



# Fabrication of polyketone-grafted multi-walled carbon nanotubes using Grignard reagent and their composites with polyketone

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## ABSTRACT

A Grignard reagent containing pyrene, 1-pyrenylmethylmagnesium bromide (PMgBr), was explored as a novel reactive compatibilizer for producing aliphatic polyketone (PK) composites with multi-walled carbon nanotube (MWCNT) that had improved interfacial adhesion and mechanical strength. 1-Bromomethylpyrene (PBr) was adsorbed on MWCNTs and reacted with Mg to produce PMgBr on MWCNTs (MWCNT-PMgBr). PK-grafted MWCNT (PK-g-MWCNT) was prepared by reacting MWCNT-PMgBr with PK, and its composite with PK was fabricated by melt extrusion. The formation of PK-g-MWCNT was examined by spectroscopy, electron microscopy, and thermal analysis. The PK interfacial adhesion energies with MWCNTs were quantified, and the mechanical strengths of their composites examined. PK-g-MWCNT had the highest interfacial adhesion energy with PK among the MWCNTs. The PK/PK-g-MWCNT composite showed better MWCNT dispersion in PK and interfacial adhesion between MWCNT and PK than the PK/pristine MWCNT composite. Consequently, the PK/PK-g-MWCNT composite exhibited higher mechanical strength than the PK/pristine MWCNT composite when the composite contained the same amount of MWCNTs.

## 1. Introduction

Aliphatic polyketone (PK) synthesized using carbon monoxide, ethylene, and propylene as comonomers is a thermoplastic polymer [1–4]. The strong attraction between PK molecules caused by polar ketone groups in the chain backbone gives PK excellent solvent and abrasion resistance, gas barrier properties, and mechanical strength. Many metal parts of automobiles and electronics are being replaced with high performance polymers and their composites with fillers to reduce cost and weight. PK is considered an engineering plastic that can be used for such applications, but its application is limited due to problems such as low heat distortion temperature, dimensional stability, and strength. It is necessary to impart electrical conductivity to the polymer for its use in the exterior panel of an automobile (requiring electrostatic painting) and electronic device parts requiring electrostatic dissipation. PK composites with improved mechanical and thermal properties and electrical conductivities might be fabricated by hybridizing PK with conductive fillers including carbon fiber and carbon nanotubes (CNTs) [5–9].

It was expected that the extraordinary mechanical and electrical properties of CNTs could be imparted to the polymer composite by

hybridizing CNTs with the polymer. However, due to strong attraction between CNTs, the excellent properties of CNTs have not been realized in polymer composites without CNT modification [10–13]. Intensive studies have been conducted to produce polymer composites containing CNTs finely dispersed in polymer matrices by modifying the CNT surfaces [6–9,14–20]. Polymer composites containing surface-functionalized CNTs by chemical reaction and physical adsorption exhibited improved mechanical strength, interfacial adhesion between CNT and polymer, and CNT dispersion in the polymer matrix relative to polymer composites containing pristine CNTs [14–20]. However, as far as we know, there are few studies dealing with the preparation of PK composites with modified CNTs that exhibit improved mechanical and interfacial properties by overcoming the strong interaction between PK molecules and the strong entanglement between CNTs.

As a preliminary study, the interfacial adhesion and CNT dispersion of PK composites containing CNTs surface-modified with various functional groups including amine, acyl chloride, and hydroxyl groups were examined. PK composites containing functionalized CNTs exhibited similar interfacial adhesion energies and CNT dispersion as those containing pristine CNTs. In this study, CNTs grafted with PK were prepared and then melt extruded with PK to produce composites

*Abbreviations:* PMgBr, 1-pyrenylmethylmagnesium bromide; PK, aliphatic polyketone; MWCNT, multi-walled carbon nanotube; PBr, 1-Bromomethylpyrene; MWCNT-PMgBr, 1-pyrenylmethylmagnesium bromide on multi-walled carbon nanotube; PK-g-MWCNT, polyketone-grafted MWCNT

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having improved interfacial adhesion between PK and CNTs and improved CNT dispersion in a PK matrix. Since aliphatic PK does not react with organic functional groups, 1-pyrenylmethylmagnesium bromide (PMgBr), a pyrene derivative containing Grignard reagent, was adsorbed on the CNT surface and then reacted with PK to form PK-grafted CNTs. The formation of PK-grafted CNTs was examined by spectroscopy, electron microscopy, and thermal analysis. PK adhesion energies with CNTs were quantified from the contact angle between PK and CNT. CNT dispersion in the composites and the mechanical properties of the composites were investigated.

## 2. Material and methods

### 2.1. Materials

Polyketone (PK, M330A, number average molecular weight: 19,500 g/mol) was provided by Hyosung (Seoul, Korea). According to the supplier, PK was a random copolymer composed of ethyl ketone and propyl ketone (mole ratio: 16/84) and its density and melting temperature were 1.24 g/cm<sup>3</sup> and 216 °C, respectively. Pristine multi-walled carbon nanotubes (MWCNTs, CM250, diameter range: 10–15 nm, average length: 1.6 μm) supplied by Hanwha Nanotech. (Seoul, Korea) were used as filler for PK composite. 1-Bromomethylpyrene (PBr; used as an interfacial agent), magnesium (Mg; used to produce Grignard compound of PBr), anhydrous tetrahydrofuran (THF; used as a dispersing agent for MWCNTs), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP; used as a solvent for PK) were purchased from Sigma-Aldrich (Milwaukee, WI, USA).

