



# Design and fabrication of morphologically controlled carbon nanotube/polyamide-6-based composites as electrically insulating materials having enhanced thermal conductivity and elastic modulus



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## ARTICLE INFO

### Article history:

Received 9 May 2016

Received in revised form

25 January 2017

Accepted 25 January 2017

Available online 30 January 2017

### Keywords:

Carbon nanotubes

Nano composites

Polymer-matrix composites

Mechanical properties

Thermal properties

## ABSTRACT

Electrically insulating polymer materials having high thermal conductivity and elastic modulus are in high demand for next-generation electric machines and electronic devices. Carbon nanotubes (CNTs) show extremely high thermal conductivity and elastic modulus; however, even the addition of a few CNTs to polymers leads to them losing their electrically insulating properties. Herein, morphologically controlled multiwalled CNT (MWCNT)/polyamide-6 (PA6)/poly(*p*-phenylene sulfide) (PPS) composites, having high thermal conductivity, electrical insulation and elastic modulus, were designed and fabricated. First, MWCNT/PA6/PPS/EGMA composites comprising a PA6 matrix and MWCNT-localized PPS domains surrounded by shell-layers formed from poly(ethylene-co-glycidyl methacrylate) (EGMA) were prepared. The thermal conductivity of the composites was improved without losing the volume resistivity. However, these composites showed low elastic modulus, especially at high temperature, due to MWCNT localization and the existence of EGMA. Therefore, MWCNT/PA6/PPS/(3-glycidyloxypropyl)trimethoxysilane (GOPTS) composites having a novel morphology were designed and fabricated using GOPTS as a highly reactive shell-forming agent. In this composite, the MWCNT ends were capped with nano-sized PPS domains (MWCNT-PPS nanodomain-linked structure) to prevent electrically conductive paths forming, and MWCNT-PPS nanodomain-linked structures were uniformly dispersed in the PA6 matrix, leading to much enhanced elastic modulus and heat resistance in addition to improved thermal conductivity and electrically insulating properties. These composites containing CNT-nanodomain-linked structures are promising as electrically insulating materials for various applications including high-performance electric machines and electronic devices.

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## 1. Introduction

Anisotropic nanocarbons, such as carbon nanotubes (CNTs) [1–6] and graphenes [7–11], have attracted extensive attention for various potential applications owing to their interesting properties, such as their extremely high thermal conductivity, electrical conductivity, and elastic modulus (Young's modulus). In particular, CNTs have already been produced by several companies and their production capacity has greatly increased over the past couple of decades [1]. However, their applications have been mostly limited to cases where electrical conduction is required, such as in polymer composites, antistatic coatings and films, and as additives for

battery electrodes [1,2]. In these applications, the individual CNTs are usually required to be homogeneously dispersed in solvents or matrices [2]. Therefore, various methods have been developed for dispersing them in solvents or polymer matrices [2,3,5,6,11–14]. The incorporation of small amounts of individually dispersed CNTs into polymer matrices leads to increased thermal conductivity, electrical conductivity and elastic modulus [2,3,15].

Recently, in the fields of next-generation electric machines and electronic devices for future vehicles and communication equipment, insulating materials having high thermal conductivity, elastic modulus and heat resistance are in high demand. Highly effective heat-dissipation from heat sources of the aforementioned applications is needed for their miniaturization, high performances and reliability [16,17]. Polymers are increasingly utilized in the automotive, packaging, and electronic industries, because they are

