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INTERFACIAL CHEMISTRY AND MORPHOLOGY OF BLENDS OF POLYBUTYLENETEREPHTHALATE AND EPOXIDE-CONTAINING RUBBER

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Abstract

Of the various ways in which polybutyleneterephthalate (PBT) can be toughened, the addition of epoxide-containing rubbers is one of the most effective. The interfacial chemistry (dissolution and fractionation experiments) and morphology (transmission electron microscopy) development in blends of PBT with ethylene-(methyl acrylate)-(glycidyl methacrylate) rubber (E-MA-GMA) has been studied as a function of the mixing time for batch kneaders and of the length along the axis of a co-rotating twin-screw extruder. First, a physics-controlled mixing regime occurs with a very fast dispersion of the rubber to the μm level. Subsequently, a chemistry-controlled regime occurs, where the interfacial area is covered with PBT/E-MA-GMA graft copolymer, which prevents coalescence and, thus, results in further refinement of the morphology to sub-μm level. The occurrence of cross-linking of the rubber phase in some cases limits optimum blend dispersion.

Introduction

The main reasons for the commercial success of PBT as engineering plastic is its high strength and stiffness, its high heat resistance and its good processability in combination with its relatively low costs [1]. An advantage over polyamides (PA) is the low water adsorption and the correspondingly good dimensional stability. This makes PBT highly suitable for electronic and automotive applications. However, PBT is sensitive to hydrolysis and brittle when subjected to impact conditions at or below ambient temperatures. To improve the impact resistance, PBT is often compounded with glass fibers or rubber. In practice, about 10 to 20 wt.% of a finely dispersed (≤ 1μm) rubber phase is required to ensure rubber toughening [2,3]. Pre-synthesised core-shell rubbers may be used for toughening of PBT, such as ABS or acrylate core-shell rubbers. Alternatively, compatible blends may be produced via reactive blending (in-situ compatibilisation [4,5]) of PBT with elastomers containing epoxides [6-9], cyclic anhydrides [10] or oxazolines [11].

Blends of PBT and epoxide-containing elastomers, such as E-MA-GMA, have found commercial application. In a previous study we have identified the chemical structures formed upon reaction of PBT with E-MA-GMA using low-molecular-weight model systems [12]. Reaction of a PBT carboxylic acid end group (PBT-COOH) with a rubber epoxide group results in epoxide ring opening, yielding an ester linkage between PBT and rubber chains (Figure 1: top, first reaction). Although it is known that alcohols can also react with epoxides, the reaction between PBT hydroxyl end groups (PBT-OH) and the rubber epoxide hardly occurs at temperatures ≤ 250 °C. From other studies there is some evidence that PBT-OH can react with acrylate rubbers via trans-esterification (Figure 1: bottom), but at more elevated temperatures [13]. In addition to formation of a PBT/rubber graft copolymer, also cross-linking of the rubber phase occurs. This is probably due to ring opening polymerisation of the pendent epoxide groups, initiated by the secondary hydroxyl present in the PBT/rubber graft structure (Figure 1: top, second reaction). Using atomic force microscopy it was shown that in PBT/E-MA-GMA blends the cross-linking of the rubber phase is initiated at the interface and proceeds towards the center of the rubber particle [14]. In blends of PBT with acid-modified E-MA-GMA, which already contains secondary hydroxyl groups, cross-linking occurs homogeneously throughout the rubber particle.

In this paper we present a study on blends of PBT with E-MA-GMA with emphasis on the interplay between chemistry, i.e. graft copolymer formation and rubber phase cross-linking on the hand, and morphology development, i.e. particle size, on the other hand. Blends have been prepared on a batch kneader, studying the physico-chemical phenomena as a function of mixing time, as well as on an extruder, studying the same phenomena along the screw axis using recently developed sampling devices [15]. Finally, the results are combined and a general description of the production of in-situ compatibilised PBT/E-MA-GMA blends is presented.

