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# One-step enrichment of silica nanoparticles on milled carbon fibers and their effects on thermal, electrical, and mechanical properties of polymethyl-vinyl siloxane rubber composites

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ABSTRACT

It is critical to develop new approaches of preparing engineered carbon-based fillers for high-performance applications. Herein, silica nanoparticles enriched milled carbon fibers (MCFs@$SiO_2$) as novel thermal conductive and electrical insulating filler was synthesized through a simple and rapid sol-gel reaction method within one hour before their incorporation into polymethyl-vinyl siloxane rubber (MVSR). Fourier transform infrared spectrometer (FT-IR) and X-ray photoelectron spectrometer (XPS) were applied to analyze the surface chemical structure of synthesized MCFs@$SiO_2$, results of which demonstrated the existence of unhydrolyzed oxyethyl groups that are beneficial to improve the compatibility with polymer matrix. Enrichment mechanism of silica nanoparticles on milled carbon fibers was also described. The MVSR composites with a 20 vol.% MCFs@$SiO_2$ loading showed 109.7% higher thermal conductivity compared to that of neat MVSR and an excellent electrical volume resistivity of $1.04 \times 10^9\ \Omega\,cm$ owing to the silica nanoparticles layer. Besides, their tensile strength increased by 145.7%, resulting from the good compatibility between MCFs@$SiO_2$ and MVSR which was confirmed by scanning electron microscope observations.

## 1. Introduction

With the rapid development of lightweight and miniaturized electronic equipment, excess heat resulting from the high-density electronics brings about irreparable damage and short lifetime to the devices [1–3]. Therefore, advanced materials with high thermal conductivity, e.g. thermal interface materials (TIMs) and packaging materials, etc., are urgently demanded [4,5].

To address this issue, high thermally conductive fillers are incorporated into polymer matrix to improve thermal conductivity of the resulting composites [6–9]. Among these fillers, carbon-based fillers, i.e. carbon nanotubes [10,11], graphite [12,13], and carbon fibers [14,15], are widely investigated owing to their high aspect ratio and thermal conductivity resulting in formation of thermally conductive network in polymer matrix easily. However, the crystalline carbon-based fillers make the composites not only thermally but also electrically conductive, which lead to electron leakage [16,17]. To overcome this issue, many attempts have been made by covering insulating materials on surface of carbon-based fillers to block electron transfer. Cui et al. [18] synthesized silica coated multi-walled carbon nanotubes. Yan and his co-workers [19] prepared boron nitride coated multi-walled carbon nanotubes. Chio et al. [20] fabricated silica coated graphite. However, these methods are either complicated (acid oxidation, etc.) or time-consuming (more than 12 h). Besides, the high cost of nanomaterials limits their further application in engineering.

Carbon fibers (CFs), due to low coefficient of thermal expansion and outstanding mechanical characteristics, have been widely used in thermal conductive polymer composites [21,22]. However, agglomeration of CFs (even short cut CFs) in thermosetting resins greatly blocks their enhancement in thermal conductivity of polymer composites. Milled carbon fibers (MCFs) recycled from CFs waste have the advantages of dispersing easily in resins and being inexpensive. Furthermore, the experience of surface heat treatment, mechanical grinding, sieving, milling, and drying during the recovery process results in free from binder of MCFs [23–25], which is in favor of further surface functionalization. Therefore, it is of practical significance to

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**Table 1**
Physical properties of MCFs.

| Item | Density (g/cm$^3$) | Diameter (μm) | Mesh | Aspect ratio | Resistivity (Ω·cm) | Thermal conductivity (W/(m·K)) |
|---|---|---|---|---|---|---|
| MCFs | 1.75 | 7 | 30–1000 | 2:1–8:1 | $1.5 \times 10^{-3}$ | 20–40 |

