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Interfacial Chemistry and Morphology of In-Situ Compatibilised PA-6 and PBT Based Blends

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Summary: Reactive blending is the preferred route for obtaining rubber-toughened engineering plastics. In this study the chemistry and morphology of in-situ compatibilised PA-6/EPM-g-MA blends and PBT/E-MA-GMA blends are compared. Despite the different chemical structures formed (PA-6: cyclic imide; PBT: ester), the different side-reactions that take place (PA-6: chain scission; PBT: rubber crosslinking) and the different reaction rates (PA-6: very fast; PBT: rather slow), a general description of reactive blending is proposed. First, a very fast physics-controlled dispersion of the rubber phase into the polycondensate matrix occurs (from milimeter to micrometer scale). Then the interface, thus generated, is covered via graft-copolymer formation. This results in a stabilisation against coalescence and in a reduction of the interfacial tension, enabling further dispersion of the rubber phase. In the case of PA-6/EPM-g-MA blends the graft formation occurs so quickly that when the physics-controlled dispersion is completed, the final dispersion is achieved. In the case of PBT/E-MA-GMA blends the graft formation is much slower and the chemistry-controlled dispersion can hence be considered as a secondary process, yielding the final morphology.

Keywords: blend, graft copolymer, in-situ compatibilisation, morphology, reactive blending

Introduction

The main reasons for the commercial success of polyamide-6 (PA-6) and poly(butyleneterephthalate) (PBT) as engineering plastics are their high strength and stiffness and their high heat resistance, combined with their relatively low cost. PA-6 has the disadvantage of high water adsorption and, consequently, has a lower dimensional stability and poorer electrical properties than PBT. Since both thermoplastics are brittle when subjected to impact conditions, they are often compounded with glass fibres or rubber. In practice about 20 wt.% of a finely

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dispersed (≤ 1 μm) rubber phase with good adhesion to the thermoplastic matrix has been shown to ensure sufficient rubber toughening.[1,2] To obtain such small rubber particles and good adhesion, pre-synthesised core-shell rubbers may be used. Alternatively, compatible blends may be produced via reactive blending, i.e. in-situ compatibilisation.[3,4] PA-6 is typically toughened with ethylene-propylene rubber (EPM) using maleic-anhydride-modified EPM (EPM-g-MA) as the reactive compatibiliser. In the case of PBT one often resorts to epoxy-containing rubbers, such as ethylene-(methyl acrylate)-(glycidyl methacrylate) terpolymers (E-MA-GMA).

In the present paper the results of our (partly published) studies on PA-6/EPM-g-MA blends and PBT/E-MA-GMA blends[5-14] will be combined. The similarities and the differences of these blends will be highlighted and conclusions with respect to reactive blending on a more general level will be drawn.

Experimental

For experimental details the reader is referred to the original studies.[5-14] Only a few general remarks will be made here. Experiments with representative low-molecular-weight model compounds have been carried out, since these allow relatively straightforward characterisation of the reaction products, in order to determine the chemical structures formed during the interfacial reactions between the polycondensate end groups and the rubber functionalities. Selective fractionation and hydrolysis schemes have been developed and applied, in order to identify the graft copolymers and to quantify the conversion of the reactive groups and/or the amount of copolymer formed. The morphology of the heterogeneous thermoplastic/rubber blends has been investigated using electron microscopy in combination with image analysis.

Besides blends produced in batch kneaders or extruders, the development of the various physico-chemical phenomena was also studied along the screw axis of a co-rotating twin-screw extruder by using special sampling devices.[15] As shown in Figure 1 (top), by turning a bolt (2) in the barrel wall, the cavity (4) can be positioned towards the opening in the wall of the extruder (1), allowing polymer melt to flow from the screw channel into the cavity. By turning the bolt 180°, the melt sample is accessible from the outside of the extruder. The sample is removed, quickly quenched and analysed off-line. Figure 1 (bottom) shows the extruder layout and typical locations of the sampling devices. They are positioned along the staggering kneading blocks and/or left elements, where inner pressure develops for forcing the melt sample into the cavity.

