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Effect of hybrid carbon nanotube/short glass fiber reinforcement on the properties of polypropylene composites

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ABSTRACT

The hybrid reinforcement effect of surface treated or untreated carbon nanotube (CNT)/glass fiber (GF); on the morphology, mechanical and electrical properties of polypropylene matrix composites were investigated. Surface treatment of the CNTs was performed by using 3-Amino propyl tri ethoxy silane (APTES). Composites were prepared by means of extrusion and injection molding techniques. FT-IR analysis of the CNT samples revealed the successful surface modification of nanotubes after silane treatment. XRD results showed that chemically functionalized carbon nanotubes have the same cylinder wall and crystalline structure with untreated carbon nanotubes. Tensile and dynamic mechanical analysis (DMA) test results revealed that GF and nanotube reinforced hybrid composites exhibited better tensile strength and modulus values than only GF or CNT reinforced composites. According to all these results, it can be concluded that simultaneous usage of glass fiber and carbon nanotube in the composites increases the reinforcing ability of nanotubes in polymer composites.

1. Introduction

Polypropylene (PP) is one of the widely used commodity polymers and its composites can be used for the production of piping systems, automobile components, flexible packaging as well as containers for food industries [1]. Fillers and reinforcements are added to PP in order to reduce its cost or enhance its mechanical properties. These fillers and reinforcements are talc, calcium carbonate, mica, glass fiber, carbon fiber, etc [2–4]. Glass fiber (GF) is one of the most widely used fiber reinforcements for PP since its properties are suitable for a large number of applications [3]. On the other hand, carbon nanotubes (CNTs) possess to become the next generation reinforcements due to the exceptional high elastic modulus, strength and resilience for PP composites [1]. As it is known from the literature, small amount of CNT in the range of 1–5% in volume increases the mechanical properties of the PP composites [5]. However poor interfacial adhesion between CNT and polymer matrix and non-homogenous dispersion hinder the improved performance of the CNT reinforced composites [6,7]. In addition to this, the chemical structure of PP limits its bonding to glass fiber or CNT surfaces [8]. For these reasons, improvement of the interfacial adhesion between the nanotubes or glass fiber and PP matrix is crucial for the increment of mechanical properties. Interfacial adhesion properties of the glass fiber or CNT reinforced PP composites are studied separately by many researchers in the literature. Some of these studies which focus on the adhesion properties of the glass fiber reinforced PP composites are as follows; Pedrazzoli and Pegoretti showed the possibility to improve the adhesion between GF and PP matrix by dispersing different types and loading level of silica nanoparticles in the polymer matrix [9]. They used non-functionalized and dimethyldichlorosilane-functionalized silica nanoparticles during composite preparation. They found that the interfacial strengths remarkably increased with addition 7 wt.% of surface treated nanoparticles. Xie et al. indicated that mechanical properties of the GF reinforced PP composites increase by using both silane treated glass fiber and matrix modification with maleated polypropylene [10]. Besides, in the absence of maleated PP, the silane types affected the mechanical performance of the PP composites. Etcheverry and Barbosa reported that metallocenic polymerization of propylene onto a GF surface resulted in a promising way to increase the adhesion for the GF reinforced PP composites [11]. They also found that the tensile strength and toughness values of the PP composites were tripled and interfacial shear strength was doubled by using

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this method. Some of the studies which investigated properties of the treated CNT reinforced PP composites are as follows; Zhou et al. prepared multi-wall CNT reinforced PP composites by using raw multi-wall carbon nanotubes (MWCNTs) and MWCNTs functionalized with a silane coupling agent [12]. They showed that functionalized MWCNTs reinforced composite has higher tensile strength than the raw MWCNTs reinforced PP composite. Lee et al. functionalized the MWCNT surface with the octadecylamine (ODA) via CF4 plasma-assisted fluorination and subsequent alkylamination [13]. They observed better dispersion when they used the treated MWCNT in the matrix. Liao et al. produced a novel PP nanocomposite bipolar plate with functionalized MWCNTs by using melt blending [14]. They showed that the flexural strength of nanocomposite bipolar plates which contain DGEBA-functionalized CNT are higher than those of the PP nanocomposite bipolar plates prepared with untreated CNT. In the literature, there are a few studies which investigated the effect of hybrid CNT and GF reinforcement on the properties of the PP composites. One of these studies was performed by Rahmanian et al. [15]. They grown the CNTs on the carbon and glass fiber surfaces by using floating catalyst chemical vapor deposition and they called this system as "hierarchical fibers". Their characterization results showed that all mechanical properties of CNT coated fiber reinforced PP composites were higher compared to those of uncoated short fiber reinforced composites. In another study Barber et al. [8], investigated the interfacial strength between E-glass fibers and an isotactic polypropylene matrix by using single-wall CNTs as stress sensors. For this purpose, an industrial sizing which includes small amount of CNTs was applied to GF surface. They found that interfacial strength variation between coated GF and PP matrix can be easily evaluated by using CNTs as stress sensors. However, to the best of our knowledge there is no study in the literature that deals with PP composites which were reinforced with CNT or treated CNT and glass fiber at the meantime.