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insulating materials having good molding processability and light weight. However, polymers show extremely low thermal conductivity ( $\sim 0.2 \text{ W m}^{-1} \text{ K}^{-1}$ ); therefore, the addition of small amounts of CNTs ( $\sim 2000\text{--}6000 \text{ W m}^{-1} \text{ K}^{-1}$ ) or graphenes ( $\sim 5000 \text{ W m}^{-1} \text{ K}^{-1}$ ) into polymers has been used to improve their thermal conductivity [2,3,18]. However, CNTs and graphenes have not actually been applied in highly electrically insulating polymers because even the addition of a few CNTs or graphenes tends to give rise to high electrical conductivity [2,15]. Meanwhile, electrically insulating thermally conductive nanofillers such as nanodiamonds (NDs) [19], boron nitride nanotubes (BNNTs) [20], and BN nanosheets (BNNSs) [21] can also be candidates. However, the thermal conductivity of ND/polymer composites containing a low ND loading ( $< 10 \text{ vol}\%$ ) is relatively low [19] compared with that of anisotropic nanocarbon/polymer composites. In addition, the cost of producing BNNTs and BNNSs is generally higher than the case of CNTs. Therefore, to use CNTs as nanofillers to increase the thermal conductivity of electrically insulating polymers, we previously fabricated a CNT/polymer composite having a controlled morphology, which exhibited enhanced thermal conductivity without losing electrical insulation [16]. This composite comprised a poly(*p*-phenylene sulfide) (PPS) matrix and multi-walled CNT (MWCNT)-localizing high-density polyethylene (HDPE) domains encapsulated by shell-layers formed from poly(ethylene-co-glycidyl methacrylate) (EGMA). Controlling the affinities of MWCNTs and the constituent polymers for each other was key to the fabrication of this novel morphology, and MWCNTs showed higher affinity for HDPE than for PPS. However, the use of HDPE led to low elastic modulus and heat resistance of the composites because HDPE itself had a very low flexural modulus (0.8–1.1 GPa) and heat resistance (glass transition temperature (T<sub>g</sub>):  $\sim 120 \text{ }^\circ\text{C}$ , melting point (mp):  $132\text{--}135 \text{ }^\circ\text{C}$ ) compared with engineering polymers and super-engineering polymers. In contrast, PPS, which is much more expensive compared with HDPE, has a very high flexural modulus ( $\sim 4 \text{ GPa}$ ) and is heat resistant (T<sub>g</sub>:  $\sim 90 \text{ }^\circ\text{C}$ ,  $\sim \text{mp}$ :  $\sim 285 \text{ }^\circ\text{C}$ ). Therefore, using PPS as the domain polymer (minor component) instead of the matrix polymer (major component) is very effective at reducing the cost. Meanwhile, polyamide-6 (PA6) is a cheap, common engineering polymer, which is very widely used in the automotive, packaging, and electronic industries. It also exhibits higher flexural modulus ( $\sim 2.8 \text{ GPa}$ ) and heat resistance (T<sub>g</sub>:  $\sim 50 \text{ }^\circ\text{C}$ , mp:  $\sim 225 \text{ }^\circ\text{C}$ ) than HDPE. Therefore, a similar type of morphology employing PA6 as matrix polymer (major component), and PPS as the domain polymer (minor component) would be very attractive as a candidate material for next-generation electric machines and electronic devices requiring high elastic modulus and heat resistance, in addition to high thermal conductivity and good electrical insulation.

Here, we demonstrate that a material with a similar morphology can be fabricated using a PA6 matrix, PPS domains, MWCNTs, and EGMA as a shell-forming agent, which achieves high thermal conductivity and good electrical insulation. Moreover, in order to improve elastic modulus and heat resistance of the composite, we design and fabricate a novel MWCNT/PA6/PPS composite having a controlled morphology containing MWCNT-PPS nanodomain-linked structures by using a highly reactive shell-forming agent. This morphology is very effective at achieving a much higher elastic modulus and heat resistance, in addition to enhanced thermal conductivity and good electrical insulation.

## 2. Experimental section

### 2.1. Materials

MWCNTs (NT-7, chemical vapor grown MWCNTs, diameter

40–90 nm (mean diameter  $\sim 65 \text{ nm}$ ), length 5–15  $\mu\text{m}$  (mean length  $\sim 9.6 \mu\text{m}$ ), purity  $> 99.5 \text{ wt}\%$ , specific gravity 2.1, Raman intensity ratio of G-band at  $\sim 1590 \text{ cm}^{-1}$  to D-band at  $\sim 1350 \text{ cm}^{-1}$ , i.e., G/D ratio,  $\sim 8.0$ ) were purchased from Hodogaya Chemical Co., Ltd., Japan and used as received. Mean diameter and mean length of MWCNTs were estimated as average values ( $N = 20$ ) using scanning electron microscope (SEM) images (Fig. S1). PPS (W202A, linear type, specific gravity 1.35) was purchased from Polyplastics, Co., Ltd., Japan. PA6 (1022B, specific gravity 1.14) was purchased from UBE industries, Ltd., Japan. EGMA (Bondfast E, ethylene/glycidyl methacrylate = 88/12 wt%, specific gravity 0.94) was obtained from Sumitomo Chemical Co., Ltd., Japan. 3-Glycidyloxypropyltrimethoxysilane (GOPTS; purity  $\geq 98\%$ , density  $1.07 \text{ g ml}^{-1}$ ) was obtained from Sigma-Aldrich Corporation, USA.

