



# Hybrid network structure and thermal conductive properties in poly(vinylidene fluoride) composites based on carbon nanotubes and graphene nanoplatelets



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## ABSTRACT

A small quantity of carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) were introduced into the poly(vinylidene fluoride) (PVDF)/GNP and PVDF/CNT composites, respectively, to prepare the corresponding ternary PVDF/CNT/GNP and PVDF/GNP/CNT composites. The results demonstrated that adding CNTs into the PVDF/GNP composites greatly promoted the formation of the hybrid network structure of fillers. This was much different from the scenario that adding GNPs into the PVDF/CNT composites. GNPs and CNTs exhibited excellent nucleation effects for the crystallization of PVDF matrix; however, the variation of the PVDF crystallinity was small. Adding CNTs into the PVDF/GNP composites greatly enhanced the electrical conductivity of the PVDF/CNT/GNP composites. This was also different from the scenario of the PVDF/GNP/CNT composites. Furthermore, the PVDF/CNT/GNP composites exhibit higher thermal conductivity and higher synergistic efficiency compared with the PVDF/GNP/CNT composites. The conductive mechanisms and the synergistic effects of the ternary composites were then analyzed.

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## 1. Introduction

Heat management materials exhibit wide application in many fields, and they have already been one of the main subjects of researches about the functional materials. Heat management materials include thermal insulating materials and thermal conductive materials. The former can be used in heat preservation field, and the wide application of them meets the requirement of energy conservation and environmental protection. The latter exhibits great potential in many fields, such as consumer electronic, microelectronic devices, generators, heat exchangers in power generation, and automobile. With the application of thermal conductive materials, the generated heat can be quickly transferred and the temperature of product can be maintained at relatively low level. This is very important from viewpoints of extending service life of products and lowering the risks.

Most of polymers are well-known the thermal and electrical insulating materials. Introducing conductive fillers into polymers has been demonstrated an efficient way to enhance the conductive properties of polymers [1,2]. Among those fillers which have

already been used to prepare the conductive polymer composites, the allotropes of carbon attract the most attention of researchers. The allotropes of carbon can be classified as several types according to the dimension of them, including carbon black (CB) and fullerene ( $C_{60}$ ) with zero-dimensional structure, carbon nanotubes (CNTs) with one-dimensional (1-D) structure, and graphite and graphene with two-dimensional (2-D) structure. Due to the extremely high aspect ratio and high conductive properties, CNTs and graphene have attracted much more attention of researchers. For example, CNTs and graphene exhibit the thermal conductivities of about 2000–6000 and 5000  $W m^{-1} K^{-1}$  [3–7], respectively. Specifically, through tailoring the content of carbon-based fillers, the thermal and electrical conductive properties of polymer composites can be simultaneously improved [8,9]. Obviously, these characteristics endow the composites with great potential in some special fields. For example, these conductive polymer composites can be used to fabricate the sensors with excellent electrically actuated shape memory behaviors [10,11].

Constructing a percolated network structure of fillers in the composites has been demonstrated the most efficient way to improve the conductive properties of polymer composites [12,13]. Generally, the formation of the percolated network structure of fillers is dependent upon several factors, such as dispersion

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state [14], aspect ratio of fillers [15], and content of fillers [16]. Factually, completely isolated dispersion of fillers is unfavorable for the enhancement of conductivities of polymer composites, because the presence of insulating matrix ligament prevents the transportation of electron or phonon vibration [17]. Introducing conductive fillers into an immiscible polymer blend with cocontinuous structure and simultaneously tailoring the selective location of fillers at the blend interface and/or in the one phase component, the conductive network structure can be constructed at relatively small filler content [12,18]. This is the so-called double percolation mechanism. However, for the composites with single polymer component, constructing the highly efficient network structure of conductive fillers is still intriguing and challenging.

Constructing the three dimensional (3-D) hybrid network structures of fillers with different dimensions attracts the attention of researchers. The pioneering work was done by Liu et al. [19]. In their work, 3-D network structure of CNTs and clay was constructed through in situ growth of CNTs from the interlayer of clay. The results demonstrated that the dispersion of CNTs and clay was simultaneously improved, and the special 3-D hybrid network structure exhibited excellent reinforcement effect for polymer composites. Subsequently, the method to construct 3-D hybrid network structure in polymer composites is widely accepted [20–22]. Specifically, much attention has been focused on constructing 3-D hybrid network structure using the two particular fillers, graphene/graphite and CNTs [21,23–28], to improve the mechanical, conductive, dielectric, or microwave shielding properties of polymer composites.

