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Characterization of polyamide 6/carbon nanotube composites prepared by melt mixing-effect of matrix molecular weight and structure

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ABSTRACT

Effects of molecular weight and structure of polyamide 6 (PA6) on morphology and properties of PA6/MWCNT prepared by melt mixing were investigated. Microscopic analysis showed fine dispersion of MWCNT within low viscosity PA6s due to domination of melt infiltration into MWCNT agglomerate at low viscosity matrices with linear structure. Rheological data indicated good interfacial interaction with no percolation of MWCNT up to 2 wt% loading. DSC thermograms showed nucleating role of MWCNT on crystallization of PA6s with marginal effect on crystallinity. Experimental data supported with micromechanical model showed limited improvement on mechanical properties, but it was closely consistent with degree of dispersion of MWCNT.

1. Introduction

Carbon nanotubes (CNTs) are remarkably attracted by researchers due to their multifunctional features such as superior electrical properties, excellent thermal characteristics and outstanding mechanical performance [1–4]. Additionally, CNTs have shown high specific surface area and extremely large aspect ratio, as high as 1000 [5,6]. Such distinctive geometrical features along with exceptional performance have made CNTs to be promising nanoparticles in polymer nanocomposites for multifunctional applications. However, the effectiveness of CNTs in polymer matrices is greatly dependent on the nanoscale dispersion and development of strong interface/interphase [7–9].

Due to large aspect ratio and strong van der Waals attractions between nanotubes, as-produced CNTs are always available as severely entangled nanotubes leading to highly agglomerated particles. This morphological feature of as-produced nanotubes restricts their dispersion in polymer matrices. However, disagglomeration is often managed by application of suitable mixing process along with an appropriate surface modification of CNTs depending on the type of polymer matrices. Solvent mixing, in-situ polymerization and melt mixing are well documented techniques for preparing polymer/CNT composites. In spite of many difficulties for uniform dispersion of CNT in thermoplastic matrices using melt mixing, the technique is still preferred due to its consistency with current industrial equipment.

In melt mixing process, it is believed that dispersion of single solid particles into viscous polymers can be achieved by the rupture of agglomerates, i.e. a bunch of single particles binding together via interparticle cohesive forces. The rupture of agglomerates basically occurs when the mixing viscous forces developed in mixing chamber overcome cohesive strength of agglomerates. The viscous forces acting on agglomerates are actually dependent on the flow type (elongational and shear flows) and the size of primary particles in an agglomerate [10]. Therefore, polymers with higher viscosity (molecular weight) promoting higher viscous forces seem to be much suitable for successful dispersive mixing. However, it was further explored that besides rupture mechanism, the dispersion of agglomerates can also be achieved by eroding the primary particles from the surface of agglomerates [11]. It was also revealed that polymer melt is also able to infiltrate into porous agglomerates like carbon black (CB) which actually results in weaker agglomerate integrity and lower cohesive strength [11]. Therefore, it is supposed that infiltration facilitates both rupture and erosion mechanisms leading to deagglomeration by applied shear stresses even at lower

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values than uninfiltrated agglomerate cohesive strength. A systematic investigation performed by Kasaliwal et al. [12] on model amorphous polymer matrices, i.e. polycarbonate (PC), exhibited that erosion mechanism could also be essential in deagglomeration of CNT agglomerates and it is most efficient in maintaining nanotube length than rupture mechanism.

Polyamide 6 (PA6) is a semicrystalline thermoplastic with remarkable mechanical properties and versatile processability. These features have made PA6 an ideal candidate for engineering applications in various forms such as films, fibers and molding articles [13,14]. By emerging nanotechnology, polymer nanocomposites based on PA6 have also attracted the attention of researchers to obtain high performance nanocomposites. Clay (silicate layers) might be the most considered nanoparticle in PA6 based nanocomposites in literature [15–18]; however, CNT could be the promising candidate to obtain multifunctional PA6 nanocomposites.

The current works dealing with the mechanical properties of PA6/CNT have examined different issues relevant to the dispersion state of CNT and interfacial interaction such as mixing method, surface characteristics of CNT and the optimum loading of CNT. Accordingly, literature shows a wide range of mechanical property enhancement by incorporation of CNT into PA6, e.g. 10–150% [19,20] improvements in stiffness strength. Significant improvement in mechanical properties of melt mixed PA6/CNT system was first reported by Zhang et al. [21] who observed 115% and 124% increments in elastic modulus and tensile strength, respectively, by incorporating only 1 wt% carboxylated CNT. However, elastic modulus of PA6 filled with 1 wt% CNT reported by Liu et al. [22] and Giraldo et al. [23] showed lower improvement, i.e. almost 30% improvement, compared to Zhang's report [21]. Whereas Bhattacharyya et al. [24] reported 15% and 11% increase in tensile modulus and yield stress, respectively, with incorporation of 1.5 wt% of Single walled carbon nanotube (SWCNT) to PA6.