Experimental

Various PBT grades were supplied by DSM. The acid and hydroxyl chain end concentrations and the number-averaged molecular weights are given in Table 1. Prior to processing PBT was dried for one night at 125 °C under vacuum. Different E-MA-GMA grades were purchased from Elf-Atochem Co. The chemical composition and the melt flow index are given in Table 2. Despite a small difference in composition it was shown that the non-reactive E-MA is fully miscible with E-MA-GMA. Modified E-MA-GMA was synthesised in the melt by mixing E-MA-GMA (8 wt.% GMA) with para-t-butylbenzoic acid according to a procedure described elsewhere [12].

(80/20; w/w) blends of PBT with (modified) E-MA(-GMA) were prepared at 250 °C using a Brabender WE 50H internal mixer purched with nitrogen. The PBT pellets were first melted for 1 min. at 30 rpm. After introduction of the rubber powder, the rotation speed was increased to 90 rpm. Zero time was taken when all rubber was introduced. At different times samples were withdrawn from the mixing cavity and quenched in liquid nitrogen in order to stop interfacial reactions and freeze in the morphology.

In a second series of experiments PBT/rubber blends were produced on a modular Leistritz LSM 30.34 intermeshing, co-rotating twin-screw extruder. The temperature was set at 280 °C and the throughput was 6 kg/h. The screw speed was varied between 50 and 250 rpm, resulting in a variation of the total residence time between 195 and 97 sec. Samples were collected along the screw axis using a series of sampling devices mounted on the extruder at locations where high pressure is developed, allowing easy removal of the samples from the barrel [15]. About 2 gram of melt sample can be collected in about 3 and 5 seconds after which it is quenched with liquid nitrogen for further analysis.

A Molau test - simple but informative - is carried out by dissolving a blend in trifluoroacetic acid under stirring and then letting the mixture stand for 2 days. A stable, milky suspension indicates sufficient compatibilisation, whereas a white skin layer at the top of the solution indicates the absence of compatibilisation or macroscopic cross-linking of the blend. Elaborate fractionation schemes have been developed and validated to determine the amount of free PBT and free rubber [12]. The blend morphology is determined using transmission electron microscopy (TEM) with a Philips EM301 microscope on 90 nm cryo-coupes after staining with RuO_4 for 6 min. The particle size (distribution) is determined using image analysis software developed at the U.S. National Institute of Health. The interfacial graft copolymer density (1/A) is calculated using the expression derived by Paul and Newman [16] assuming that the molecular weight of the grafted PBT is equal to that of the original PBT.

Results and discussion

Although in this paper only blend morphology data are presented, the interpretation is supported by the fractionation data. In figure 2 some results are given for the PBT blends produced on the batch kneader. The average particle sizes are as low as 0.1 μm, the PBT graft contents are up to 30 wt.%, the epoxide conversion is far from complete and there is substantial cross-linking. The results obtained for the twin-screw extruder blends (figure 3) are similar, i.e. the particle size is as low as 0.1 μm, but the chemical conversion is less, i.e. PBT graft contents up to 15 wt.% only. Visual inspection indicates that the PBT has already been completely melted at the location of the second sampling device at L/D = 9. TEM shows that at this position a μm level dispersion of rubber in PBT is already obtained, which is further refined along the screw axis, but reaches plateau values at L/D~15. In all blends the rubber is the minor phase (20 wt.%) and thus the dispersed phase in agreement with previous studies [17]. PBT occlusions in the rubber dispersion are not observed. For blends with E-MA always smooth spherical particles are observed. For blends with E-MA-GMA smaller particles with less regular shape and interface are observed, suggesting cross-linking during blending.

Based on these results a general description for the production of PBT/E-MA-GMA blends can be drawn. Two different regimes can be distinguished during PBT/E-MA-GMA blending, the first being physics-controlled and the second being chemistry-controlled. In the first regime a very fast dispersion of E-MA-GMA rubber in the PBT matrix to μm level occurs, which is similar to the morphology development in blends of non-reactive polymers. The latter blends have been studied quite extensively [2,3] and it has been shown that the final blend morphology is the result of a dynamic equilibrium between particle break-up, leading to a more refined dispersion, and coalescence, leading to a coarser morphology. Particle break-up is determined by the interfacial tension (σ_{12}), the matrix phase viscosity (η_m), the shear rate ($d\gamma/dt$) and the critical Weber number ($W_{e,c}$). Coalescence is determined by the interfacial tension, the probability of coalescence after collision (α), the volume fraction of the dispersed phase (Φ), the matrix viscosity and the slope of the frequency of particle break-up versus the Weber number at $W_{e,c}$ (f). In a semi-quantitative approach the equilibrium particle diameter (d_p) is given by the equation derived by Fortelny et al. [18]:

$$d_p = \sigma_{12} W_{e,c}/\eta m(d\gamma/dt) + \sigma_{12}\alpha\Phi/\eta_m f \qquad (I)$$

