The effect of filler functionalization on dispersion and thermal conductivity of polypropylene/multi wall carbon nanotubes composites

Antonella Patti [a], Pietro Russo [b, *], Domenico Acierno [c], Stefano Acierno [d]

[a] Department of Chemical, Materials and Industrial Production Engineering, University of Naples Federico II, P.le Vincenzo Tecchio 80, 80125, Naples, Italy
[b] Institute for Polymers, Composites and Biomaterials, National Research Council, Via Campi Flegrei 34, 80078, Pozzuoli, Naples, Italy
[c] Centro Regionale di Competenza (CRdC Tecnologie Scarl), Via Nuova Agnano 11, 80125, Naples, Italy
[d] Department of Engineering, University of Sannio, Piazza Roma 21, 82100, Benevento, Italy

ARTICLE INFO

ABSTRACT

This paper deals with melt blended polypropylene based nanocomposites filled with multi wall carbon nanotubes. The effect of the content of unfunctionalized, amino- and carboxyl-functionalized carbon nanotubes having the same aspect ratio on their actual dispersion is investigated by dynamic rheological measurements and transmission electron microscopy observations. In particular, the former tests highlight a greater propensity to percolate of non functionalized nanotubes with respect to amino surface modified ones and even the absence of terminal effects in presence of carboxyl functionalized carbon nanotubes. Morphological observations, instead, show dispersion and agglomeration effects typically expected by increasing the carbon nanotubes loading. Moreover, through-plane steady-state evaluations of their thermal conductivity reveal a cubic polynomial trend of this parameter as a function of the filler content. This behaviour is interpreted in terms of the "average inter-aggregate distance (AID)" related to competitive dispersion/agglomeration phenomena to which added multi wall carbon nanotubes are subjected during the preparation of compounds with concentrations over specific threshold values.

1. Introduction

Polyolefins are widely used in several applications ranging from automotive to appliances, from constructions to housewares, and so on due to their attractive properties and low costs [1,2]. Nowadays, further expansion in new areas is expected by including carbon nanotubes (CNTs) as reinforcement to develop novel multifunctional composites combining improved mechanical [3], thermal [4], electrical [5], and flame resistance [6] properties at low nanotubes contents. In many cases enhancements of the thermal conductivity of obtained composites are also reported.

Wu et al. showed a linear increase in thermal diffusivity of high density polyethylene-based composites for multiwalled carbon nanotubes (MWNT) content up to 40% in vol. Results, interpreted by an effective medium approach model, showed an intrinsic longitudinal thermal conductivity of individual as-grown MWCNTs in the range of 40~60 $Wm^{-1} K^{-1}$ [7].

Chen et al. analysed high density polyethylene/multiwall carbon nanotube (HDPE/MWCNT) composite films by laser pulse method, finding a rapid increase of their thermal conductivity for MWCNT contents up to 3.35% in volume followed by slight effects at higher contents. This trend was interpreted by authors as due to a sort of percolation [8].

Kim et al. investigated thermal conductivity and diffusivity of different samples prepared by melt-blending polypropylene (PP) with non-treated, nitric acid (HNO_3)-treated, and potassium hydroxide (KOH)-treated nanotubes, respectively. Thermal conductivities were enhanced by a factor of about two in presence of acid-functionalized and base-treated carbon nanotubes with respect to non treated ones [9].

Kashiwagi et al. studied thermal and flammability properties of melt compounded polypropylene/multi-walled carbon nanotube (PP/MWNT) systems, with a filler content up to 20 wt.%. In details, the authors measured thermal conductivities in the range from 30

to 260 °C, confirming higher values for nanocomposites with respect to pure PP, with significant effects above 160 °C [10].

In general, the compatibility between carbon nanotubes and polymer matrices, especially non-polar ones like polyolefins, is limited by the remarkable tendency of the former to agglomerate, leading to mean defect sites in the composites and compromising their efficiency in "reinforcing" the polymer matrices. The dispersion is usually hindered by their large aspect ratio and strong Van-der-Waals attractions between nanotubes such that commercial products are always available as severely entangled nanotubes [11]. The extent of this drawback is usually limited by covalent and non-covalent functionalization routes [12–14] and by using appropriate processing conditions [15]. Indeed, agglomerates, formed by clusters of aggregates of primary particles, being less cohesive with respect to these latter [16], may be destroyed if the applied shear stress exceeds their cohesive strength, and their ratio is higher than a critical threshold, referred as fragmentation number (Fa) [17]. Otherwise, dispersion and agglomeration become competitive.

Another critical issue, associated with the use of CNTs as thermally conductive fillers, is related to the interfacial thermal resistance between the polymer and the filler, best known as "Kapitza resistance" [18], which causes a drastic phonon scattering and dramatically reduces the thermal conduction in a composite. Thus, perfectly dispersed particles and improved interfacial adhesion can inhibit the phonon transportation along carbon nanotubes reducing the effectiveness of heat transport.