In an attempt to investigate the role of surface characteristics of CNT, Meng et al. [25] showed that the diamine modified CNT had larger influence on the mechanical properties improvement of PA6/CNT nanocomposites compared to carboxylated ones, while the unmodified CNT exhibited almost no improvement. According to them, increment in elastic modulus and tensile strength by incorporating 1 wt% aminated CNT was 42% and 18%, respectively. Sahoo et al. [26] reported that the melt mixing equipment, i.e. extrusion mixer versus internal mixer, can also influence the final mechanical properties of PA6/CNT. They concluded that the internal mixer leads to higher improvement in tensile strength, i.e. 22% improvement at 1 wt% CNT loading and 70% improvement at 10 wt% loading.

Literature shows that the research on the influence of molecular weight/structure and viscosity of PA6 on PA6 based nanocomposites is mainly limited for the clay filled PA6 systems [27–30]. It was shown that the degree of dispersion of clay and the mechanical properties of PA6/clay nanocomposites are greatly dominated by the molecular weight of PA6. According to Fornes et al. [29], high molecular weight PA6 led to higher degree of exfoliation and significant enhancement in mechanical properties. In the field of CNT based nanocomposites, the same investigation was indeed limited to the influence of matrix properties on the dispersion state of CNT, while the correlation between matrix characteristics and the mechanical properties has not been well explored. In an attempt to investigate the role of melt viscosity of various polymers (except PA6) on the degree of dispersion of CNT, Socher et al. [31] observed that the high matrix viscosity is often resulted in nano-dispersion of CNT due to the higher shear forces; however, fiber shortening becomes worse at this situation [32,33]. As the CNT length is essential on the final mechanical properties of the nanocomposites [34], therefore such nano-dispersion is not necessarily helpful for the mechanical property enhancement with polymers having higher melt viscosity.

As mentioned above, the research works dealing with PA6/CNT nanocomposites reported a wide range of mechanical properties enhancements. In many cases, such improvements have been attributed to the state of dispersion of CNT and strong interfacial interaction. As it is expected, processing (viscosity) and molecular characteristics of PA6 can dominate the dispersion state in melt mixing process. However, as the molecular structure (linearity or branching) of PA6s (as dominant parameters on dispersion state) and their viscosity have not been reported in such studies, the comparison of different results may be difficult. Basically, in addition to the nanoscale dispersion and strong interfacial interaction, other issues such as CNT length, *trans*-crystallinity induced by CNT and filler–filler networking can also be effective in mechanical properties enhancement. Literature is also sparse to correlate these issues with the molecular characteristics of PA6s. Therefore, it seems that a systematic investigation to correlate the molecular structure/melt viscosity with the mechanical performance of polymer/CNT system is missing in literature. Therefore, the aim of this work is to examine the role of molecular characteristics and melt viscosity of PA6 on the morphological and mechanical properties of PA6/MWCNT nanocomposites.

2. Materials and method

Four different PA6s were obtained from different manufactures including Akulon F223D (marked as D) from DSM company of Netherland, Kopa KN 136 (marked as KN) produced by Kolon plastic Inc. Korea, Tecomid NB40 (marked as NB) from Eurotec engineering plastic and Zisamide TP6802 (marked as T) by Zig Sheng Industrial company, Taiwan. The first three PA6s, i.e. D, KN and NB, are injection grades with low viscosities and Zisamide (T) was used as high melt viscosity grade. Multi walled carbon nanotube (MWCNT) functionalized by carboxylic groups (TNMC2, COOH content of 2.5 wt.%, purity > 95%, specific surface area >233 m^2/g) was procured from Timesnano, China.

PA6/MWCNT nanocomposites were prepared by an internal melt mixer (350 E, Brabender, Germany) at 225 °C and 140 rpm. First, PA6s were added into mixing chamber and allowed to be melted for five minutes. Then, MWCNT was added gradually within five minutes and mixing process continued for further 12 min. MWCNT was loaded at various contents of 0.25, 0.5, 1 and 2 wt%. After preparation of samples in internal mixer, the samples were milled slightly using a grinder. The grinded samples were injection molded to obtain test specimens. The temperature zone of injection molding machine was tuned at 220–225–230–235 °C. From injection molding machine, samples for tensile experiments were attained. Each sample was designated by a code indicating type of PA6 and content of MWCNT. For example, sample with KN 136 and 0.25 wt% of MWCNT is denoted by KN-0.25C. Before each stage of preparing or testing, samples were vacuum dried for 18 h at 75 °C.

Tensile properties were measured using HIWA 2126 universal testing machine from Hiwa Eng, Co. Iran, equipped with incremental extensometer. Tensile tests were performed based on ASTM D 638 using a 3 mm thick and 13 mm width of dumbbell shape samples. Optical microscopy (OM) was carried out using Olympus BX51m microscope in transmission mode. Scanning electron microscopy (SEM) images were captured by Field emission SEM (FESEM) using MIRA TESCAN-LMU at voltage of 15 kV. Samples were coated by nano-metric golden layer before image capturing.

Crystallization behavior was investigated using a TA instrument Q100 DSC under nitrogen atmosphere. The samples with the weight of about 5 mg were heated from 40 °C to 250 °C at rate of 10 °C/min and kept for 5 min at this temperature to erase any