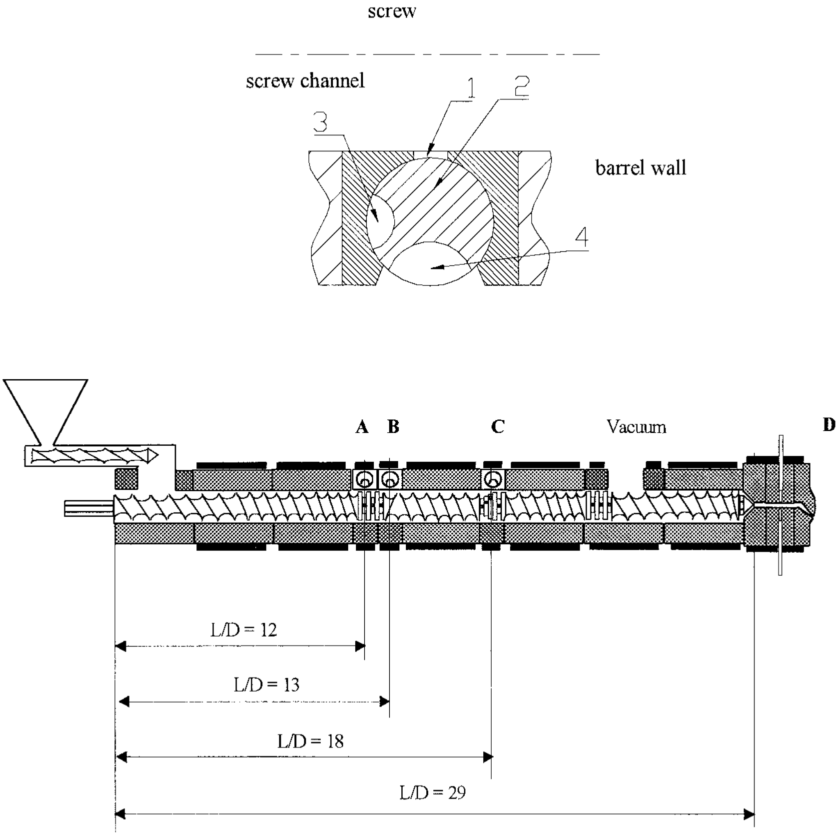

Fig. 1. Schematic drawing of sampling device (top) and set-up of extruder with positions of sampling devices along screw axis (bottom).

PA-6/EPM-g-MA Blends

In the case of PA-6/EPM-g-MA blends produced in the melt, the graft copolymer is formed upon reaction of the PA-6 amine end group (PA-NH_2) with the cyclic anhydride of EPM-g-MA, yielding a cyclic imide link under formation of water (Figure 2).[5,6,16-18] If the concentration of anhydride is larger than that of the amine groups, an indirect reaction between the PA-6 amide group (PA'-CONH-PA) and the anhydride will occur, again resulting in an imide link, but also in a new PA-6 carboxylic end group (PA'-COOH) due to scission of the PA'-6 chain. The reaction between anhydride and amine group is extremely fast, that between anhydride and amide is much slower.

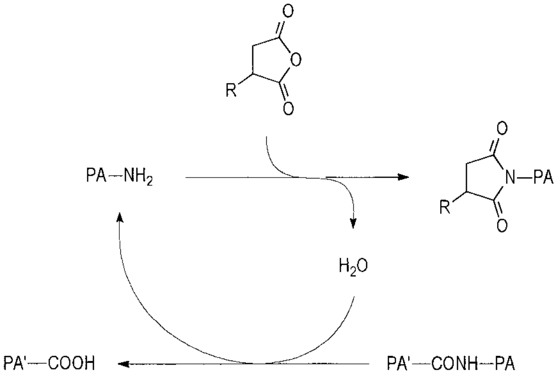

Fig. 2. Reaction scheme illustrating in-situ compatibilisation of PA-6/EPM-g-MA blends.

