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Enhanced thermal conductive property of epoxy composites by low mass fraction of organic–inorganic multilayer covalently grafted carbon nanotubes

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) have been widely used as thermal conductive filler for polymers during the past decades. However, the high electrical conductivity and serious agglomerate phenomenon of MWCNTs hamper their applications in some specific fields. In this work, multi-walled carbon nanotubes (MWCNTs) were coated with insulated inorganic nanosilica (nano-SiO_2) *via* the Stober method and further modified by the organic 1,1′-(Methylene di-4,1-phenelene) bismaleimide (BMI) *via* nucleophilic addition reaction to prepare MWCNTs@SiO_2-g-BMI nanocomposite and then used it to modify the epoxy resin (EP). The new chemical-functionalization method can improve the homogeneous dispersion of MWCNTs in many organic solvents. The MWCNTs@SiO_2-g-BMI/EP nanocomposites at a low loading fraction of 1.25 wt % showed a 125.5% higher thermal conductivity compared to the neat EP composite. Moreover, an excellent electrical volume resistivity (about 2.9076×10^{15} Ω cm) of MWCNTs@SiO_2-g-BMI/EP nanocomposite was also realized. The high thermal conductivity and electrical resistivity can be explained in terms of the reduced thermal boundary resistance and restrictive inter-tube charge transport by the nano-SiO_2 shell. Besides, the well-chosen BMI can enhance the dispersity and interfacial interaction between MWCNTs and EP matrix. This approach provides a strategy to enhance the thermal conductivity and simultaneously possess electrical insulation of EP materials with ultra-low filler content.

1. Introduction

The development of miniaturized and lightweight electronic equipment yields high density electronics resulting excess heat which leads to irreparable damage to the electronic device. For implementation in these emerging markets, advanced thermal interface materials with high thermal conductivity and electrical insulating properties need to be developed and fabricated [1–3].

Carbon nanotubes (CNTs) as fillers have been widely studied in view of their admirable intrinsic properties such as thermal conductivity (K) [4], mechanical strength [5] and electrical conductivity (σ) [6]. In theory, according to Nan's model, CNTs should increase a polymer's thermal conductivity by six times at a weight fraction of 0.1 wt % [7,8], and the thermal conductivity of a composite filled with 1 vol % CNTs can be fifty times than pure polymer using Maxwell's mixing theory [9]. However, based on experimental findings [10], the thermal conductivity of CNTs/polymer materials was inconsistent with these predictions due to the huge boundary resistance of heat transfer between matrix material and CNTs (about 10^{-7} m^2 kW^{-1}) [11]. This originated from the modulus mismatch and large difference in the phonon density of states called Kapitza resistance [12]. Moreover, CNTs tend to form entangled agglomerates just like ropes and bundles due to the high aspect ratio (up to 1000) of CNTs and the very strong van der Waals forces among CNTs having underdeveloped solubility in most solvents [13], which leads to poor dispersion of CNTs when incorporated the CNTs into the polymer matrix. Furthermore, the surfaces of nanotubes are atomically smooth and lack of interfacial bounding sites, which restricts the heat transfer from the polymer matrix to the CNTs. Therefore, enhancing the homogeneous dispersion and

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the interfacial interaction between the CNTs and the polymer matrix along with decreasing the thermal boundary resistance will be the critical technique to effectively utilize the intrinsic properties of CNTs.

Much attention has been paid to overcome these issues by chemical-functionalization methods to modify the CNTs [14]. Carlos et al. [15] used *in situ* polymerization, Gong et al. [16] employed an non-ionic surfactant and Zhu et al. [17] used chemical acid treatment and subsequent fluorination to promote the dispersion of CNTs in polymer matrices. However, the chemical-functionalization that works well for improving the homogeneous dispersion and the interfacial interaction may not necessarily result in reducing the thermal boundary resistance between the CNTs and the polymer matrix [6]. Moreover, in the microelectronics industry, it is not only very important to increase thermal conductivity, but also to maintain high electrical insulation properties and mechanical properties of the polymer materials, especially in electronic packaging and printed circuit board (PCB) fields. However, after conventional chemical-functionalization, the uniform dispersion of CNTs doesn't contribute to the electrical insulation and even easily lead to a fall in electrical insulation of the final composites. Thus, new chemical-functionalization methods should be further researched and developed for highly thermal conductive and electric-insulating composites.

