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# Co-continuous nanostructured nanocomposites by reactive blending of carbon nanotube masterbatches

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## ABSTRACT

Masterbatches of reactive polymers containing carbon nanotubes are used to prepare nanocomposites by reactive blending. By mixing masterbatches of low molecular-weight amino-terminated polyamide-6 (PA6) containing ~10 wt% or ~17 wt% of multi-walled carbon nanotubes (MWNT) with maleic anhydride functionalized polyethylene (PE*) at temperatures above melting of PA6 it is possible to obtain fine and homogeneous dispersions of carbon nanotubes. In the PA6 concentration range explored, from 19 wt% to 37 wt%, nanostructured co-continuous blend morphologies are achieved. Selective extractions show that a high amount of graft copolymer PE*-g-PA6 is synthesized during mixing. The swelling experiments in selective solvents demonstrate co-continuous blend morphologies. Electron microscopy confirms good quality of MWNT dispersion and shows structures on mesoscopic scales. Fine dispersion of carbon nanotubes and the matrix co-continuity concur to yield a unique combination of properties such as solvent resistance, electrical conductivity, mechanical strengthening and ductility.

## 1. Introduction

Among the existing polymer morphologies, co-continuous structures are certainly one of the most promising as they can combine in unique and synergistic ways the advantages of various polymer components [1–4]. The polymer materials with co-continuous structures of sub-micrometer size are interesting for many applications such as solar cell panels or separation and catalytic membranes [5–8]. Introduction of fillers in such microstructures may bring added functionalities such as mechanical reinforcement and electrical conductivity. In this respect, multi-walled carbon nanotubes (MWNT) are promising because of their unique intrinsic electrical and mechanical properties [9,10], which are combined with a diameter between 10 and 20 nm and a high length over diameter ratio (from 100 to 1000).

Achieving stable co-continuous sub-micrometer structures is challenging and only a few successful strategies have been proposed so far. Moreover, carbon nanotubes (CNT) are difficult to disperse in polymer matrices and potentially toxic when used as powders [11,12]. To alleviate dispersion and toxicity problems in industrial compounding it is desirable to be able to use polymer masterbatches containing high concentration of carbon nanotubes rather than carbon nanotube powders. Masterbatches allow for a safer transport and loading into compounding machines and also facilitate CNT dispersion in a matrix [13]. Here, we propose to use a masterbatch not only as a convenient carrier for CNT, but as a mean to structure the composite on sub-micron scale: the masterbatch is indeed a reactive component.

As mentioned above, only a few methods allow for the obtention of polymer materials with stable co-continuous morphologies. Indeed, by adequately matching component viscosities and proportions, micrometer size co-continuous morphologies can be achieved by melt mixing of two polymer species A and B [2,14,15]. Fast cooling can quench the morphology. However, the system is out of equilibrium, the morphology is metastable and delicate to preserve during (re)processing and/or thermal treatment. In the development of composites the incorporation of carbon fillers, e.g. carbon black and carbon nanotubes, in such morphologies has two major interests. First, the selective localization of the fillers in one phase or at the interface can considerably decrease the amount of fillers needed to achieve electrical conductivity [16–19]. Second, the introduction of fillers at the interface of macro-phase separated polymer blends can reduce the coarsening of the domains during annealing [20].

The first way to obtain stable co-continuous materials is based on self-assembly of block copolymers with two or more monomer sequences of precise molecular weights linked together [21–24]. The composition range in which co-continuous morphologies are

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observed is very narrow. Another strategy, inspired by oil/water microemulsions, employs A-B block copolymers to stabilize co-continuous structures of a mixture of A and B homopolymers [25–28]. In a similar way, blends of A-B-A triblock copolymer with low molecular weights A homopolymer also lead to bicontinuous structures [29]. In such polymeric micro-emulsions, the structures obtained are thermodynamically stable but the co-continuous morphology can be obtained only in a very narrow domain of compositions. It is also possible to use functionalized nanoparticles rather than block copolymers to stabilize interfaces and form Pickering-like emulsions [30]. Particles designed to segregate at the interface of A-B diblock copolymer enable, above a critical concentration of particles, a transition from lamellar to stable bicontinuous microstructure [31].

In quite a different vain, reactive blending provides a very robust and easy to scale-up method of blend synthesis [32]. The method employs various functional group pairs [33] to synthesize during the blending block or graft copolymer at the interface. Depending of the reactivity of the pairs and the chemical structures of the two polymers chains, various amount of copolymer can be synthesized. The level and the structure of the formed copolymer defined the final morphology: nodular or co-continuous [34,35]. In this study, the efficient amine–anhydride reaction is used to synthesize by end grafting a large quantity of graft-copolymers and obtain materials with co-continuous morphologies [36–39]. While the abovementioned methods [25–28] rely on precise control of copolymer architectures and low polydispersity, the reactive blending strategy depends on concurrence of chain polydispersity and of random distribution of reactive groups along the chains backbones to yield co-continuous structures. Structures thus obtained are stable for a large composition domain. Two families of systems have been previously investigated [36,37]: functionalized polyethylene (PE*) and functionalized poly(methyl methacrylate) blended with end-reactive polyamide-6 (PA6). Whether co-continuous structures can be also obtained in the presence of fillers and whether stable co-continuous morphology can maintained in a composite is an open question, which we address in the present work for the case of MWNT. The beneficial role of MWNT on material properties has also been investigated.