Therefore, increasing the PBT matrix molecular weight (= viscosity) or increasing the screw rotation speed result in decreasing rubber particle size. In this physics-controlled regime, i.e. for batch mixing times smaller then 30 sec., the Molau tests yielded unstable emulsions, indicating that the rubber is finely dispersed, but graft copolymer formation has not yet occurred. However, once a μm level dispersion of E-MA-GMA in PBT is obtained a chemistry-controlled regime takes over. Upon dispersion with a factor of 10^3 from mm rubber powder to μm particles, the diffusion distance of reactive polymers to the interface is decreased with a factor of 10^3 and the amount of interface is increased with a factor of 10^6. As a result, the rate of PBT/rubber graft copolymer formation is dramatically enhanced. The presence of graft copolymer reduces the interfacial tension and prevents coalescence via steric stabilisation of the dispersed particles [2,3], thus allowing a further refinement of the rubber dispersion to a sub-μm level. Molau tests on blends, produced on the batch kneader with mixing times larger then 30 s., yielded stable emulsions. Therefore, increasing the PBT carboxylic end group content or the rubber epoxide content results in decreasing rubber particle size. At interfacial graft copolymer densities $\geq$ 0.05 chain/nm^2 dynamic coalescence is prevented and the finest dispersions are obtained. During batch kneading the rubber particle size in the PBT/E-MA reference blend continues to decrease up to mixing times of several minutes, which is probably because of slow PBT/rubber graft copolymer formation via transesterification of PBT-OH with acrylate rubber moieties (Figure 1: bottom). Blends with acid-modified E-MA-GMA or produced at a relatively high temperature favour cross-linking of the rubber phase, which limits optimum dispersion and yields relatively coarse morphologies. For blends produced in the batch kneader at very long mixing times (> 15 min.) the Molau test yielded unstable emulsions again. Dispersed rubber particles are probably linked by PBT chains via HOOC-PBT-COOH chains reacting on both ends with epoxide-containing rubber particles, resulting in macroscopic cross-linking of the blend without affecting the rubber dispersion.

The transition between the physics- and chemistry-controlled regimes is affected by the experimental conditions. Increasing the melt temperature favours the chemical reactions and the transition is at relatively short mixing times. On the other hand, increasing the shear rate delays the occurrence of the chemistry-controlled regime. In the case of PBT/E-MA-GMA blends the distinction between the physics-controlled and chemistry-controlled regimes can be made, because the reactivity between PBT-COOH and the rubber epoxide is not that high. In contrast, in blends of PAs with anhydride-modified rubbers, the formation of PA/rubber graft copolymer is extremely fast [19]. As a result, a distinction between the two regimes cannot be made and the final morphology is obtained within a few seconds upon melting of the PA [20,21].

Figure 4 shows a plot of the average rubber particle size as a function of the free PBT content - a measure for the amount of PBT/rubber graft copolymer formed - for PBT/E-MA/E-MA-GMA blends produced in the batch kneader and in the extruder [14]. Although a fair correlation is obtained, this does not tell à priori whether the particle size is determining the degree of grafting or vice versa. However, from the above discussion it is clear that the degree of dispersion is indeed determining the degree of grafting.