Selective extraction with formic acid at room temperature allows quantification of the PA-6 graft content in PA-6/EPM-g-MA blends. Hydrochloric acid treatment allows identification of the cyclic imide and quantification of the MA conversion. The ratio of the PA-6 graft content and the degree of anhydride conversion provides an estimate of the number-average molecular weight of the PA-6 grafts. Some typical results for 50/50 (w/w) blends of PA-6 and PA-6.6 with EPM-g-MA and poly(styrene-co-MA) (SMA)[5] and for 80/x/20-x (w/w/w) PA-6/EPM/EPM-g-MA blends[7] are presented in Tables 1 and 2, resp. The amount of PA-6 graft and the MA graft conversion depend clearly on the type of blend components used and the blend composition. The MA graft conversion is high and the molecular weight of the PA-6 grafts is low in comparison with that of the initial PA-6 polymer, both demonstrating the occurrence of PA-6 chain scission.

Table 1. Characteristics of 50/50 (w/w) blends of polyamides and MA-containing polymers produced on a co-rotating twin-screw extruder (240/255 °C, 200 rpm).[5]

blend	grafted PA (wt.%)	MA graft conversion (%)^a	M_n free PA (kg/mol)^b	M_n PA graft (kg/mol)^b
PA-6/EPM-g-MA	14	100		2.0
PA-6/SMA	12	42		0.2
PA-6.6/EPM-g-MA	13	100	16	1.8
PA-6.6/SMA	10	44	8.5	0.16

a: MA content of original EPM-g-MA and SMA is 1.4 and 28 wt.%, resp.; b: M_n of original PA-6 and PA-6.6 is 13 and 20 kg/mol, resp.

Table 2. Characteristics of PA-6/EPM/EPM-g-MA blends produced on a co-rotating twin-screw extruder (220 °C, 200 rpm, 6 kg/hr).[7]

PA-6/EPM/EPM-g-MA blend (w/w/w/)	grafted PA (wt.%)	MA graft conversion (%)^a	M_n PA graft (kg/mol)^b	average particle size [range] (μm)
80/20/0	0	-	-	9.0 [2.0 – 31]
80/15/5	0.38	100	1.4	2.6 [1.5 – 23]
80/10/10	0.8	96	1.7	2.3 [1.5 – 8.0]
80/5/15	0.8	89	1.2	2.2 [1.5 – 5.2]
80/0/20	0.8	86	1.0	0.33 [0.1 – 0.7]

a: MA graft content of original EPM-g-MA is 0.49 wt.%; b: M_n of original PA-6 is 13 kg/mol.

The low molecular weight of PA grafts has also been explained by the high concentration of low-molecular-weight PA at and/or the fast diffusion to the interface.[17, 18] The morphology of the PA-6/EPM-g-MA blends consists of a (sub-)micrometer dispersion of rubber spheres. The rubber dispersion often contains PA-6 occlusions. When PA-6.6. is used instead of PA-6, crosslinking of the rubber phase via H_2N-PA-NH_2 oligomers (including 1,6-hexanediamine) occurs, yielding a coarse and irregular morphology,[5] which corroborates the results found by Paul et al.[19]

