) indicated with " − " having no or bad adhesion; (b) indicated with " ± " having a moderate adhesion and partially disrupted PPE particles; (c) indicated with " + " having good adhesion and strongly disrupted PPE particles; (d) indicated with "++" having excellent adhesion and fully disrupted and fractured PPE particles.

Table 2
Influence of BHPPA functionality content on PPE particle size and adhesion in blends of BHPPA-modified PPEs (Scheme 2B) (40 wt%) with PBT (60 wt%)

Functionality content wt% BHPPA	PPE $\bar{M}_w$ (kg/mol)	PPE particle size (μm) before annealing TEM	PPE particle size (μm) before annealing SEM	PPE particle size (μm) after annealing TEM	Adhesion before annealing SEM
1.09	12.95	2	3	2	±
2.71	15.21	2	3	3	++

Table 3
Influence of HPPA functionality content (Scheme 2A) on PPE particle size and adhesion in blends of HPPA-modified PPEs (40 wt%) with PBT (60 wt%)

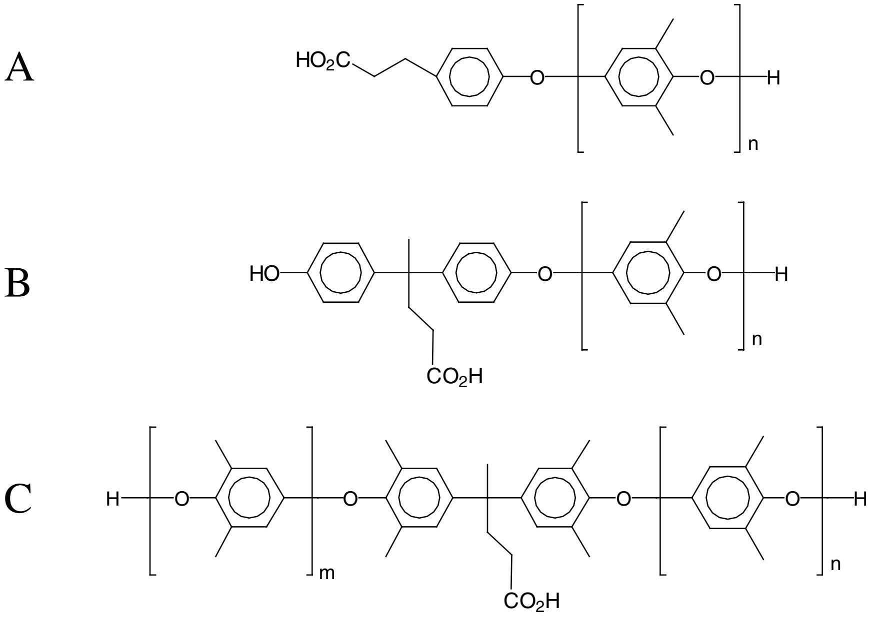
Functionality content wt% HPPA	PPE $\bar{M}_w$ (kg/mol)	PPE particle size (μm) before annealing TEM	PPE particle size (μm) before annealing SEM	PPE particle size (μm) after annealing TEM	Adhesion before annealing SEM
1.31	18.82	1	2	> 25	−
1.84	14.18	2	2	4	++
1.87	14.56	0.5	1	2	++
2.66	13.66	1	1	2	++

The initial particle size can be partially ascribed to a difference in viscosity between unmodified and functionalized PPE. Only adhesion and annealing are really conclusive. For successful compatibilization the obtained morphology should be stable upon annealing and after subsequent processing. In this paper, as mentioned in the introduction only annealing experiments were performed to test qualitatively the effectiveness of in situ compatibilization as a function of PPE-functionality type and content. This can be determined by SEM, but is more clear from TEM analyses. Fig. 2A–D shows the TEM micrographs before and after annealing for unmodified (Fig. 2A and B) and bis(hydroxyphenyl)pentanoic acid (BHPPA)-modified PPE (Scheme 2B; Fig. 2C and D).

