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Ultrasonic twin screw compounding of polypropylene with carbon nanotubes, graphene nanoplates and carbon black

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ABSTRACT

The effect of ultrasonic treatment on dispersion of carbon nanotubes (CNT), graphene nanoplates (GNP) and carbon black (CB) in polypropylene (PP) using twin screw extrusion (TSE) was investigated. The ultrasonic power consumption as a function of filler concentration was found to increase for PP/GNP, decrease for PP/CNT and slightly increase for PP/CB. The difference in behavior of the ultrasonic power consumption was related to the void (bubble) concentration in the polymer composites. The efficiency of the ultrasonic treatment was verified through measurements of rheological, electrical and mechanical properties as well as by morphological studies. Ranking of ultrasonic dispersion in composites from best to worse was PP/CB, PP/CNT and PP/GNP. Ranking of the rheological and electrical percolation threshold of composites from low to high was PP/CNT, PP/CB and PP/GNP. The storage modulus and complex viscosity of PP/CNT and PP/CB composites in the low frequency region increased with the ultrasonic treatment while little changes occurred in the PP/GNP composites. In the percolation region, the electrical resistivity of ultrasonically treated composites dropped by 8, 4 and 2 orders of magnitude for PP/CNT, PP/CB and PP/GNP, respectively, compared with the untreated ones. The Young's modulus, yield stress and elongation at break of the PP/CNT and PP/GNP composites were not affected by ultrasonic treatment, but the elongation at break of the treated PP/CB composite at a concentration of 10 wt% increased from 230% to 310%. Morphological studies showed that agglomerates size and agglomerates area ratio of PP/CNT and PP/CB composites reduced with ultrasonic treatment, but not for PP/GNP composites. The incorporation of various fillers increased the crystallization temperature, melt temperature and lamella thickness and decreased the spherulites size. The fillers acted as γ form crystal nucleation agents with the ranking of nucleation ability of CNT > GNP > CB.

1. Introduction

Carbon black (CB), carbon nanotube (CNT) and graphene nanoplatelets (GNP) are three widely used carbon-based nanofillers tailoring the properties of polymers. CB is used for over 100 years, but it was not valued until mixing into the rubbers by S.C. Mote [1]. The main purpose of an addition of CB in rubbers and plastics is to enhance their performance. The size of CB primary particles is usually in the range of 5–100 nm with their aggregates size of 70–500 nm [2]. More recent carbon nanofillers are CNTs and graphene with potentials for applications in various areas, such as catalyst, energy, composites, and

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sensors [3] Tubular structure of CNTs was first found by Iijima [4] who used the arc-discharge evaporation method for their production, similar to production of the fullerene. In the following years, CNTs have gained tremendous attention from both academia and industry, due to their high aspect ratio (~1000), high mechanical properties and high electrical and thermal conductivity. Graphene was known earlier than CNT, but the interest to graphene was not attracted attention until the success in isolating the free-standing single-layer graphene in 2004 [5]. Since then, tremendous research on graphene as well as its composites and applications has been conducted. Several graphene based fillers are expanded graphite, graphite oxide and GNP. As a commercially available filler, GNP is usually obtained from a graphite intercalation compound prepared by treating graphite with sulfuric and nitric acid followed by thermally expanding it in a furnace or microwave [6]. GNP contains tens of graphene layers with the thickness of only about 10 nm [7]. CB, CNT and GNP are considered as zero, one and two dimensional fillers, respectively.

