



Dispersion of carbon nanotubes in polypropylene via multilayer coextrusion: Influence on the mechanical properties



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ABSTRACT

Multilayer coextrusion was used to disperse Carbon Nanotubes (CNT) in polypropylene (PP). The dilution of commercially available masterbatches using a twin-screw extruder was first applied to produce several formulations, which were then mixed with PP using a multilayer coextrusion device to obtain films or pellets with CNT concentrations between 0.1 and 1%wt. The influence of the specific mechanical energy (SME) during the dilution step, of the addition of a compatibilizer, and of the multilayer tool on the CNT dispersion within the matrix was highlighted. The effect of the dispersion on the thermo-mechanical properties of the resulting materials was studied. We showed notably that films containing 0.2%wt CNT, 1%wt of PPgAm, prepared at high SME presented a Young's modulus increase of 25–30% without significant decrease in the elongation at break. These results, using low amounts of CNT and industrially available devices, may show a new path for producing nanocomposites.

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1. Introduction

Carbon nanotubes (CNT)/polymer composites have received a huge amount of interest over the past ten years due to the unique combination of properties of nanotubes, mainly their large aspect ratio (typically in the 100–1000 range), low density, extremely high tensile moduli and strengths, toughness and high electrical conductivity [1]. In consequence, they have been for quite a long time [2] considered as potentially ideal fillers in high performance polymer composites, with the idea that despite their high price even for industrial MultiWall CNT (MWCNT), a very low fraction of CNT compared to classical fillers could lead to higher reinforcements [3].

To achieve good mechanical properties of the composite, one however does need to achieve a good dispersion/distribution of the nanotubes [1]: because of large surface areas of contact possibly creating physical entanglements and interactions, nanotubes are often agglomerated, which can decrease the efficiency of the filler (local stress concentrations and smaller effective aspect ratio). Moreover, orientation of the nanotubes and compatibility between

the polymer matrix and the nanotubes, due to their chemical structures, play an important role in the final properties of the composites.

Several methods have been studied to prepare CNT-based composites and thoroughly reviewed in the literature (see for example Refs. [1,3,4]).

Solution processing may be the most common method used at small scales to obtain such composites. Chemical processing can be achieved via in-situ polymerization or covalent functionalization of nanotubes [3]. However, melt processing is the only way to produce CNT-composites that is compatible with standard industrial processes (injection, extrusion, compression molding), due to its speed, cost and relative simplicity. An alternative route, solid-state shear pulverization appears promising but is still in its early stages [5–7].

Melt mixing actually has been less fundamentally studied than the others, and to this day gave the least interesting results, despite few exceptions [4]. This is mainly due to the fact that one is dealing with relatively high viscosities that affect the ability to disperse efficiently CNT in the matrixes, especially if the polymer and the CNT do not have favorable interactions (polyolefines). Reviews mentioned above list techniques or combinations of techniques to produce CNT nanocomposites in varieties of polymers but a “universal” and comprehensive method has yet to be proposed to achieve commercially relevant materials.

One of the most common industrial techniques for melt mixing is extrusion, and especially twin-screw extrusion in the case of CNT. However, only few recent papers use this method to create CNT

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composites. Pötschke et al. (for example references [8–11]) have published a large amount of work over the past few years in order to study extensively the role of different parameters using a twin-screw extruder in obtaining good dispersion of CNT within different polymer matrixes. In particular, these studies have pointed out the crucial importance of factors like matrix infiltration, masterbatch dilution technique, specific mechanical energy, screw configurations... In this paper, we propose the use of multilayer coextrusion to improve the dispersion and distribution of CNT in a polypropylene matrix to achieve interesting mechanical properties at low contents of CNT. Multilayer coextrusion is a quite old technique [12] that received under slightly various forms growing interest over the past years [13–15], following the pioneer work by Baer and his coworkers [16–21] and has been developed in our group recently [22]. In the context of this study, the idea is to use the multilayer coextrusion as a “mixing” tool: in this work we produce “layers” of the same polymer smaller than the typical size of the CNTs aggregates. Hence, the shear stress created by multilayer coextrusion should disperse and simultaneously orientate them in the extrusion direction and the confined structure should force breaking of the aggregates [23].

This idea has been scarcely studied to our knowledge: Jana et al. studied a similar mixing method to develop multilayer morphologies [24] and to disperse oxidized carbon nanofibers in PMMA and thermoplastic polyurethane with promising results in the viscoelastic region [25,26]. Very recently, Guo et al. studied the conductivity of polypropylene nanocomposites made using a similar device based on single extrusion [27,28] but no mechanical measurements have been performed.

In this paper we show that this method is effective and scalable to industrial processes to reinforce a commodity plastic such as Polypropylene (PP). PP is, for example, widely used in the automobile industry and increasing its mechanical properties without making it brittle could lead to lighter cars.