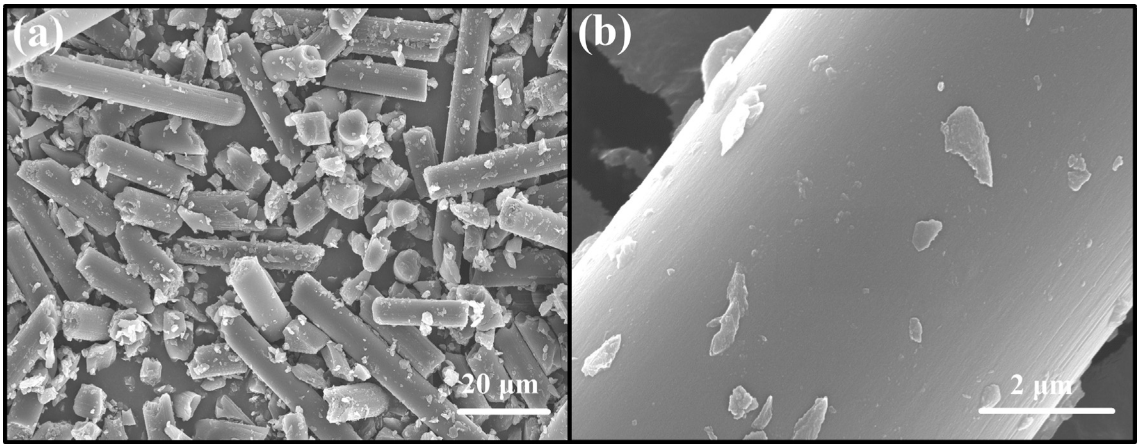



**Fig. 1.** Microscopy images of MCFs: (a) ×1000 and (b) ×15,000.

**Table 2**
The amounts of $NH_4OH$ for silica nanoparticles enrichment on MCFs.

| NO. | $NH_4OH$ (wt. %, 4.0 g) | Ammonia solution (25.0–28.0 wt.%, g) | $H_2O$ (g) | MCFs (g) | EtOH (mL) |
|---|---|---|---|---|---|
| 1 | 1 | 0.165 | 3.835 | 0.2 | 50 |
| 2 | 5 | 0.814 | 3.186 | | |
| 3 | 10 | 1.600 | 2.400 | | |
| 4 | 15 | 2.356 | 1.644 | | |

**Table 3**
The amounts of TEOS for silica nanoparticles enrichment on MCFs.

| NO. | TEOS (wt.% to MCFs) | TEOS (g) | MCFs (g) | EtOH (mL) |
|---|---|---|---|---|
| 1 | 25 | 0.05 | 0.2 | 50 |
| 2 | 50 | 0.10 | | |
| 3 | 75 | 0.15 | | |
| 4 | 100 | 0.20 | | |

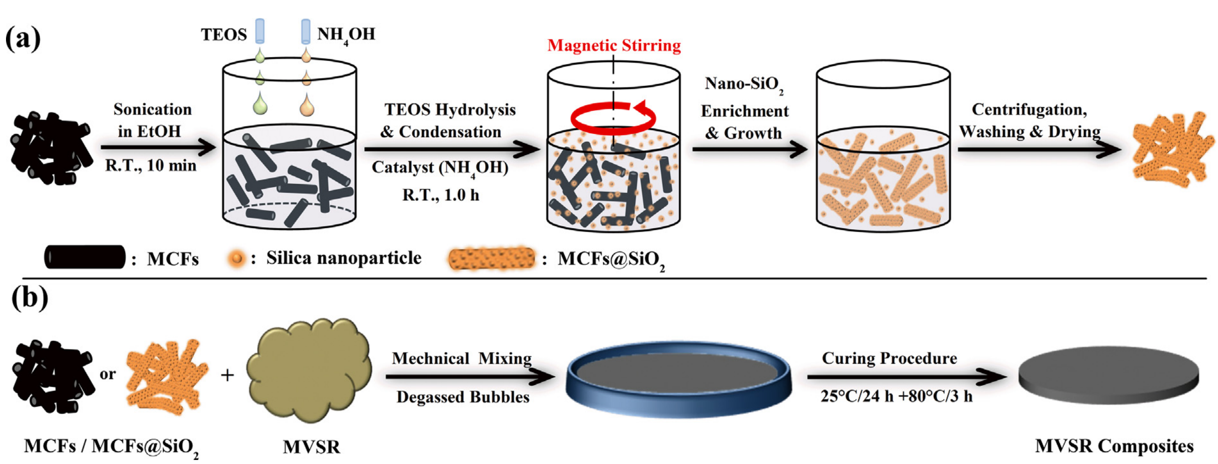
investigate insulating materials coated MCFs for improving thermal conductivity and electrical insulating properties of polymer composites.

In this paper, for the first time, silica nanoparticles were enriched on the surface of MCFs directly within 1.0 h, and the effect of amounts of $NH_4OH$ and TEOS on morphology of silica nanoparticles enriched MCFs (MCFs@$SiO_2$) was investigated. MCFs@$SiO_2$ was applied as thermal conductive and electrical insulating fillers in polymethyl-vinyl siloxane rubber. The thermally conductive, electrical insulating, rheological, and mechanical properties of MCFs@$SiO_2$ filled polymethyl-vinyl siloxane rubber composites (MCFs@$SiO_2$/MVSR) were studied systematically to guide practical application.

## 2. Experimental

### 2.1. Materials

Polydimethyl-vinyl siloxane (viscosity 3000 mPa·s, vinyl content 0.22 wt.%), ploymethyl-hydro siloxane (viscosity 29 mPa·s, hydride content 0.12 wt.%) was synthesized in our laboratory. Polymethyl-vinyl siloxane rubber (MVSR) was prepared by mixing polydimethyl-vinyl siloxane and ploymethyl-hydro siloxane in proportion (Si—H/




**Scheme 1.** Preparation processes of (a) MCFs@$SiO_2$ and (b) MVSR composites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)