### 2.2. Preparation of MWCNT/PA6-based composites

#### 2.2.1. Preparation of MWCNT/PA6/PPS/EGMA composites

1 vol% (1.78 wt%) of MWCNTs, 71 vol% (68.61 wt%) of PA6, 21 vol% (24.03 wt%) of PPS, and 7 vol% (5.58 wt%) of EGMA were fed into a twin-screw microrheology compounder (HAAKE-MiniLab, Thermo Scientific) and melt-blended at a temperature of  $290 \text{ }^\circ\text{C}$  and a screw rotation rate of 200 rpm (co-rotational twin screw) for 5 min in an  $\text{N}_2$  atmosphere. The MWCNT/PA6/PPS/EGMA (1/71/21/7 vol%, 1.78/68.61/24.03/5.58 wt%) composites were obtained after drying under vacuum at  $80 \text{ }^\circ\text{C}$  for 12 h.

#### 2.2.2. Preparation of MWCNT/PA6/PPS/GOPTS composites

1 vol% (1.76 wt%) of MWCNTs, 77.5 vol% (74.03 wt%) of PA6, 21 vol% (23.76 wt%) of PPS and 0.5 vol% (0.45 wt%) of GOPTS were fed into a twin-screw microrheology compounder (HAAKE-MiniLab, Thermo Scientific) and melt-blended at a temperature of  $290 \text{ }^\circ\text{C}$  and a screw rotation rate of 200 rpm (co-rotational twin screw) for 5 min in an  $\text{N}_2$  atmosphere. The MWCNT/PA6/PPS/GOPTS (1/77.5/21/0.5 vol%, 1.76/74.03/23.76/0.45 wt%) composites were obtained after drying under a vacuum at  $80 \text{ }^\circ\text{C}$  for 12 h.

## 3. Results and discussion

Fig. 1 (a) and (b) show schematic diagrams of a CNT/polymer composite having high thermal conductivity and good electrical insulation, which we previously designed and fabricated [16], and a novel CNT/polymer composite having high elastic modulus in addition to high thermal conductivity and good electrical insulation, respectively. In previous work [16], the CNT/polymer composites shown in Fig. 1 (a) consisted of a PPS matrix and CNT-localized HDPE domains surrounded by shell-layers formed from EGMA. HDPE showed higher affinity for CNTs than PPS, and EGMA exhibited a very low affinity for CNTs, resulting in the CNTs being locked into the HDPE domains. This morphology counts on its phase structure wherein CNTs are selectively existed in HDPE domains encapsulated by EGMA, which prevents forming electrically conductive pathways between the CNTs in the whole composite.

In this study, PA6 was selected as the major component (matrix polymer) instead of PPS. PPS was used as the minor component (domain polymer) because it has relatively high affinity for CNTs due to  $\pi\text{--}\pi$  interactions between the phenylene groups of PPS and the CNT surface [22–24], in addition to its higher elastic modulus and heat resistance than HDPE. MWCNT was used as CNT because it is much cheaper than single-walled CNTs. As a preliminary study, MWCNT (1 vol%), PA6 (78 vol%), and PPS (21 vol%) were mixed by melt-blending using a twin-screw microrheology compounder under conditions of  $290 \text{ }^\circ\text{C}$  and 200 rpm. The viscosity of PPS (melt viscosity at  $1216 \text{ s}^{-1}$  and  $290 \text{ }^\circ\text{C}$ :  $57.4 \text{ Pa s}$ ) is higher than that of PA6 (melt viscosity at  $1216 \text{ s}^{-1}$  and  $290 \text{ }^\circ\text{C}$ :  $39.9 \text{ Pa s}$ ). Therefore, from

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