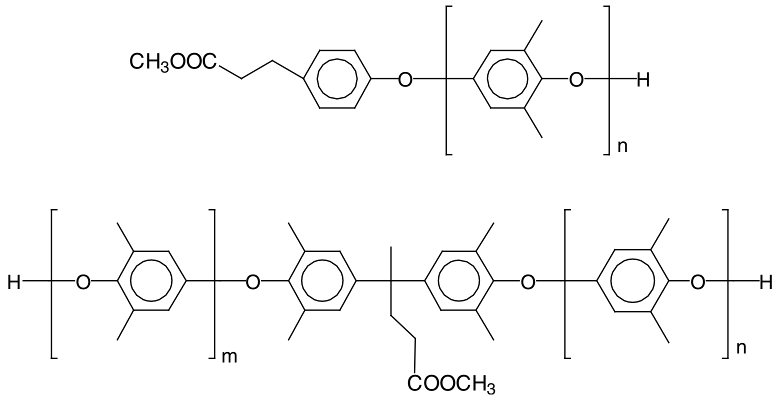
While the PPE particles in blends with unmodified PPE grow macroscopically due to coalescence (Fig. 2A and B), the morphology is stable in the PPE/PBT blends with the carboxylic-acid-modified PPE (Fig. 2C and D). Morphology stability testing by annealing (at 260°C, 10 min), above the melting temperature of PBT (ca. 225°C) can be considered as a screening test to determine whether compatibilization is successful.

As shown in Fig. 2, blends of BHPPA-modified PPEs (Scheme 2B) and PBT show finely dispersed PPE particles which are stable upon annealing (Fig. 2D). When studying blends containing PPEs with different BHPPA content, the TEM pictures did not show large differences, although SEM pictures show better adhesion for blends containing PPEs with higher functionality content (Table 2). The addition of compatibilization promoter TPP decreases the particle size of the PPE dispersed phase approximately by a factor two.

A larger effect of functionality content on the extent of the compatibilization is found when propionic-acid-modified (HPPA-modified) PPEs (Scheme 2A) are used instead of BHPPA-modified PPEs. In Table 3 the dependence of the obtained morphology and stability on functionalization content is demonstrated for HPPA-modified PPE. In all cases a stable morphology was obtained after annealing, except for the lowest functionalization content. When using the epoxy resin (2 wt%) as co-reactant, morphology, adhesion and morphology stability improve a great deal because of faster reaction of carboxylic acid endgroups with epoxy, epoxy mobility and probable reaction of epoxy with carboxylic acid groups of both components. Coupling reactions are favored, because typically a small excess of carboxylic acid is used. When the epoxy resin only



Scheme 2.

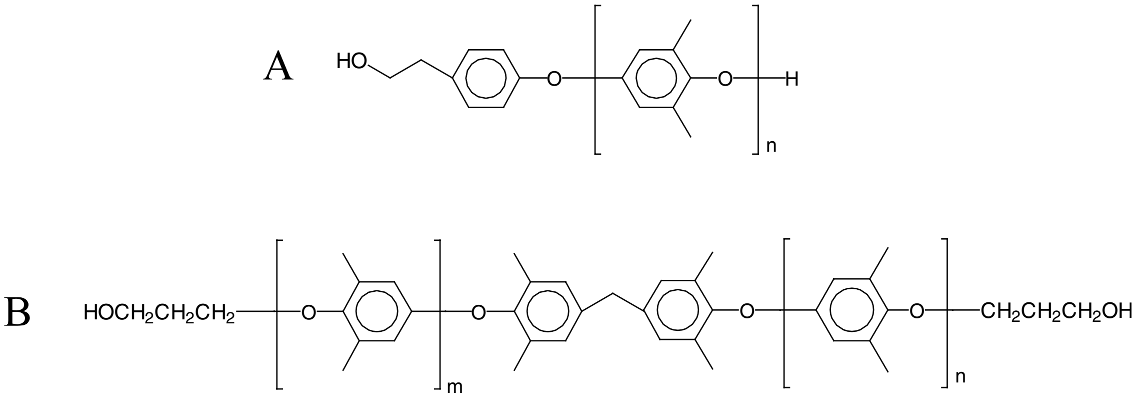


Scheme 3.

reacts with the PBT endgroups and not with the carboxylic acid endgroups of the PPE chain, extension of the PBT occurs, resulting in increasing the relative viscosity of the PBT phase. This increase in relative viscosity could also have a positive effect on the blend dispersion and stability. Similarly to epoxy resins, phenoxy resins have been reported as effective compatibilizing agents for PPE/polyester blends [69]. Phenoxy resins are polyhydroxyethers obtained by condensation of bisphenol acetone and epichlorohydrin leading to polymers with a higher molecular weight than similar epoxy resins. The higher mobility of epoxy resins in comparison with phenoxy resins benefits their use as compatibilization promoters.

