Glassy-Crystalline Nanostructured Polymers Via Reactive Blending

Ilias Iliopoulos,1* Ludwik Leibler,1 Mathilde Freluche,1 Jean-Jacques Flot,2 Pierre Gerard3

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-