Besides the effect of interfacial resistance, other possible heat transfer mechanisms between fillers have been considered. Zhong and Lukes [19] investigated the thermal transport between carbon nanotubes, by molecular dynamics simulation and analytical thermal modelling, showing a clear reduction of the contact resistance between tubes with increasing overlap and reducing space between themselves. Thus, a percolating 2-D network, realized by oriented, interconnected and overlapped particles, seems to be the desirable goal to produce thermal conductive compounds. At this regard, functionalization could be also aimed to reduce thermal contact resistance between adjacent CNTs, since stronger interactions can arise between chemical groups on their surfaces [20].

It is well established that the nature and the molecular weight of the matrix, the properties of included carbon nanotubes, the presence of surface defects and the processing conditions affect the dispersion of added nanotubes and, therefore, final properties of products. Thus, according to previous considerations, many research efforts have been spent to assess the actual state of filler dispersion in nanocomposite systems. In particular, this aspect has been widely monitored by optical [21] and electron microscopy techniques [22] but each one have benefits and limitations. Indeed, optical microscopy allows for a resolution down to about 0.2–0.5 μm while electron microscopy, even if allowing for inspection of individual nanotubes, is limited to 2D observations while carbon nanotubes are arranged in 3D-networks. Alternative methods to investigate the actual dispersion of nanoparticles in polymer matrices are essentially based on the consideration that the distribution of fillers in polymer melts influences their viscoelastic behaviour [23–26]. In particular, it is known that at a critical filler threshold the viscoelastic behaviour of the systems changes from liquid-like to solid-like. This effect, especially due to filler-–filler interactions, is characterized by a plateau of the storage modulus at low frequency values (non-terminal effect) and it is known as rheological percolation. The concentration threshold at which it occurs depends on several variables such as processing conditions, quality of dispersion, aspect ratio and shape of fillers.

Methods normally employed to prepare CNT-based composites include solution mixing [27], melt blending [28,29], and in situ polymerization [30]. Among these, melt compounding, although less effective in dispersing nanotubes compared with other techniques, has attracted a continuous growing interest representing an economically feasible process consistent with common industrial equipments as well as having a negligible environmental impact.

In this work, with the goal to develop new nanocomposite systems with improved thermal conductivity, three different types of multiwalled carbon nanotubes, one not functionalized (MWNT) and two chemically modified with amino (MWNT-NH₂) and carboxyl (MWNT-COOH) groups, have been included in the melt of a commercial polypropylene resin. The polar nature of both filler functionalizations, reducing the affinity with the non-polar hosting matrix, leads to poor wetting and infiltration of carbon nanotubes agglomerates and, due to mutual interactions and geometrical constrains, may give rise to internal structures with higher cohesive strength and, consequently, more resistant to dispersion mechanisms than pristine ones. All considered compounds obtained by melt blending were characterized in terms of rheological behaviour and morphological aspects to get qualitative information about the achieved level of MWNTs dispersion. Further tests aimed to evaluate the thermal conductivity of investigated materials permitted to relate this parameter to content and dispersion/agglomeration of included fillers.

2. Experimental

2.1. Materials

Commercial polypropylene resin (Monsten MA524, M_n = 32,400 g/mol; M_w = 250,084 g/mol, melt flow index 24.0 g/10 min at 230 °C, 2.16 kg) supplied by UNIPETROL RPA, was used as matrix. Three types of multi-wall carbon nanotubes, one neat, one chemically modified with carboxyl −COOH, and one modified with amino −NH₂ groups, supplied by Nanocyl S.A. (Sambreville − Belgium), were used as fillers. The nanotubes have the same purity, length and aspect ratio but different bulk densities. Their properties are summarized in Table 1 where the porosity was evaluated according to the Equation (1) [31]:

$$\varepsilon = 1 - \frac{\rho_b}{\rho_t} \tag{1}$$

where ρ_b and ρ_t are respectively the bulk and the true density values of the carbon nanotubes.

2.2. Sample preparation

Formulations, containing up to 5 vol. % of each type nanotubes, were prepared in a batch mixer (Brabender Plastograph EC- Brabender GmbH & Co. KG, Germany) at mixing temperature of 190 °C and rotational speed of 60 rpm. Polypropylene pellets were loaded as-received in the fed chamber and processed for 2 min in order to guarantee a complete melting of the polymer. Afterwards, the filler was added and the mixing continued for further 5 min. Specimens,

Table 1
Nanotubes datasheets for different types of carbon nanotubes utilized.

Commercial code	NC3150	NC3151	NC3152
Functionalization	None	−COOH	−NH₂
Carbon purity	>95%	>95%	>95%
Average length (μm)	<1	<1	<1
Average diameter (nm)	9.5	9.5	9.5
True density (g/ml)	1.94	1.94	1.94
Bulk density (g/l)	100	250	150
Porosity	0.95	0.87	0.92