When PPE modified with the tetramethyl derivative of BHPPA (bis(3,5-dimethyl-4-hydroxyphenyl)-pentanoic acid) (BDMHPPA) (Scheme 2C) is used in the reactive compatibilization experiments, small particle size and a moderate adhesion are obtained, although the morphology is very unstable after annealing compared to the PPEs modified with the non-methylated carboxylic acid functional phenols. In this case, the initial smaller particle size might be entirely due to the lower viscosity of the PPE, with no interfacial reaction. Furthermore, there are two basic differences. First, methylated bisphenols are incorporated in the middle of the PPE chain (Scheme 2C), resulting in graft copolymers, in contrast to non-methylated PPE-derivatives (Scheme 2A and B) which yield block copolymers after reaction with PBT. The second difference as regard to reactivity could be steric hindrance of the carboxylic acid group in the tetramethylated derivatives, which might prohibit copolymer formation. This is proposed to be the main reason for the poor compatibilization found in case of the tetramethylated PPE-derivatives (Scheme 2C). The effect of the shape (block or graft) of the formed interfacially active copolymer on the compatibilization is not clear from this experiment because a blend of PBT with BDMHPPA-modified PPE (Scheme 2C) might form less copolymer during reactive extrusion.

Upon comparing carboxylic acid derivatives of PPE (HPPA-, BHPPA- and BDMHPPA-modified PPEs) steric hindrance appears to have a large effect on copolymer formation and compatibilization. The most freely moving and unhindered carboxylic acids in the HPPA-modified PPEs (Scheme 2A) and BHPPA-modified PPEs (Scheme 2B) give the best compatibilization results. Poor compatibilization is achieved using the tetramethylated derivative of the carboxylic-acid-modified PPE (BDMHPPA-modified PPE) (Scheme 2C), which in addition to the steric hindrance of carboxylic acid group provides graft copolymer instead of block copolymer. In this case the functionality located in the middle of the chain is less mobile and its appearance at the surface of a polymer coil is less probable.



Scheme 4.

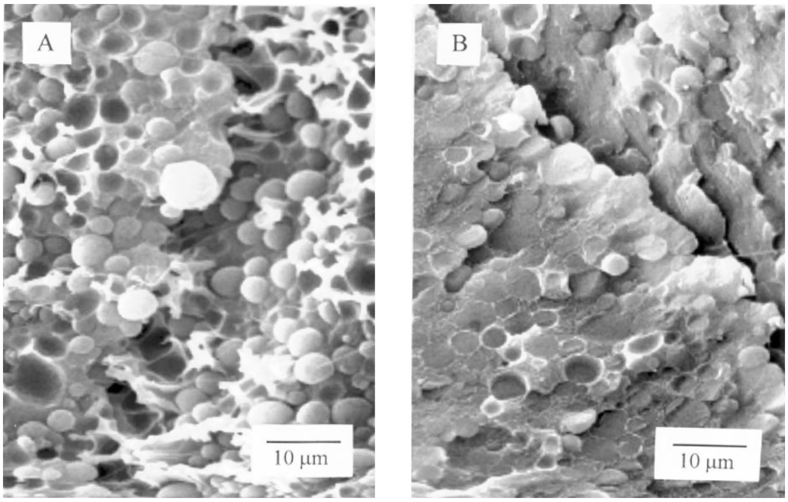


Fig. 3. SEM pictures of blends containing 40 wt% bis(hydroxypropyl)-modified PPE (Scheme 4B) and 60 wt% PBT. (A) Without promoter. (B) With 6.5 wt% sodium stearate.

3.3. Blends of PBT and methyl ester-modified PPE

Two types of methyl-ester-modified PPEs are used for in situ compatibilization of PPE/PBT blends, as shown in Scheme 3 (Methyl-ester-modified PPEs), both prepared using PPE redistribution [2].

Methyl-ester-modified PPEs, blended with PBT, show in general a coarse morphology and possess a poor adhesion and annealing stability, in comparison with the carboxylic-acid-modified PPEs, especially for the PPEs modified with the methyl ester of bis(3,5-dimethyl-4-hydroxyphenyl)pentanoic acid. These results are related with their lower reactivity towards the hydroxyalkyl endgroups and/or the main-chain ester groups of PBT. Transesterification, which occurs using methyl-ester-modified PPE, is proposed to give slower reaction rates than esterification, which occurs in the case of the reactive blending PBT with carboxylic-acid-modified PPEs.