In this study, CNT and/or GF reinforced PP composites were prepared by using melt blending and injection molding methods. In the first part of the study, effects of the surface treatment and loading level of CNT on the properties of the PP matrix composites were evaluated. In the second part, it was aimed to investigate the hybrid reinforcement effect of the glass fiber and treated carbon nanotubes on the mechanical properties and electrical resistivity values of the PP matrix composites.

2. Experimental

2.1. Materials

In this study, PP (Emoplen® HP) supplied from Emas Plastik A.S was used as the matrix material. Carbon nanotubes (CNTs) and glass fibers (GFs) were also used as reinforcement materials. Detailed information about the properties of CNT and GF were given in Table 1.

2.2. Carbon nanotube surface treatment

Firstly, CNTs were treated with sulfuric acid (H_2SO_4)/nitric acid (HNO_3) (1:1) mixture to form reactive sites on their surfaces and to remove catalytic residues. The procedure was as follows: 3 g. portion of as-received CNTs were added to 300 ml of acid mixture. The mixture was sonicated for 4 h at 80 °C. Sonication was carried out in a Bandelin sonorex ultrasonic bath and frequency was 35 kHz. Then the mixture was diluted with distilled water/acetone mixture 1:5 by volume, followed by filtering in order to recover the CNTs from the acid mixture. After this, filtered CNTs were washed with excess distilled water/acetone mixture until no residual acid was present (pH of the filtrate distilled water/acetone mixture was greater than 5). Finally, CNTs were dried in the vacuum oven for 24 h at 100 °C.

Acid treated CNTs were treated with 3-Amino propyl tri ethoxy silane (APTES) to modify their surface chemical structure. Firstly, 1.8 g. acid treated CNTs were mixed with 100 ml. of silane/distilled water (2 ml. silane/98 ml. distilled water) solution and were stirred for 5 min so that hydrolysis and silanol formation takes place. Then 300 ml. of ethanol/distilled water (95:5) mixture was added to CNT/silane/distilled water mixture and they were sonicated in the ultrasonic bath for 4 h at 70 °C. After sonication, this mixture was filtered out and silane treated CNTs (SCNTs) were washed with distilled water/acetone mixture. Finally SCNTs were dried in the vacuum oven for 24 h at 100 °C.

2.3. Composite preparation

Carbon nanotube, glass fiber and hybrid reinforced composites were prepared via melt mixing method by using a laboratory scale co-rotating twin-screw mini extruder (DSM Xplore). Compounding was performed at 230 °C barrel temperature for 3 min, with a screw speed of 100 rpm. Compositions of all samples were given in Table 2. Composites were subsequently injection molded with a laboratory scale injection molding machine (DSM Xplore) at 230 °C barrel temperature and injection pressure was 10 bars.

2.4. Carbon nanotube and composite characterization

Fourier Transformed Infrared Spectroscopy (FTIR) analysis was performed by using a Perkin–Elmer Spectrum 100 spectrometer to investigate the surface chemistry of CNT and SCNT and observe the differences between as-received and surface treated CNTs. The infrared spectra of CNT and SCNT were recorded in the range of 400–4000 cm^{-1} by using an Attenuated Total Reflectance (ATR) apparatus. The crystal structure of nanotubes was monitored by using a X-ray diffractometer (XRD, Rigaku MiniFlex II) with a Cu Kα radiation, $\lambda = 0.15418$ nm. The X-ray detector scanned in a 2θ range from 10° to 70° at a speed of 0.02° per minute.

Tensile tests were conducted by using a Lloyd Instrument-LRX Plus model universal testing machine according to ASTM D 638-10 standards at a crosshead speed of 5 mm/min. The izod impact strength tests were performed by using a Ceast machine model 9050 according to ISO 180 standards. Ten specimens were mechanically tested and results were given as an average value with standard deviations. Dynamic mechanical analysis (DMA) was conducted by using a DMA 50 analyzer from 01 dB-Metravib in the tension mode. Storage modulus (E′) values of composites were determined under the dynamic force of 0.001 N, at a constant frequency of 1 Hz, in a temperature range of 25–180 °C and at a heating rate of 1 °C/min. Electrical resistivity values of the composites containing CNT and SCNT were measured with two point probe

Table 1
Carbon nanotube and glass fiber properties.

Material	Trade name and supplier	Properties
Multi walled carbon nanotube	Nanocyl 7000; Nanocyl (Belgium)	Average diameter 10 nm, average length 1.5 μm, purity 90%
Glass fiber	PA1, Cam Elyaf A.Ş.	Average length 4.5 mm, average diameter 13 μm, sized with silane coupling agent