Recently, the effect of 3-D hybrid network of fillers on thermal conductivities of polymer composites attracts attention of researchers. For example, Yu et al. [29] introduced graphite nanoplatelets (GNPs) and CNTs into epoxy composites. They found that there was a synergistic effect between GNPs and CNTs in improving the thermal conductivity of the epoxy composites. The increased thermal conductivity was ascribed to the formation of denser percolating network structure of fillers. Zhou et al. [30] introduced the hybrid CNTs/micro-silicon carbide (SiC) fillers into epoxy composites. They found that the thermal conductivity of the composites was greatly enhanced compared with the composites with only CNTs or micro-SiC. The formation of the 3-D percolated network structure was proposed to explain the largely enhanced thermal conductivity, although such network structure was not demonstrated in their work. Im and Kim [31] introduced CNTs and graphene oxide (GO) into the epoxy composites. The composites also exhibited largely enhanced thermal conductivity. They proposed that the improved thermally conductive properties were mainly related to the formation of 3-D heat conduction paths induced by addition of CNTs. However, they also observed that extremely high content of CNTs also led to the decreased thermal conductivity because of the increased phonon scattering.

However, although constructing 3-D hybrid network structure of fillers has been demonstrated an efficient way to enhance the conductivity of composites, it is still unclear how to construct the highly efficient 3-D conductive network structure of fillers. For example, there are two strategies to prepare the ternary composites with 1-D and 2-D fillers. One is introducing a small quantity of 1-D filler into the composites with 2-D filler and the other is introducing a small quantity of 2-D filler into the composites with 1-D filler. So, the question is proposed that which strategy is more favorable for constructing the highly efficient 3-D conductive network structure in the composites.

In our previous work, we have already attempted to prepare poly(vinylidene fluoride) (PVDF) composites with high conductive properties [22,32,33]. For example, we demonstrated that the addition of a small quantity of GO (1 wt%) promoted the dispersion of CNTs in the PVDF/CNT composites and the 3-D network structure

of CNT/GO was constructed. Consequently, the PVDF/CNT/GO composites exhibited largely enhanced thermal conductivity compared with the PVDF/CNT composites at the same CNT load [22]. However, it is worth noting that GO is insulating and it has no apparent effect in improving the conductive properties of the PVDF composites [34]. In other words, GO and CNTs hardly exhibit the synergistic effect in enhancing the conductive properties of materials. Furthermore, the 3-D network structure of boron nitride (BN) and CNTs was also constructed in the PVDF composites. Similarly, we observed that the ternary PVDF/BN/CNT composites exhibited largely enhanced thermal conductivity compared with the PVDF/BN composites at the same BN content [32]. However, due to the intrinsic difference in microstructures, the interfacial thermal resistance between BN and CNTs is very high, which is unfavorable for the transportation of phonon vibration across the interface of BN and CNTs. This is possibly one of the reasons why the enhancement of the conductivity of the PVDF/BN/CNT composite is not as high as expected.

This work is then motivated by the above unclear but interesting questions. GNPs and CNTs are simultaneously introduced into PVDF to prepare the ternary composites. Firstly, CNTs and GNPs exhibit the similar chemical structures. It is expected that the interfacial thermal resistance between CNTs and GNPs is smaller than that between CNTs and BN and therefore, the ternary PVDF composites possibly exhibit better conductive properties. Secondly, it is expected to propose a more efficient way to construct the highly efficient 3-D conductive network structure of fillers in the PVDF composites.

## 2. Experimental section

### 2.1. Materials

PVDF (with a trade name of Kynar 720, a melt flow rate (MFR) of 22.8 g/10 min (230 °C/3.8 kg) and a density of 1.78 g/cm<sup>3</sup>) was purchased from Arkema (France). CNTs and GNPs were obtained from Chengdu Institute of Organic Chemistry, Chinese Academy of Science (Chengdu, China). CNTs were chemically treated using strong acid. The carboxyl content is about 0.51 wt%. The outer diameter of CNT is more than 50 nm and the length of a single CNT is about 10–30 μm. The layer numbers of GNPs are smaller than 30 and a median size is about 5–7 μm. The purity of CNTs and GNPs is above 90%.

### 2.2. Sample preparation

The composites were prepared through a two-step processing strategy, i.e. solution compounding and subsequent melt compounding. First, PVDF, GNP and CNTs were dissolved in the N,N-dimethylformamide (DMF) to prepare the PVDF/DMF, GNP/DMF and CNT/DMF solution, respectively. The dissolution of GNPs and CNTs were carried out at 55 °C with the aid of sonication for 2 h, and the dissolution of PVDF was stirred for 20 min. Second, the three mixtures were mixed together with sonication and continuously stirring at 55 °C for 2 h, and then the solution temperature was increased up to 100 °C and maintained at this temperature for more than 2 h to remove most of the solvent. After that, the mixture was transferred into a watch glass and placed in an oven with a setting temperature of 80 °C for more than 24 h until the weight of the sample was not invariant and in this condition, the residual solvent could be completely removed. Subsequently, the composite was continuously melt-compounded using a micro-extruder for about 6 min. The melt compounding was carried out in a nitrogen atmosphere to avoid the thermal degradation of PVDF. Then, the final composite was prepared. To obtain the

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