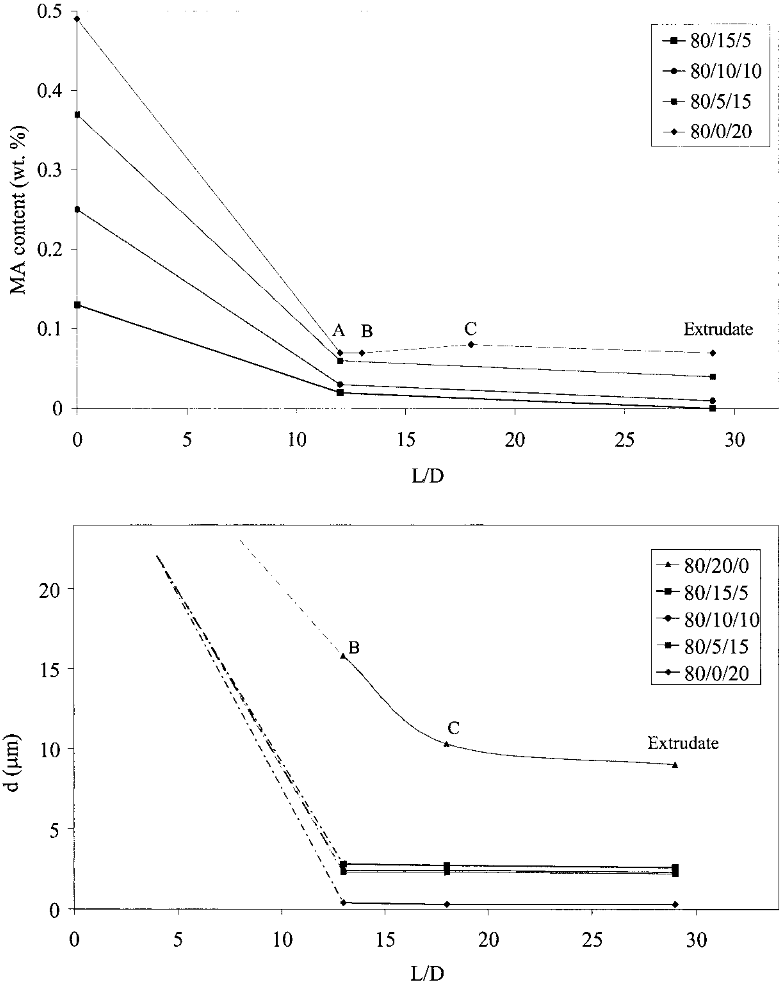

Fig. 3. MA graft content of EPM-g-MA (top) and of average rubber particle size (d) (bottom) along screw axis during production of 80/20-x/x (w/w/w) PA-6/EPM/EPM-g-MA blends.[7]

Samples were taken along the screw axis during the production of PA-6/EPM/EPM-g-MA blends.[7] For all compatibilised blends the reaction between PA-6 and EPM-g-MA occurs in the first kneading zone, resulting in a MA graft conversion of 80% (Figure 3; top). With the exception of the non-compatibilised blend, the dispersion of the rubber phase occurs also extremely fast, i.e. from milimeter granulate to sub-micrometer particles within the first kneading zone (Figure 3; bottom). Another extruder lay out with 6 sampling devices in series at the first kneading zone has shown that the PA granulate melts over an axial distance of only a few centimetres and both chemical and morphological development occur over the same distance. The actual dispersion process seems to be rather chaotic,[8, 9] which confirms the observations by Scott and Macosko:[20] very large domains, sheets, elongated threads, threads breaking up into droplets and small droplets are all observed in the same sample. Further along downstream, the PA-6 graft content, the residual MA content and the average rubber particle size do not change significantly. However, some last large rubber particles are finely dispersed along the screw axis, resulting in a decrease in the particle size distribution, and also degradation of the PA-6 matrix occurs.[10]

PBT/E-MA-GMA Blends

In the case of PBT/E-MA-GMA blends produced in the melt the main reaction is the opening of the epoxide rings of E-MA-GMA as a result of attack of PBT carboxylic end groups (PBT-COOH), resulting in ester linkages (Figure 4: top: first reaction).[11] This reaction is not that fast and the epoxide conversion is far from complete, but it still predominates over the similar reaction between PBT hydroxyl end groups (PBT-OH) with rubber epoxide[21] and over PBT-OH/E-MA transesterification (Figure 4: bottom). The latter reaction does occur in non-compatibilised PBT/E-MA blends though, but is very slow and the degree of conversion is too low to obtain a fine rubber dispersion.[12, 22] In addition to the graft reaction, also crosslinking of the E-MA-GMA rubber occurs (Figure 4: top: second reaction), initiated by the secondary hydroxyl group actually formed during graft formation.

Selective extraction with trifluoroacetic acid allows the determination of the non-grafted PBT content. Subsequent extraction with chloroform yields the amount of free E-MA-GMA. The remaining residue consists of both E-MA-GMA and PBT. Using m-cresol, a common solvent for PBT and E-MA-GMA, at 130 °C it was shown that this residue is crosslinked. Hydrolysis with t-butylammonium hydroxide shows that the crosslinking is not due to HOOC-PBT-COOH chains acting as a crosslinker. Table 3 gives some typical results obtained for PBT/E-MA/E-MA-GMA blends produced in an extruder.[12-14] Increasing the GMA content of E-MA-GMA clearly results in higher PBT graft contents, but also in increased crosslinking of the rubber phase.