In this study a PA6-CNT masterbatch is used with the blending strategy depicted in Fig. 1. The use of low molecular weight PA6 allows to easily obtain a PA6-CNT masterbatch with a high loading of CNT. The PA6-CNT masterbatch with amino-terminated ($NH_2$) PA6 are melt mixed with PE* bearing randomly distributed maleic anhydride functions (MAH). A reaction between hydroxyl or carboxylic groups, present on the nanotubes surface, and the $NH_2$ terminal group of the PA6 is possible. But regarding the effort made by various teams [40,41] to graft PA6 on CNT, we assume that this reaction during the extrusion is negligible compared to the reaction between the $NH_2$ group and the MAH function. The formation of graft copolymers during the reactive blending increases the viscosity of the blend and favors the quick dispersion of the CNT. From the combination of MWNT and the co-continuous morphology we obtain a unique combination of properties such as solvent resistance, high temperature creep resistance and electrical conductivity. The approach developed here could be generalized to many reactive systems starting from a masterbatch, safe to use, in order to achieve nanostructured nanocomposites.

## 2. Experimental section

### 2.1. Materials

Both the PA6 and PE* were provided by Arkema. The PA6 synthesized by polycondensation, is terminated at one end by a primary amine function and at the other by a methyl group, its number-average molecular weight ($M_n$) is equal 2.5 kg·mol$^{-1}$ with a polydispersity index (PDI) of 2. The PE* consists in a random copolymer of ethylene, ethyl acrylate and maleic anhydride (2.9 wt %) with a $M_n$ of 16 kg·mol$^{-1}$ and a PDI around 5.

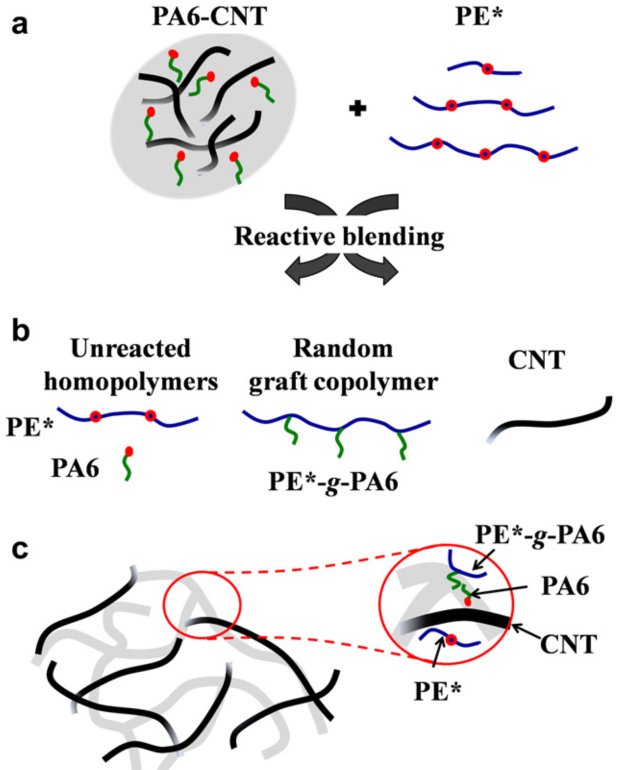

**Fig. 1.** Reactive blending strategy: a) PA6-CNT masterbatch is melt mixed with PE*. b) Species in presence after reactive blending. c) Co-continuous morphology: the PA6 phase is in gray and the PE* in white. The zoom in the microscale organization shows the graft copolymer at the interface between the PA6 and the PE* co-continuous domains.

MWNT produced by catalytic chemical vapor deposition were provided by Arkema (Graphistrength™ C100) and purified by refluxing in sulfuric acid. Their average diameter is about 10 nm with a length between 0.1 and 10 μm.

### 2.2. Samples preparation

Before use the polymers were dried at 80 °C under vacuum to remove moisture. Melt compounding was done using a DACA micro-compounder under nitrogen flux. This compounder is a 5 cm$^3$ capacity co-rotating twin-screw compounder with a feed-back channel allowing various mixing times.

The PE*/PA6-NT nanocomposites were prepared in a two step process. First, the CNT and the PA6 were melt mixed to obtain PA6-CNT masterbatches with 9.3 wt% (MB1) or 16.5 wt% (MB2) of carbon nanotubes. The conditions taken were 8 min mixing at 220 °C with a screw rotational speed of 200 rpm. Second, the PE* was extruded (220 °C, 200 rpm, 4 min) with the PA6-CNT masterbatch to reach the nanocomposites; these lasts are designed as PE*/*x*PA6-*y*NT were *x* represents the weight fraction of PA6 and *y* the weight fraction of CNT (Table 1).

For comparison purpose composites with 78 wt% PE*, 20 wt% PA6 and 2 wt% CNT were achieved with a different blending sequence. This time, the PE* and the PA6 were melt mixed at 220 °C during 4 min at the screw rotational speed of 200 rpm prior to the introduction of CNT. These nanocomposites are named [PE*/20PA6]-2NT-