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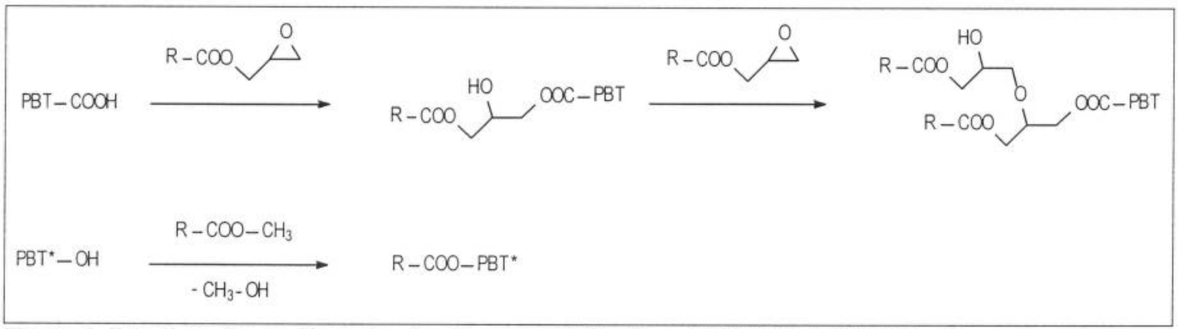

Figure 1. Reaction scheme illustrating in-situ compatibilisation of PBT/E-MA-GMA blends.