3.4. Blends of PBT and hydroxyalkyl-modified PPE

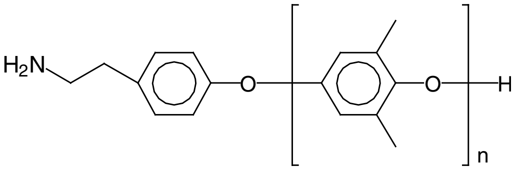
We employed two different hydroxyalkyl-modified PPEs, i.e. hydroxyethylphenol (HEP)-modified PPE prepared by redistribution [2] (Scheme 4A (Hydroxyalkyl-modified PPEs. (A) Prepared from PPE redistribution with hydroxyethylphenol. (B) Prepared via modification of phenolic endgroups)) and PPE telechelics functionalized with hydroxypropyl (propanol) functionalities prepared via modification of the phenolic endgroups [42] (Scheme 4B). These hydroxyalkyl-modified are proposed to react with the carboxylic acid endgroups and/or main-chain ester units of PBT.

The morphology after extrusion using 1.85 wt% hydroxyethylphenol (HEP)-modified PPE (Scheme 4A) or 1.96 wt% HEP-modified PPE with similar molecular weight ($\bar{M}_w = 20$ kg/mol) is comparable (TEM, dispersed PPE particles 1–3 μm). In both cases the morphology, adhesion and morphology stability are substantially better than for an unmodified PPE/PBT blend.

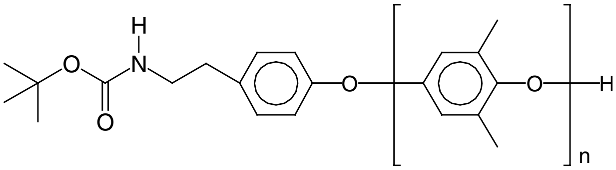
The influence of promoters is illustrated by the example of PPE telechelics functionalized with hydroxypropyl (propanol) functionalities (Scheme 4B). The most illustrative are SEM pictures after extrusion. Adhesion improvement is clear when using a catalyst to promote esterification reactions between the hydroxypropyl functionality of PPE and the carboxylic acid endgroups of PBT. Sodium stearate is more efficient than titanium isopropoxide. Chain extension agent TPP) did not improve adhesion. These examples confirm the dominant effect of reactivity on compatibilization. Fig. 3A and B shows the difference of a moderate and good adhesion in blends of hydroxypropyl-modified PPEs and PBT obtained subsequently for a blend without promoter (Fig. 3A) and with addition of 6.5 wt% sodium stearate (Fig. 3B) (modified PPE: $M_w = 39.1$ kg/mol).

3.5. Blends of PBT and amino-terminated PPE

The amino-terminated PPE, shown in Scheme 5



Scheme 5.



Scheme 6.

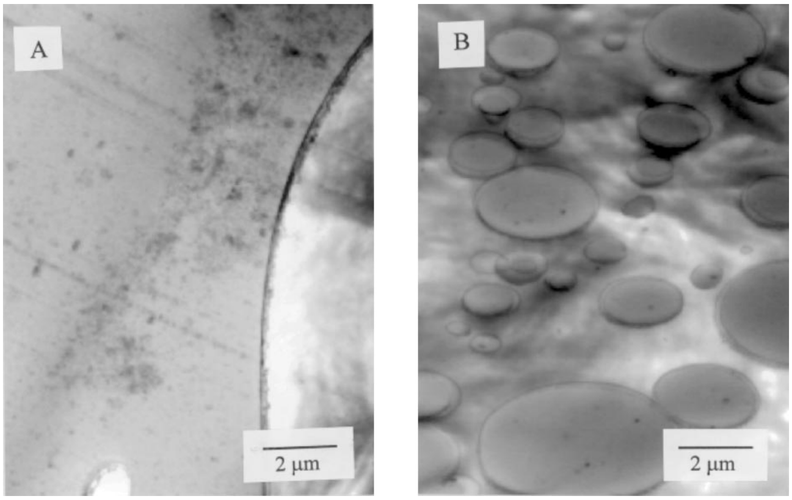


Fig. 4. TEM pictures of annealed blends of 40 wt% *t*-BOC-tyramine-functionalized PPE ($\bar{M}_w = 12.99$ kg/mol, functionality content = 3.52 wt% *t*-BOC-tyramine) and 60 wt% PBT. (A) Without Ti(*i*-OPr)$_4$. (B) With 0.7 wt% Ti(*i*-OPr)$_4$.