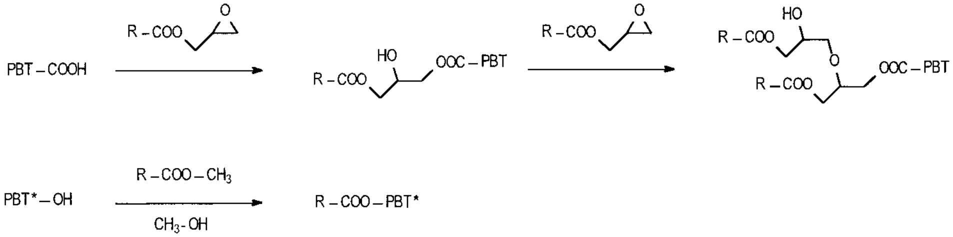

Fig. 4. Reaction scheme illustrating in-situ compatibilisation of PBT/E-MA-GMA blends.[11]

Table 3. Characteristics of 80/20 (w/w) PBT/E-MA-GMA blends produced on a co-rotating twin-screw extruder (280 °C, 200 rpm, 10 kg/hr) [12-14].

E-MA-GMA	free PBT (wt.%)	free rubber (wt.%)	molecular weight between crosslinks (kg/mol)[a]	average particle size (μm)	interfacial copolymer density (chain/nm²)
0 wt.% GMA[b]	80	18	3.8	0.97	0
1 wt.% GMA	78	5.7	1.8	0.26	0.044
2 wt.% GMA	74	0.68		0.26	0.11
8 wt.% GMA	68	4.3	1.1	0.12	0.19
8 wt.% GMA (48% modified[c])	71	0.23	0.58	0.21	0.27
E-MA/E-MA-GMA (10/10; w/w)	72	5.0	1.7	0.17	0.21

a: of dispersed rubber phase determined with solid-state ^{1}H NMR relexation time measurements; b: E-MA copolymer; c: E-MA-GMA modified with p-*t*-butylbenzoic acid.

The morphology of PBT/E-MA-GMA blends is usually a fine sub-micrometer dispersion. However, the rubber particles are somewhat irregular in shape and do not have a smooth interface, which is probably due to the crosslinking of the E-MA-GMA phase.[11] Using Atomic Force

Microscopy in the electrostatic resonance mode it is shown that in the case of PBT/E-MA-GMA blends the crosslinking reaction is indeed initiated at the interface by the graft reaction and then proceeds towards the centre of the rubber particles.[14] In blends of PBT with acid-modified E-MA-GMA the crosslinking occurs homogeneously throughout the rubber particles, since the modified rubber already contains the secondary hydroxyl groups. Still, even when this modified E-MA-GMA is used, a sub-micrometer rubber dispersion is obtained.

Samples were taken along the screw axis during PBT/E-MA-GMA blend production.[14] The formation of PBT grafts proceeds relatively slowly and continues to the end of the extruder. The crosslinking of the rubber phase also continues to the end of the extruder. The dispersion of the rubber phase seems to follow a two-stage process, viz. first a fast dispersion to micrometer scale, followed by a final dispersion to sub-micrometer scale (Figure 5). Characterisation of samples obtained via batch kneader mixing at 250 °C as a function of time showed that during short mixing times (< 30 sec) a very fast dispersion occurs, but hardly any grafting.[12, 13] At intermediate mixing times the small rubber particles are grafted. At prolonged mixing times (> 15 min), rubber

