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Polyhedral oligomeric silsesquioxane functionalized carbon nanotubes for high thermal conductive poly(vinylidene fluoride) composite membrane

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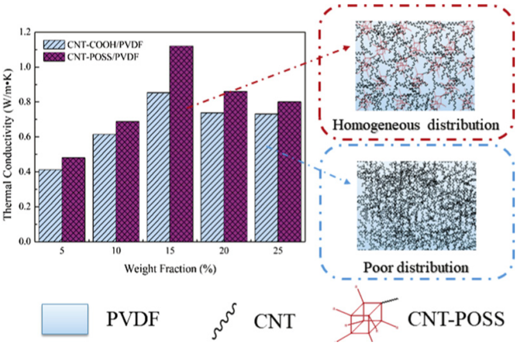
HIGHLIGHTS

- POSS functionalized CNTs was applied to improve the dispersion state of fillers and PVDF matrix.
- The nucleation effect of CNTs increased the crystallinity of the pure PVDF from 42.9% to 51.2%.
- The mechanical, thermal stability and conductivity were further enhanced by the incorporation of POSS nanoparticles.
- Compared with the pure PVDF, the thermal conductivity of 15 wt % CNT-POSS/PVDF composite was increased 7.4 times.

GRAPHICAL ABSTRACT



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ABSTRACT

To achieve high thermal conductivity of polymer-based composites at low filler loading is still a challenge because of the insufficient contact area and incomplete thermal percolation pathway. In this work, PVDF composite membrane with high thermal conductivity is fabricated using polyhedral oligomeric silsesquioxane (POSS) functionalized carbon nanotubes (CNTs) as fillers. Surface modification promotes the uniform dispersion of CNT-POSS in PVDF matrix and enlarges the contact area. Through the thermal analysis of the CNT-COOH/PVDF and CNT-POSS/PVDF composites, the results indicate that the nucleation effect of CNTs increases the crystallinity of the pure PVDF from 42.9% to 51.2%. In addition, the addition of POSS nanoparticles to the CNT-PVDF composites significantly improves its thermal stability, mechanical and thermal conductivity properties. The CNT-POSS/PVDF composite membrane with 15 wt% CNT-POSS presents an extremely high thermal conductivity of 1.12 W/m·K (vs. 0.15 W/m·K for pure PVDF) and exhibits great superiority in comparison with the thermally conductive PVDF-based composites reported before.

1. Introduction

Recently, thermal conductive polymer composites have attracted extensive academic attention and industrial interest due to their advantages of lightweight, easy processing, corrosion resistance and low cost.

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Poly(vinylidene fluoride) (PVDF) with the characteristics of good chemical stability, mechanical strength, easiness fabrication, piezoelectric and pyroelectric properties [1,2] has been selected as the matrix materials of the polymer composites. However, the intrinsic thermal conductivity of PVDF (0.1–0.5 W/m·K) falls within a relatively inferior range [3], which seriously limits its practical application for energy storage, automotive, microelectronic packaging and heat exchanger industries [4]. Therefore, the development of PVDF composites with remarkable thermal properties is crucial to meet the requirement of heat conduction and dissipation devices.

In order to overcome this shortcoming, carbon-based materials, such as carbon nanotube [3,5], graphene [6–10], graphite [11] etc., have been exploited as the promising candidate fillers to improve the thermal conductivity of polymer materials. Carbon nanotubes (CNTs) with the advantages of excellent mechanical and thermal properties (2000–3000 W/m·K) is considered to be an idea filler for polymer-based composites [12–14]. In particular, CNTs with high aspect ratio tend to form a thermal percolation network to promote the thermal performance of the polymer composites.

Nevertheless, it is regrettable that the actual research results of the CNTs/polymer composites are far from the anticipated results, which is mainly originated from the intrinsic weak chain bonds and phonon scattering [15,16]. Moreover, the crystallinity, interface interaction and geometric characteristics (such as length, size, and aspect ratio) of the filler or matrix have great influence on their thermal properties.

More importantly, the aggregation of CNTs caused by van der Waals interactions plays an unfavorable role in the dispersion state and leads to phonon scattering, thus degrading the thermal conductivity of the composites. Surface modification of fillers, including covalent or non-covalent treatment [17], has been proved to be an effective strategy to regulate the poor interfacial interaction and strengthen the affinity with polymers [18,19]. Huang [20] systematically elucidated the effect of interfacial interaction on the thermal conductivity of highly filled epoxy composites, which were prepared by modifying AlN with six different types of modifiers. The physicochemical properties of the modifiers and the filler loading were the critical factors to obtain the advanced thermal performance of the compounds, and surface modification could obviously compensate the interface defects. Compared with the other modifiers, 65 vol% AlN treated by silane coupling agents (KBM 803) showed the highest values of the thermal conductivity, which was about 6.5 W/m·K. Therefore, homogeneous dispersion as well as intensified interfacial interaction between fillers and polymer matrix was conductive to the formation of the consecutive thermal conductive network [21,22]. At the same time, some investigation strategies have been pushed forward to construct the well-developed conductive network, such as synergistic effect of hybrid fillers [23,24], aligned fillers in polymer matrix [9,25–28] and selective distribution of fillers [29,30].