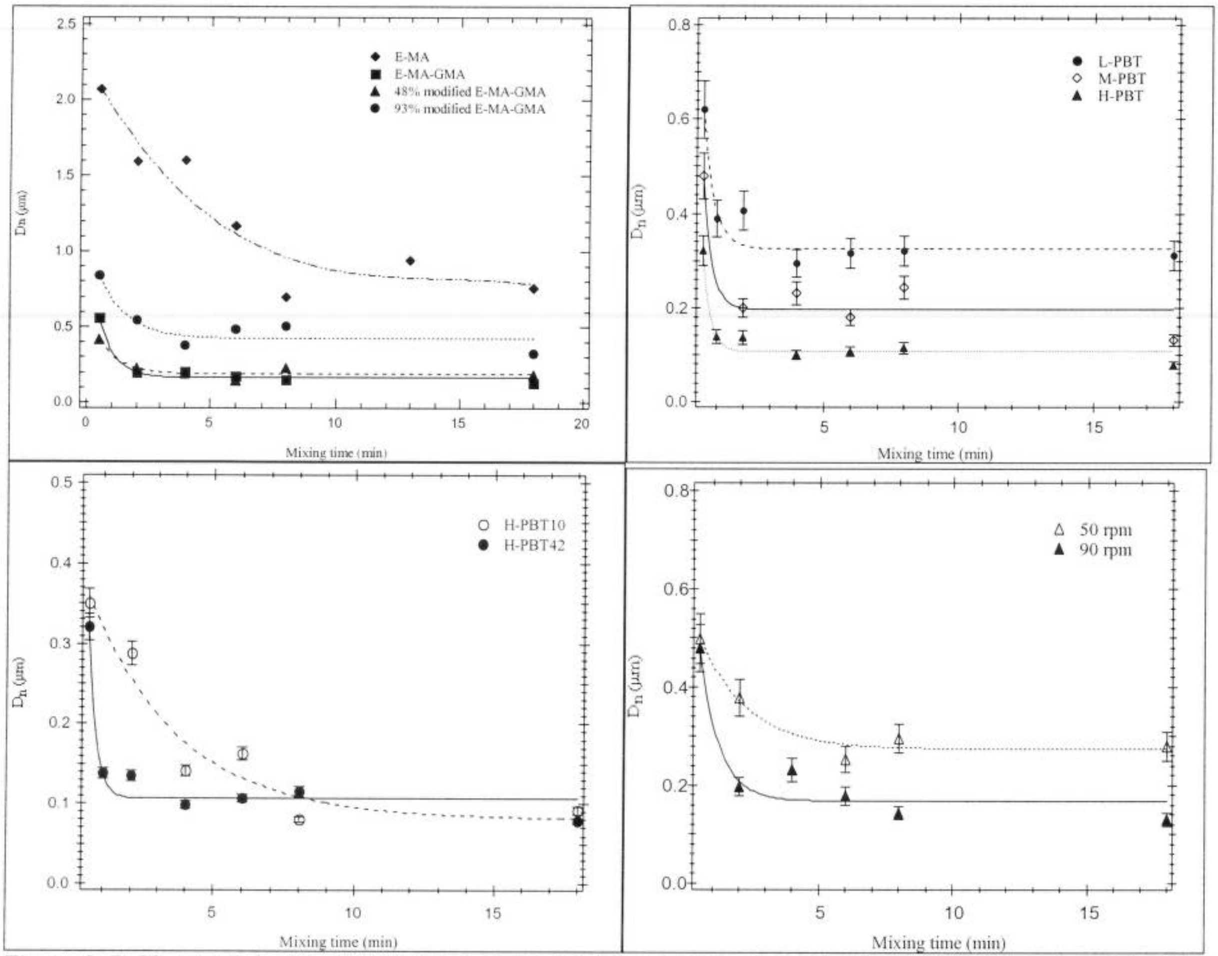

Figure 2. Rubber particle size of PBT/E-MA-GMA (80/20; w/w) blends as a function of batch kneader mixing time: a: effect of rubber epoxide content; b: PBT molecular weight, c: PBT carboxylic end group content and d: rotation speed.

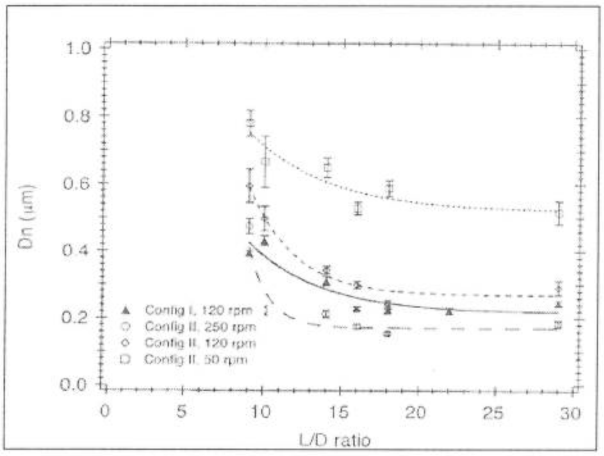

Figure 3. Rubber particle size (D_n) along screw axis during production of 80/20 (w/w) PBT/E-MA-GMA blends in the extruder: effect of screw speed and configuration

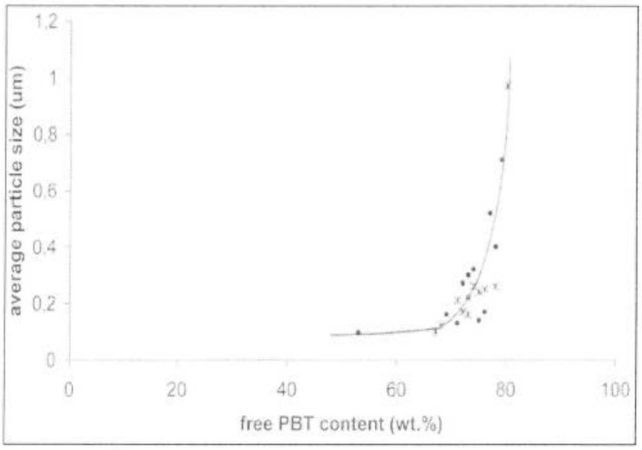

Figure 4. Average rubber particle size as a function of free PBT content for PBT/E-MA/E-MA-GMA blends produced in the batch kneader and the extruder.

Table 1. PBT characteristics.

PBT[a]	[-COOH] (µeq/g)	[-OH] (µeq/g)	M_n (kg/mol)
L-PBT-45	45	66	16.1
M-PBT-49	49	31	19.8
H-PBT-10	10	60	31.4
H-PBT-42	42	10	30.9

a: L, M and H indicate low, medium and high-molecular weight, resp.; the number indicates [-COOH].

Table 2. E-MA-GMA characteristics.

E-MA-GMA	E content (wt.%)	MA content (wt.%)	GMA content (wt.%)	MFI (g/10 min.)[a]
E-MA	70	30	0	6
E-MA-GMA8	68	24	8	6
48% modif. E-MA-GMA8[b]	68	24	4[b]	6
93% modif. E-MA-GMA8[b]	68	24	0.6[b]	6

a: melt flow index at 190 °C under 315 g;
b: residual GMA content of E-MA-GMA modified with para-t-butylbenzoic acid.

Keywords

PBT, blend, morphology, graft copolymer