(Amino-terminated PPE) was obtained by redistribution of PPE with aminoethylphenol (tyramine) [2]. Amino endgroups could react with the carboxylic acids endgroups in amidation reaction and/or with the main-chain ester units of PBT.

The influence of functionality content is illustrated with the use of amino-terminated PPEs in Table 4. A finer morphology of PPE dispersed particles in a PBT matrix is observed for amino-functionalized PPEs with higher functionality content after reactive blending. The blended sample with modified PPE containing 1.74 wt% aminoethylphenol result in the finest morphology, which was stable after annealing.

When 3 wt% TPP is added to a blend of amino-modified PPE and PBT, small PPE particle sizes (2 μm) are obtained, which even become smaller after annealing (1 μm) (amino-terminated PPE: $\bar{M}_w = 21.87$ kg/mol, functionality content = 0.77 wt% aminoethylphenol). Without the addition of TPP, no stable morphology is obtained after annealing. This suggests that besides the reaction of hydroxyl endgroups of PBT also the amino endgroups of PPE react as a nucleophile with TPP, yielding a phosphoramidite (–NH–P(OPh)$_2$) [62,63]. Subsequent reaction of a carboxylic acid endgroup of PBT with a phosphoramidite (derived from TPP and amino-functional PPE) yields a PPE–PBT copolymer with an amide linkage. While the reaction of a carboxylic acid endgroup of PBT with a modified phosphite (–CH$_2$–O–P(OPh)$_2$) (derived from reaction of TPP and a hydroxybutyl endgroup of PBT) yields subsequently an extended PBT [62,63]. The coupling of PPE terminated with a phosphoramidite endgroup with carboxylic acid-terminated PBT presumably occurs faster than a traditional amidation reaction of amino-terminated PPE with carboxylic-acid-terminated PBT. Next to the chemistry, which occurs when TPP is used as promoter, not only copolymer formation can be enhanced but also the molecular weight (relative viscosity) of PBT can increase. A higher relative viscosity of this in situ chain-extended PBT will enhance fine dispersion of the PPE particles in the continuous PBT matrix. The resulting larger interfacial area will promote reaction between the PBT and modified PPE as well.

3.6. Blends of PBT and t-BOC-protected amino-functionalized PPE

Besides the amino-terminated PPEs prepared from redistribution [2] with 4-hydroxyphenyl-ethylamine (tyramine), we studied similar PPEs in which the amino group was protected with a *tert*-butoxycarbonyl (*t*-BOC) group [2] (Scheme 6 (*t*-BOC-protected amino-functionalized PPE)).

The *tert*-butoxycarbonyl (*t*-BOC)-protected amine-modified PPEs can yield the free amine after thermal decomposition. Upon reaction of this modified PPE with PBT, the

Table 4
Influence of functionality content in amino-functional PPEs on particle size and adhesion in PPE/PBT blends

Functionality content (wt% aminoethyl phenol)	PPE $\bar{M}_w$ (kg/mol)	PPE particle size (μm) SEM	Adhesion SEM
1.74	18.22	2	++
1.25	22.25	4	+
0.77	21.87	5	+
< 0.5	19.82	10	−

