



Functionalized multi-walled carbon nanotubes with stereospecific Ziegler–Natta catalyst species: Towards facile *in situ* preparation of polypropylene nanocomposites

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were functionalized with a stereospecific Ziegler–Natta catalyst species for *in situ* preparation of polypropylene (PP)/MWCNT nanocomposites. The functionalization process involved initially treating MWCNTs containing a few (~3.0% w/w) surface hydroxyl groups (MWCNT-OH) with an excess amount of Grignard reagent followed by further reaction with TiCl₄. Triethylaluminum (TEA) and dimethoxydiphenylsilane (DDS) were used as co-catalyst and external electron donor, respectively. The resulting MWCNTs (MWCNT/Mg/Ti) only behaved as a fair isospecific Ziegler–Natta catalyst, promoting propylene polymerization at a moderate rate and resulting in PP with moderate isotacticity indices (76.4–91.0%). To improve the catalytic performance, the electron-donating reagent 9,9-bis(methoxymethyl)fluorine (BMMF) was added into the MWCNT functionalization process, incorporating BMMF into the catalytic material and simultaneously reducing the quantity of TiCl₄ immobilization. The BMMF-incorporated functionalized MWCNTs (MWCNT/Mg/BMMF/Ti) produced PP with a high isotacticity index (92.0%) without the use of an external electron donor. PP with an isotacticity index greater than 98% was achieved when DDS was used as external electron donor during the polymerization process.

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1. Introduction

Carbon nanotubes (CNTs), including multi-walled and single-walled carbon nanotubes (MWCNTs and SWCNTs, respectively), possess excellent mechanical properties, with Young's modulus values as high as 1.2 TPa and tensile strengths ranging from 50–200 GPa [1]. The combination of these exceptional mechanical properties with low density, high aspect ratio, and high surface area make CNTs ideal reinforcement candidates for polymers. Moreover, the addition of CNTs has proven remarkably advantageous to carbon fibers, which are otherwise brittle and easily fractured during composite processing, because CNTs are highly flexible, and thus their composites possess good processability properties without significant losses to the aspect ratios. CNTs have become the filler of choice for many polymer composite materials targeting various performance improvements because they maintain their excellent electrical and thermal conductivity properties [2].

Polypropylene (PP, predominantly isotactic) is a large-volume thermoplastic polymer of extremely high commercial significance

[3]. The incorporation of CNTs into PP generates PP/CNT nanocomposites that are highly desirable, with a loading of no greater than a few percent of CNTs greatly enhancing many of the mechanical properties of PP, including elastic modulus, tensile strength, impact resistance and fracture toughness, without deteriorating its light weight characteristics [4]. In a recent review, Tasis et al. summarized a series of literature reports concerning the reinforcing effect of CNTs on PP. It was reported that, depending on types of CNTs and processing and testing methods employed, increases in tensile strength and Young's modulus of as much as 400% and 300%, respectively, could generally be achieved with CNT loadings of less than 10% (w/w) [5]. In addition, a nucleation effect has frequently been reported for both MWCNTs and SWCNTs in PP [6,7], which also contributes to improvements in the mechanical and processing properties of PP. Besides conventional reinforcement, CNTs can also impart their electrical conductivity on to PP, transforming the typically insulating polymer into an antistatic or even semi-conductive material [8,9].

There are currently three major approaches for the fabrication of PP/CNT nanocomposites, including melt compounding [10–12], solution/latex mixing [13,14], and *in situ* polymerization [15–20]. The former two are essentially polymer mixing methods and, although they are direct methods of processing, they suffer

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