We can mention to conclude some studies devoted to the reinforcing effect of CNT dispersed in polypropylene matrix by melt mixing. Lopez-Manchado et al. [29] studied isotactic PP (iPP) with single wall carbon nanotubes (SWCNT) and found that Young's modulus is increased by roughly 30% at 0.75% of CNT. The authors show an increase in T_c with increasing content of CNT, and conclude that CNT act as nucleating agents for PP crystals with no substantial changes in the crystalline structure. Similar observations were made by Leelapornpisit et al. [30]: the mechanical reinforcement would then be due principally to the ordered zone rather than the CNT, which could explain the somewhat “limited” effect. More recent papers looked at promising routes toward industrial processes [5–7] or combined melt processing techniques with chemical engineering, especially surface modifications of the CNT [31–33], or commented on the effect of adding a compatibilizing agent between the PP and the CNT such as maleic anhydride grafted polyolefine [34–36].

The goal of this study is to use only industrially relevant apparatus (twin-screw and multilayer coextrusion), to identify the relevant mechanical and compositional parameters and methods leading to effective nanocomposites for the automobile industry, eg cost effective (small amount of CNT), with improved thermo-mechanical properties.

2. Materials and methods

2.1. Materials

Polypropylene PPH5060 is a homopolymer polypropylene grade developed by Total Petrochemicals suitable for extrusion, and will be used as the matrix in the nanocomposites produced. The Melt Flow Index is 6 g/10 min (230 °C/2.16 kg).

Polypropylene grafted with maleic anhydride (PPgAM) (see Fig. 1) was used in small quantity (between 0.5 and 7%wt) to increase the compatibility between the matrix and the CNT (“coupling agent”). Noncommercial Orevac PPgAM similar to the CA100 (high content of maleic anhydride) was obtained via Arkema. Due to defects occurring during their fabrication, MWCNT present polar groups such as hydroxyl groups at their surface. It has already been shown that polymers grafted with anhydride maleic improves the interactions between matrix and CNT fillers because of the polarity of the anhydride groups [34,37]. However, the exact mechanism and its consequences on the macroscopic properties are not yet fully understood since PPgAM will also affect the crystallization of the matrix [34].

CNTs were obtained in masterbatch form from Nanocyl. Plasticyl PP2001 is a concentrate of MultiWall Carbon Nanotubes (MWCNT) dispersed at 20%wt in a polypropylene matrix (PP2001, reference from Nanocyl) suitable for extrusion process. According to Nanocyl datasheets, their industrial grade MWCNT produced via catalytic carbon vapor deposition process (CVD) have a mean diameter of 9.5 nm, length about 1.5 μm and the carbon purity is 90% while the CNT contain 10% metal oxide impurities.

All products were used as received (under pellet forms).

2.2. Methods: sample preparation

2.2.1. Twin-screw extrusion

The twin screw extruder used in this study was a Thermo Haake PTW 16-40D. The goal with twin-screw extrusion is here to dilute the CNT concentration from 20%wt to a lower concentration by diluting the masterbatch with PPH5060. This first step is necessary since the masterbatch cannot be extruded as is using the multilayer coextrusion process, due to its high viscosity.

Following the work of Pötschke and coworkers [8–11], the influence of the specific mechanical energy (SME) in the dispersion of the CNT was studied. SME is defined by

$$\text{SME} = \frac{\tau N}{\dot{m}}$$

where τ is the torque of the screw, N the speed of the screw and \dot{m} the throughput. The absolute value will indeed depend from the extruder used, especially the extrusion temperature and the ratio L/D of the screw and its profile. SME is given in kJ/kg and basically defines a “good mixing”: the faster and the longer, the better.

The SME cannot be easily fixed before the experiment, since all the parameters are related and can vary slowly during the experiment. Work by Pötschke also show that the dispersion increases with increasing SME values but reaches a plateau.

As a consequence, the SME was calculated a posteriori, and we defined roughly 3 SME regimes: low SME for values below 500 kJ/kg, medium SME for values between 500 and 2500, and high SME for values higher than 2500.

In this work, the twin-screw extrusion temperature is fixed at 240 °C. The varying parameters in the different formulations

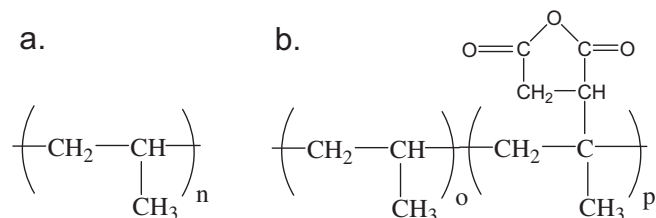


Fig. 1. a. Polypropylene. b. Polypropylene grafted with maleic anhydride PPgAM.

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