Glassy-Crystalline Nanostructured Polymers Via Reactive Blending

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Summary: Nanostructured glassy-crystalline blends were obtained by reactive blending of poly(methyl methacrylate) (PMMA), or of poly(methyl methacrylate)-*b*-poly-(n-butyl acrylate)-*b*-poly(methyl methacrylate) (MBM) triblock copolymer, with polyamide-6 (PA). The PMMA chain, or block, contains a low fraction of glutaric anhydride units which are strongly reactive toward the terminal amino group of PA. Under the blending conditions the grafting reaction is very efficient leading to a high fraction of graft copolymer. When the PA is short, $M_n = 2500$, nanostructured blends are obtained with both PMMA and MBM while for longer PA, $M_n = 15000$, nanostructures form only with the triblock MBM copolymer. The intrinsic property of MBM to self-organize in lamellar-like morphology seems to favour the nanostructure formation in the final blend. The resulting materials exhibit unique properties such as transparency, creep resistance and solvent resistance.

Keywords: nanostructure; PMMA; polyamide; reactive blending

Introduction

Reactive blending is widely used for the compatibilization of polymer blends. The presence of reactive groups at the end or along the backbone of the blended polymers leads to the formation of graft and block copolymers which stabilise the polymer/polymer interface and confer improved stability and interesting properties to the final material.[1,2] If the blended polymers are designed to have the right reactive groups at the right position, high fractions of graft or block copolymers are formed and yield to nanostructure formation. In that case reactive blending can be used as a tool for the synthesis of copolymers capable to self-assemble and form mesophases.[2] It is thus possible to synthesize copolymers or copolymer architectures that are impossible to obtain by conventional synthesis techniques.[3,4]

In this study we report on acrylic/polyamide nanostructured materials obtained by reactive blending. Two types of acrylic backbones are used, the simplest one is a functionalized poly(methyl methacrylate) (PMMA) chain, the second is a triblock copolymer poly(methyl methacrylate)-*b*-poly(n-butyl acrylate)-*b*-poly(methyl methacrylate) (MBM) with functionalized PMMA end-blocks and an elastomeric poly(n-butyl acrylate) (PBA) mid-block. The PMMA chain and blocks have few glutaric anhydride groups which react with the amino end-group of the polyamide (PA) to form the corresponding graft copolymers as schematically shown in Figure 1. We focus on blends where polyamide is the minor component.

Materials and Methods

The polymers were a gift from Arkema. Their characteristics are summarized in Table 1. Blends were prepared in a twin-

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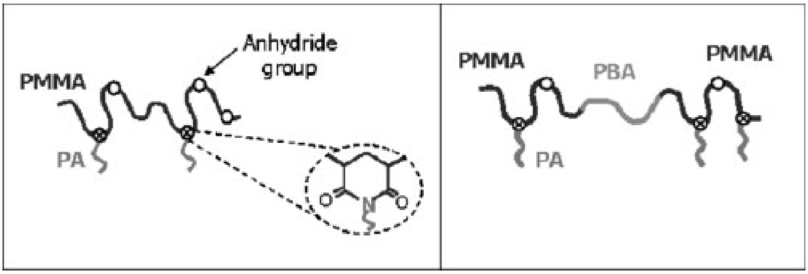

Figure 1.
Structure of the graft copolymers formed during reactive blending.

screw micro-extruder equipped with a feedback channel for cyclic extrusion (DACA Instrument). Typical blending conditions are: 250 °C, 6 minutes, 200 rpm, N_2 atmosphere. Transmission Electron Microscopy (TEM) observations were done on ultrathin sections of the extruded strands (cut perpendicular to the flow direction) stained with phosphotungstic acid. On the TEM images polyamide appears in black, poly(n-butyl acrylate) in white, while poly(methyl methacrylate) appears white or gray depending on the staining conditions.

Results and Discussion

Table 2 summarizes data on the aspect and the degree of crystallineity, of blends containing 30% polyamide. Visual inspection suggests, and transmission electron microscopy observation confirms, that blends containing non-functionalized polyamide (PA-nf) are heterogeneous. Large polyamide domains (several hundreds of nm in size) are dispersed in a continuous PMMA or MBM phase (TEM images not shown). On the other hand, blends containing short polyamide (PA-2500) are transparent and the TEM images show very thin morphologies (Figure 2). This can be taken as an evidence of the grafting efficiency of PA-2500 on both PMMA and triblock MBM copolymer.[5] Size exclusion chromatography analysis of the blends (130 °C in benzylalcohol) confirms that most of PA-2500 has been grafted.[6] A condition for the formation of nanostructured blends is the good mixing of the in situ formed graft copolymer with the remaining ungrafted components.[3] Obviously this condition is satisfied for the blends containing PA-2500.

Table 2.
Macroscopic aspect of blends containing 30% polyamide. In parenthesis: % of crystallinity of polyamide.

	PMMA	triblock MBM
PA-nf	White (33)	White (35)
PA-2500	Transparent (24)	Transparent (20)
PA-15000	white	slightly opaque (25)

Table 1.
Polymers used in this study.