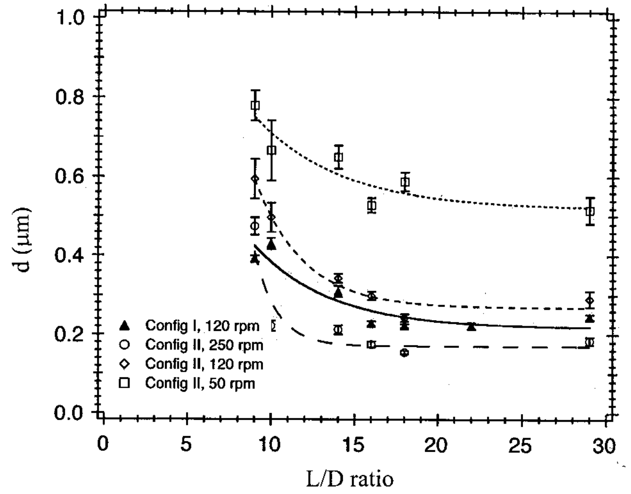

Fig. 5. Average rubber particle size (d) along screw axis during production of 80/20 (w/w) PBT/E-MA-GMA blends.[14]

particles seem to be linked by HOOC-PBT-COOH chains. Increasing the screw speed enhances clearly the dispersion in the physical regime.

A plot of the average particle size versus the free PBT content shows a fair correlation for a large set of PBT blends produced in both a batch kneader and an extruder (Figure 6).[12-14] This suggests strongly that graft formation is limited by the available interface. The interfacial graft density can be calculated by combining the PBT graft content and the rubber particle size. This quantity varies by an order of magnitude and is dependent on all the experimental variables (PBT molecular weight and carboxylic end group content, rubber epoxide content, blend composition, processing temperature and screw speed).

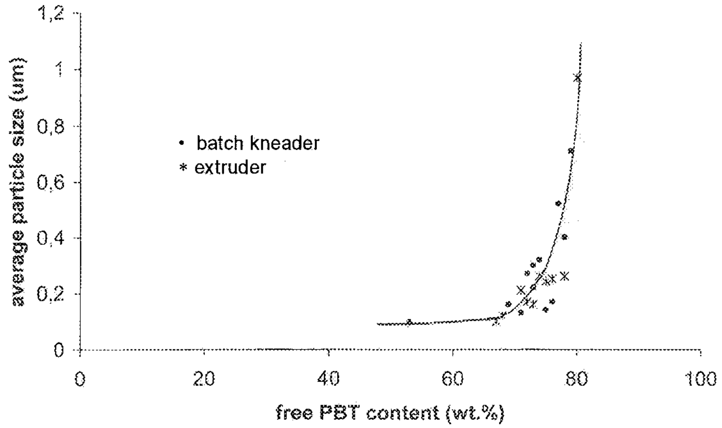

Fig. 6. Average rubber particle size as a function of free PBT content for PBT/E-MA/E-MA-GMA blends produced in a batch kneader and an extruder.[12-14]

Conclusions

Reactive blending of PA-6/EPM-g-MA and PBT/E-MA-GMA blends is obviously a complex process with continuous and reciprocal interactions between chemistry, morphology and rheology. In spite of the facts that the chemical structures formed in these two types of blends differ (PA-6: cyclic imide; PBT: ester), different side-reactions take place (PA-6: chain scission; PBT: rubber crosslinking) and the reaction rates are also quite different (PA-6: very fast; PBT: rather slow), general conclusions may nevertheless be drawn. First, the physical dispersion, governed by the viscosity (ratio) and the interfacial tension, results in the rapid formation of a fine rubber dispersion, i.e. from milimeter to micrometer scale within a few seconds. This results in a decrease of the diffusion distance between the polycondensate chains and the rubber interface by a factor of 10^3 and an increase of the available interface by a factor of 10^9, enhancing dramatically the rate of interfacial reactions. In the case of the PA-6/EPM-g-MA blends, the graft reaction is so fast that the interface is immediately covered with PA-6 chains. This results in a fast reduction of the interfacial tension and in prevention of coalescence and, hence, in an immediate further refinement of the dispersion. These phenomena occur so quickly that this sequence cannot be experimentally observed. In the case of the PBT blends the graft reaction is much slower and the subsequent morphology refinement takes place at a lower rate, which does allow the distinction between a physics- and a chemistry-controlled dispersion regime.

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