### 2.2. Preparation of functionalized MWCNT and PK-grafted MWCNT

Pristine MWCNTs were functionalized by the physical sorption of PBr. As shown in Fig. 1, PBr (0.25 g) was dissolved in THF (200 mL) and then pristine MWCNTs (0.5 g) were dispersed in THF solution under sonication at 30 °C for 2 h. The resulting solution was vacuum filtered and dried in an oven at 70 °C for 24 h to remove the remaining solvent (hereafter referred to as “MWCNT-PBr”). The provided PK pellets (5 g) were dissolved in HFIP (500 mL) and then precipitated in acetone (2000 mL) to form PK fine powder. The resulting precipitate was filtered and dried in a vacuum oven at 100 °C for 48 h to remove moisture and the remaining solvent.

The prepared MWCNT-PBr (0.5 g) was dispersed in anhydrous THF (200 mL) under nitrogen to avoid contact with moisture, and Mg powder (1 g) was added to the solution using a dropping funnel to form

1-pyrenylmethylmagnesium bromide (PMgBr) on MWCNTs (hereinafter referred to as “MWCNT-PMgBr”). The prepared PK powder (3 g) was added to the solution and reacted with MWCNT-PMgBr at 30 °C for 12 h to graft PK on the MWCNTs. The recovered product was dispersed in HFIP (200 mL) under sonication at 30 °C for 2 h and vacuum filtered to remove PK ungrafted on MWCNTs. This procedure was repeated five times to completely remove unreacted PK from MWCNTs. The resulting product was dried in an oven at 100 °C for 24 h (hereafter referred to as “PK-g-MWCNT”).

Preparation of MWCNT-PBr and PK-g-MWCNT was explored by Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Scientific, USA), X-ray photoelectron spectroscopy (XPS, K-Alpha+, Thermo Scientific, USA), field emission scanning electron microscopy (FE-SEM/EDS, Sigma, Carl Zeiss, Germany), and high resolution transmission electron microscopy (HR-TEM, JEM 2000EXII, Jeol, Japan). The amount of PK-grafted on MWCNT was examined by thermogravimetric analysis (TGA, TGA-2050, TA Instruments, USA).

### 2.3. Preparation and characterization of PK composites

Melt extrusion was performed with a twin extruder (BA-30, Bau Technology, Kyunggi-do, Korea) to fabricate PK composites containing MWCNTs. PK pellets and the desired amount of MWCNTs were fed into an extruder using a feeding equipment and melt extrusion was performed in the temperature range 235–250 °C with screw speed 200 rpm. The pelletized extrudates were dried at 100 °C for 12 h and subjected to injection molding to prepare specimens for tensile testing according to American Standards Testing Method (ASTM) specification D-638. Injection molding was conducted at 240–260 °C with mold temperature 70 °C.

The tensile test was conducted using a universal testing machine (UTM-301, R&B Co, Korea) at cross-head speed 5 mm/min. Five specimens were tested to determine the tensile properties of the composite and the average value was reported. The morphology of the fractured surface after tensile test was observed with FE-SEM to examine MWCNT dispersion in the PK matrix and PK adhesion with MWCNT at the interface. The amount of PK remaining on the MWCNTs after extrusion was measured with TGA. The PK composite (1 g) dissolved in HFIP (100 mL) was vacuum filtered to remove ungrafted PK. Further PK extraction from the resulting MWCNTs was conducted using a Soxhlet extractor. The obtained MWCNTs were first dispersed in HFIP and PK extraction was performed at 50 °C for 24 h. After extraction, the amount of PK-grafted on MWCNT and its morphology were examined using TGA and HR-TEM, respectively. The melting temperature and crystal

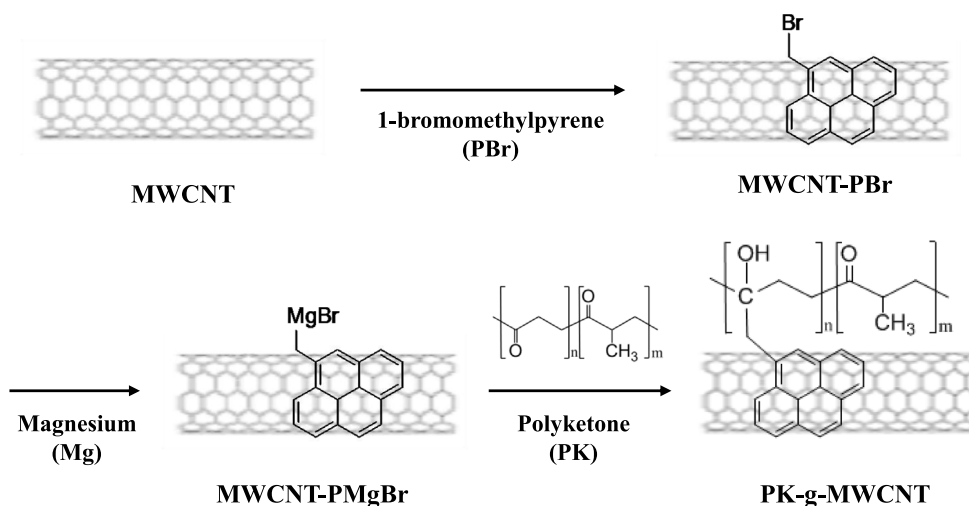


Fig. 1. Synthetic procedure for PK-g-MWCNT using Grignard reagent containing pyrene.

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