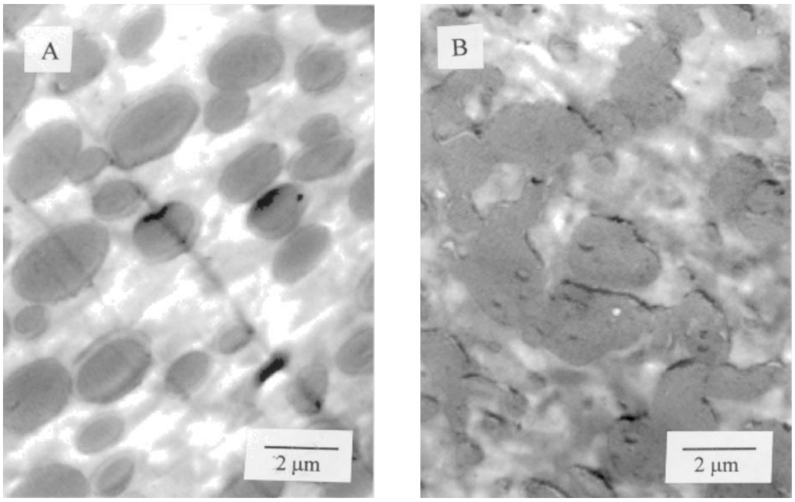


Fig. 5. TEM pictures of PPE/PBT blends, weight ratio PPE/PBT = 40/60, either with amino endgroups (functionality content: 1.74 wt% tyramine) or with hydroxyethyl endgroups (functionality content: 1.96 wt% 4-hydroxyethylphenol), both polymers $\bar{M}_w = 18.2$ kg/mol. (A) Blend with amino-terminated PPE after extrusion. (B) Blend with hydroxy-ethyl-functionalized PPE after extrusion.

t-BOC groups need to be deprotected first. Decomposition yields carbon dioxide, isobutene and free amine. When we studied this *t*-BOC-tyramine-functionalized PPE in reactive compatibilization, the influence of the functionality content is reflected, although not as strong when using PPEs with free amino-groups. This is reflected also in the stability of the PPE/PBT blend, which is not stable after annealing. Comparing tyramine versus *t*-BOC-tyramine-functionalized PPEs of the same functionality content (1.7 wt%) results in a stable morphology of the first one, and unstable morphology of the latter. Unstable morphologies were obtained using the *t*-BOC-tyramine-modified PPEs, even when using PPEs with a functionality content of 3.52 wt% *t*-BOC-protected tyramine (Fig. 4A). When titanium(IV) isopropoxide is added as compatibilization promoter, a fine morphology is obtained which is stable after annealing (Table 5) as shown in Fig. 4B. The titanium catalyst probably promotes both *t*-BOC-decomposition, as well as subsequent amidation.

3.7. Type of reaction, esterification versus amidation

The influence of the type of reaction is most clear when different reactive PPEs are used with comparable molecular weight in the PPE/PBT blends (Fig. 5). For example, we extruded PBT with differently functionalized PPE having comparable molecular weights ($\bar{M}_w = 18.2$ kg/mol), in one case with amino endgroups derived from tyramine, and in a second case with 2-hydroxyethyl endgroups derived from 4-hydroxyethylphenol. Both can react with the carboxylic acid endgroups and/or with the ester main-chain units of PBT. Finer and more stable morphology is shown for the blend with the tyramine-modified PPE, despite of the lower functionality content (Fig. 5A). This means that amidation is more efficient than esterification for these two comparable polymers. When instead of a hydroxyalkyl-modified PPE, a carboxylic-acid-modified PPE is reacted with PBT, esterification might be more efficient than amidation, e.g. in the case of HPPA-modified PPEs.

4. Conclusions

Reactive compatibilization of blends of functionalized PPE and PBT can result in fine and stable morphologies. The outcome of these investigations revealed that several factors influence compatibilization of the PPE/PBT blends: type and concentration of functionality on PPE, molecular weight of the polymers and the presence of a catalyst or chain extension agent. The overall conclusions of the study are as follows: morphology, morphology stability and adhesion of the blend is improved by — PPE functionalization

Table 5
Compatibilization of blends of 40 wt% *t*-BOC-tyramine-modified PPE and 60 wt% PBT

Functionality content wt% *t*-BOC-tyramine	PPE $\bar{M}_w$ (kg/mol)	wt% Ti(i-OPr)$_4$	PPE particle size (μm) SEM	Adhesion SEM
1.72	18.96	0	4	±
3.52	12.99	0	2.5	+
3.52	12.99	0.7	1	++

in general, and using accelerators, in particular epoxy resins or triphenyl phosphite. In general, the effectiveness of the type of functionality attached to the PPE chain on the compatibilization decreases in the following order: carboxylic acid > amino > hydroxy alkyl ≈ *t*-BOC protected amino > methyl ester. The preliminary results from the small scale extrusion experiments clearly demonstrate the feasibility of PPE/PBT blend compatibilization via copolymer formation between PBT endgroups and functionalized PPE.

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