Based on this, we synthesized a core–shell structured MWCNTs@SiO_2-g-BMI nanocomposite (Scheme 1) which had the features of high heat conduction and electric-insulating. For the core–shell structured MWCNTs@SiO_2-g-BMI nanocomposite, the main factors for the construct are as follows: (i) The function of nano-SiO_2 shell can reduce the modulus mismatch between MWCNTs and polymer matrix. Thus, the interfacial thermal resistance will be reduced and the thermal conductivity of MWCNTs-based materials will be improved. Besides, inorganic insulating nano-SiO_2 shell can increase tunneling potential barriers and restrict the inter-tube charge transport [18]. Furthermore, the electrically conductive network of MWCNTs is effectively avoided. (ii) The effect of BMI can increase the uniform dispersion and interfacial interaction between MWCNTs and polymer matrix. Additionally, since the well-chosen BMI organic molecule has symmetric properties of the polar group, the polarity activity of BMI is constrained and offset. Consequently, the BMI can enhance the dispersity of MWCNTs without degrading the insulating performance of the polymer materials. Epoxy resins have been extensively used in various electronic devices, because of their unique properties such as excellent bonding strength, outstanding chemical stability, superior electric insulation performance and low cost [19–21], however, their low thermal conductivity has limited its further development. To overcome these problems, the novel structured MWCNTs@SiO_2-g-BMI was introduced into the commercial EP and its potential applications as heat conductors and electric insulation for EP composites were investigated and discussed.

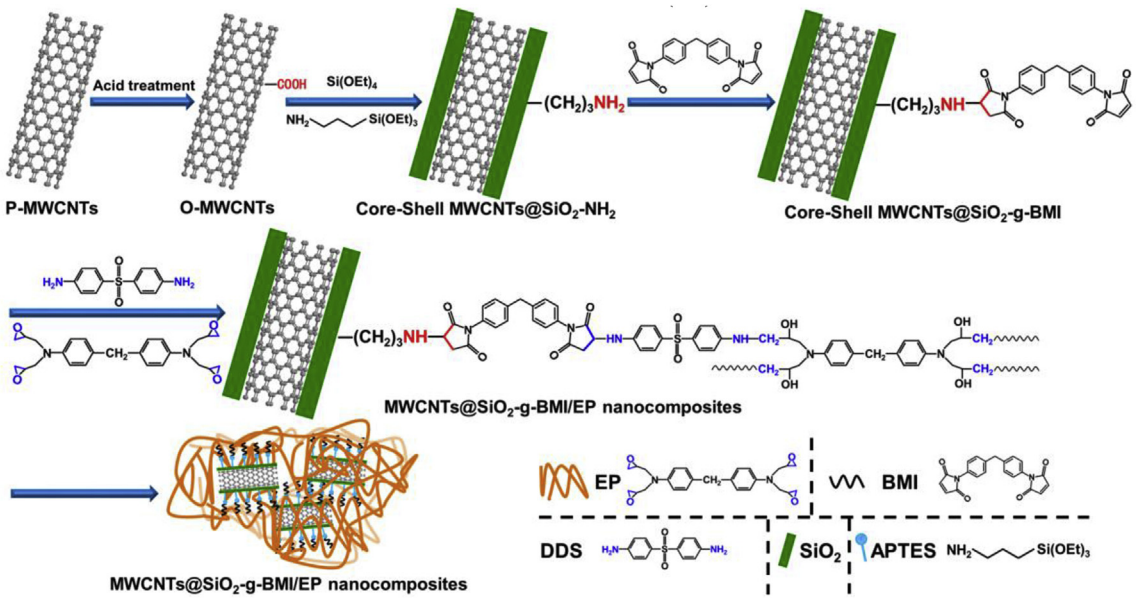
2. Materials and experimental methods

2.1. Materials

Pristine MWCNTs (P-MWCNTs; purity > 95%) with an average length of 5–15 μm and diameter of 30–130 nm were purchased from J&K Chemical Reagent Co., Ltd. γ-aminopropyltriethoxysilane (APTES) was supplied by Yaohua chemical plant (Shanghai, China). 1,1′-(Methylene di-4,1-phenelene) bismaleimide (BMI, purity >95%) were used as received from Shuangma new material technology Co., Ltd. (Honghu, China). Tetraethyl orthosilicate (TEOS), sulfuric acid (95%–98%), nitric acid (65%–68%), hydrochloric acid (36%–38%), chloroform, N, N-dimethylformamide (DMF) and acetone were all obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and the purity level was analytical grade. Epoxy resin (tetraglycidyl 4,4′-diaminodiphenyl methane) was supplied by Huayi resin Co., Ltd. (Shanghai, China). 4,4′-diaminodiphenyl sulfone (DDS) was purchased from Yingyuan Chemical Co., Ltd. (Shanghai, China). Deionized water was employed in the syntheses.

2.2. Experimental methods

After carboxylation of pristine MWCNTs (P-MWCNTs), the tetraethyl orthosilicate (TEOS) solution was slowly dropped into the



Scheme 1. Overall procedures for functionalization of P-MWCNTs by nano-SiO_2 and subsequent BMI and the schematic of the MWCNTs@SiO_2-g-BMI/EP nanocomposite preparation. For simplicity, on the surface of MWCNTs, only one functional group is shown.