Based on the previous studies shown in Table 1, PVDF-based composites exhibited high thermal conductivity have a great relationship with high filler loading (50–70 vol%). Although it has been investigated in many researches that the thermal percolation behavior is related to the sufficient filler content to construct the percolation network, there is still no strong support evidence to explain mechanism clearly. It is necessary to consider that high filler loading will inevitably increase the costs and deteriorate mechanical properties of the products. Thus, how to exploit polymer materials with outstanding thermal performance at relatively lower filler loading is becoming one of the key issues.

So far, it is worth noting that high thermal conductivity of PVDF/CNT composites has not been extensively exploited. The poor thermal conductivity of PVDF materials limits its application in heat transfer industry. Therefore, the enhanced thermal properties of PVDF composite will lead to more applications in the field of heat dissipation and heat transfer. Polyhedral oligomeric silsesquioxane (POSS) with unique cage-like molecular structure has been demonstrated to be a novel organic-inorganic hybrid nanomaterial for reinforcing the mechanic [44], dielectric, thermal [45,46] and flame retardant performance [47] of the polymers composites [48]. POSS nanoparticles with the diameter of 1–3 nm have the cube structure of Si—O as the inorganic bonds and organic substitutive groups on the Si atom. These organic substituents on the surface of POSS make it compatible or miscible with most polymers.

Table 1
The thermal conductivity of the PVDF-based nanocomposites in previous literature.

Filler type[a]	Filler loading[b]	Thermal conductivity[c]	Method	Ref.
AlN	60 vol%	11.5	Surface modification	[31]
SWCNTs	49 vol%	0.54	Surface modification	[32]
BT/SiC	60 vol% BT/20 vol% SiC	1.67	Hybrid fillers	[33]
Al	50 vol%	3.26		[34]
GS	10 wt%	<0.6		[35]
Al	70 wt%	1.74	Core–shell structure	[36]
SiC	23 vol%	1.48	Selective localization	[29]
FGS/NDs	45 wt%	0.66	Surface modification & hybrid fillers	[37]
GNF	25 vol%	10	Orientation	[38]
AlN	70 wt%	5.85	Surface modification & hybrid fillers	[39]
CNT/PVP	10 wt% CNTs/1 wt % PVP	0.63	Surface modification	[22]
Graphene	20 wt%	0.56	Orientation	[40]
GS	20 wt%	2.06		[41]
CNT/GNP	20 wt% GNP/2 wt% CNT	1.92	Hybrid fillers	[23]
BN/CNT	20 wt% BN/2 wt% CNT	1.30	Hybrid fillers	[42]
CNT	15 wt%	0.51	Orientation	[43]

[a] In this column: SWCNTs = single-walled carbon nanotubes, BT = barium titanate, GS = graphene sheet, FGS = functionalized graphene sheet, NDs = zero-dimensional nanodiamonds, GNF = graphene nanoflake, GNP = graphene nanoplatelets.

[b] In this column: The filler loading with the highest thermal conductivity in the literature.

[c] In this column: the units of thermal conductivity = W/m·K.

In this study, we proposed a simple and effective method for fabricating PVDF composites with high thermal conductivity by incorporating POSS functionalized multi-walled carbon nanotubes (MWCNTs) as fillers. The function of POSS in CNTs is concluded as: (1) improve the dispersibility of CNTs in DMF solvent and compatibility with PVDF matrix; (2) with the cage-like structure as the core and the grafted CNTs as the end points to form the thermal conductive network; (3) intensify the thermal stability and mechanical strength. Moreover, the crystallinity, thermal stability and mechanical properties of the PVDF composites are also investigated in detail. The homogeneous dispersion state and the enlarged contact area are facilitated to the effective thermal network. The obtained CNT-POSS/PVDF composite membranes with low filler loading exhibits high thermal conductivity and great potential industrial application prospects.

2. Experimental section

2.1. Materials

The PVDF with a purity of 99% and molecular weight of one million was purchased from Beijing HWRK Chem Co., Ltd. (Beijing, China). Multi-walled carbon nanotubes (outer diameter of 10–20 nm, length of 10–30 μm and purity of 98%) were supplied by Chengdu Organic Chemicals Co., Ltd. (Chengdu, China), which were prepared by a chemical vapor deposition (CVD) method. Tetrahydrofuran (THF, AR), *N*, *N* dimethylformamide (DMF, AR), absolute ethyl alcohol (AR), sulfuric acid (H_2SO_4, 98 wt%) and nitric acid (HNO_3, 65 wt%) were purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. (Tianjin, China). Aminopropyllsobutyl POSS (AM0265, $C_{31}H_{71}NSi_8O_{12}$) was purchased from Hybrid Plastics Inc. (Mississippi, USA). The chemical structure of POSS is shown in Fig. 1, which is a hybrid molecule with an inorganic