Polymer	Mn	NH_2/chain	Xc^b (%)	n-butylacrylate (mol%)	anhydride (mol%)
PA-nf	2500	0^a	35	—	—
PA-2500	2500	1	35	—	—
PA-15000	15000	1	32	—	—
PMMA	45000	—	—	0	4
MBM	70000	—	—	34	2

[a] This polyamide does not have free amino-ends.
[b] Xc = degree of crystallinity measured by DSC.

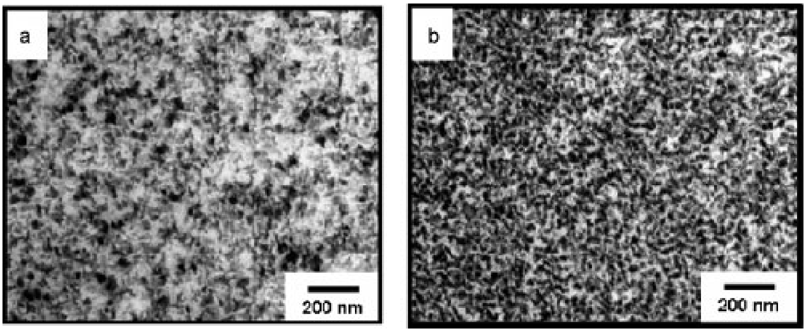

Figure 2.
Transmission electron microscopy images characteristic of blends containing short polyamide. (a) PMMA/PA-2500 80/20; (b) MBM/PA-2500 80/20. Polyamide appears in black.

On the other hand, blends containing long polyamide (PA-15000) exhibit substantial differences. Remarkably we find that the blends with the triblock MBM copolymer have a very fine morphology while those with PMMA have a very coarse one (Figure 3). This is also reflected on the macroscopic aspect of the blends, see Table 2. The higher efficiency of reactive blending in the case of triblock copolymer is attributed to the ability of the ungrafted triblock to mix with the grafted derivative formed during the blending process.

Similar results were obtained for blends containing 10 to 50% polyamide. The opacity of the MBM/PA-15000 blends however increases when the polyamide content increases above 30%. Note that highly heterogeneous blends were obtained when non-reactive PMMA or MBM are blended with PA-15000.

Interestingly the semicrystalline character of the polyamide persists in the nanostructured blends (Table 2). As a result the nanostructured blends exhibit good solvent resistance. For instance, after several days immersion in chloroform, they swell slightly but conserve their shape.

An example of the temperature dependence of the elastic modulus of neat triblock copolymer and of the blend with 30% PA-15000 is shown in Figure 4. The plateau modulus at $T > Tg_{\text{-PMMA}}$ is increased due to the connectivity of the crystalline polyamide domains via the triblock backbone. Finally the blend recovers the behavior of the neat triblock above the melting temperature of polyamide.

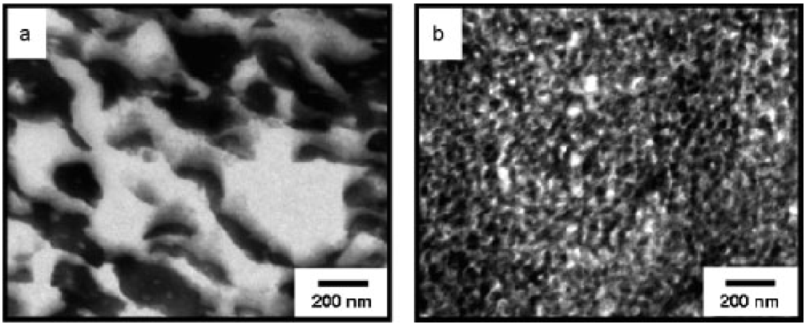

Figure 3.
Transmission electron microscopy images characteristic of the blends containing long polyamide. (a) PMMA/PA-15000 70/30; (b) MBM/PA-15000 70/30. Polyamide appears in black.

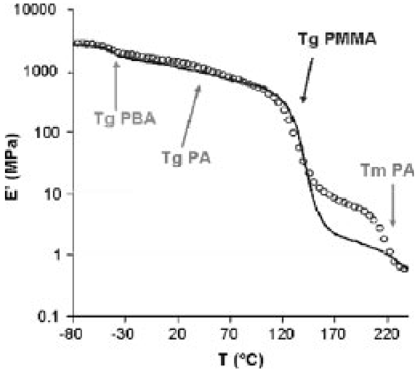

Figure 4.
Temperature dependence of the elastic modulus. Continuous line: neat MBM triblock copolymer. Circles: MBM/PA-15000 (70/30) blend.

Conclusion

Nanostructured blends of PMMA (or PMMA block copolymers) with polyamide-6 can be obtained by reactive blending providing that the PMMA chain has few anhydride units. The nanostructure formation is especially effective for blends based on a triblock PMMA-*b*-PBA-*b*-PMMA copolymer. Despite their very small size (10–40 nm) the dispersed polyamide domains conserve their crystalline character. As a consequence the resulting nanostructured blends exhibit solvent resistance and improved mechanical properties at temperatures above the Tg of PMMA.

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