The usage of carbon-based nanofillers in polymers is growing fast. From the viewpoint of industrial application, a polymer nanocomposites preparation method providing good dispersion of nanofillers is highly desirable. Three methods have been widely used to manufacture the composites: in-situ polymerization, solution mixing and melt mixing [8]. Although the solution mixing and in-situ polymerization may achieve better dispersion, the melt mixing is preferable in the industrial practice. Several melt mixing devices have been used to prepare the composites including DSM [9], and DACA [10] microcompounder, ultrasonic twin screw extruder [11], BUSS kneader [12] and HAAKE mixer [13]. The biggest challenge in preparation of polymer-carbon composites is the dispersion of primary agglomerates and the reaggregation. Therefore, how to achieve good dispersion in melt mixing is a challenging problem. To overcome this problem, several methods for surface pretreatment were proposed. In particular, Ajayan and Tour [14] suggested methods to modify the CNT surface through π-π interactions, covalent and non-covalent polymer wrapping. Bose et al. [15] modified CNT using sodium salt of 6-amino hexanoic acid and phosphonium based modifiers. Boehm [16] also provided methods to modify CB by oxidizing the surface of CB and initializing radical polymerization on surface of the CB. During treatment of GNPs by sulfuric acid and nitric acid, oxidation groups may be created. Specifically, due to the presence of hydroxyl, epoxides, carboxyl, and carbonyl groups [17], GNP can be modified by octadecylamine (ODA) [18], maleic anhydride grafted copolymers [19,20] and unsaturated polyesters [21]. These modification methods are aimed to increase the adhesion between the polymer and filler. Several studies have proven that these methods indeed increased the filler dispersion. Liu et al. [22] reported a homogenous dispersion of functionalized MWCNT in PA6. Bhattacharyya et al. [23] encapsulated SWCNTs with styrene maleic anhydride (SMA) and then melt mixed with PA 12. They found a uniform dispersion of SWCNTs in PA 12 due to an increased interfacial adhesion between PA 12 and SWCNTs. Katbab et al. [20] found that the PP-g-MA could help to separate expanded graphite (EG) layers leading to a decrease of the electrical conductivity percolation threshold of PP/EPDM/PP-g-MA/EG from 15 wt% to 7.5 wt%. Kodgire et al. [24] used a modifier, sodium salt of 6-aminohexanoic acid (Na-AHA), to increase the dispersion of MWCNT in PA 6. The existence of 'cation-π' reaction between Na-AHA and MWCNT assisted the debundling of MWCNTs, provided an improved dispersion of MWCNTs in PA 6 and reduced electrical percolation threshold to 0.5 wt%. Another method to increase the nanofiller dispersion is physical pretreatment. The primary agglomerates of CNTs are microns in the size. Therefore, mechanical shearing using ball milling, before melt mixing could be used to induce breakage of the primary agglomerates. Isayev et al. [25] used ball milling to pretreat the carbon nanofibers and then mixed them with polyetherimide (PEI). They found the pretreatment lowered the electrical percolation threshold. Jiang and Drzal [26] used solid state ball milling (SSBM) and solid state shearing pulverization (SSSP) to prepare HDPE/GNP composites reducing the electrical percolation threshold from 10–15 vol% to 3–5 vol%. Clearly, the mechanical and chemical pretreatments could increase the dispersion of nanofillers in polymer matrix.

The first study on ultrasonic treatment of polymer melt under static conditions was carried out in 1954 by Bernhardt [27]. He found that the ultrasonic treatment reduced the viscosity of polymer melts. Later, the ultrasonic treatment was utilized to improve the processability of PP, HDPE, LLDPE, PS and POE during extrusion by lowering torque and die pressure [28–32]. In 1973, Panchenko et al. applied the static ultrasonic treatment to assist the dispersion of kaolin in amino-containing monomer [33]. A number of studies on the ultrasonic treatment of polymer composites were carried out including PEI/CNT [11], polyetherimide (PEI)/CNF [25], LLDPE/clay [30], HDPE/clay [34], PP/clay [35,36], polymethyl methacrylate (PMMA)/clay [37], PS/LDPE/clay [38] and PP/PS/clay [39]. The majority of these studies on the polymer/clay composites indicated a possibility of the ultrasonic exfoliation of the layered structure of clay and its better dispersion. Ryu et al. [38] found the disappearance of the X-ray diffraction peak of clay along with a more uniform dispersion of clay in polymer matrix, as indicated by TEM. Swain and Isayev [34] reported a similar effect on ultrasonic treatment of HDPE/clay composites during extrusion. They found that the exfoliation was related to the residence time in the ultrasonic zone: the longer residence time the more exfoliation level. They also reported improved mechanical properties of the treated composites compared to the untreated ones. CNT and CNF based composites were studied by Isayev et al. [11,25] using ultrasonic single and twin screw extrusion. The dispersion of CNT and CNF in PEI was improved by the ultrasonic treatment as reflected by a higher value of the storage modulus and a lower electrical percolation threshold after the treatment. Although the validity of ultrasonic treatment on improving dispersion of various nanofillers has been proven in the aforementioned studies, our previous study [40] indicated that the ultrasonic treatment only improved dispersion of the expanded graphite, but not of the original graphite in PEI. Therefore, it is very important to compare the efficiency of ultrasonic treatment of polymer composites containing various carbon nanofillers and investigate the most important factors affecting their dispersion.

The main goal of the present study is to carry out a systematic investigation of compounding of various carbon fillers in PP using recently developed ultrasonic TSE in order to elucidate the mechanism of action of ultrasound on their dispersion.