Thermal conductivity of polymers and polymer nanocomposites

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ABSTRACT

Polymers are widely used in industry and in our daily life because of their diverse functionality, light weight, low cost and excellent chemical stability. However, on some applications such as heat exchangers and electronic packaging, the low thermal conductivity of polymers is one of the major technological barriers. Enhancing the thermal conductivity of polymers is important for these applications and has become a very active research topic over the past two decades. In this review article, we aim to: 1). systematically summarize the molecular level understanding on the thermal transport mechanisms in polymers in terms of polymer morphology, chain structure and inter-chain coupling; 2). highlight the rationales in the recent efforts in enhancing the thermal conductivity of nanostructured polymers and polymer nanocomposites. Finally, we outline the main advances, challenges and outlooks for highly thermal-conductive polymer and polymer nanocomposites.

1. Introduction

Polymers and polymer composites are used ubiquitously in a wide range of industrial applications ranging from structural materials to electronics and in our daily life from chopsticks to trash bins due to their diverse functionality, light weight, low cost, and excellent chemical stability. However, the low thermal conductivity of polymers limits in their applications in some fields. For example, the low thermal conductivity of polymers can be one of the major technological barriers for the polymer-based flexible electronics due to the limited heat spreading capability [1–3]. If a polymer can be engineered with high thermal conductivity, polymeric heat spreaders and heat exchanger can be manufactured with superb features including structural compactness, light weight, resistance against corrosions, and ease of processing and low-cost, which could in turn find many applications in electronics, water and energy industry. [4,5] Thus, enhancing the thermal conductivity of polymers and polymer composites are of great interests.

Over the past two decades, with a better understanding of the fundamental heat transfer process at the micro-, nano- and even molecular- scales, there have been significant efforts devoting to enhancing the thermal conductivity of polymers and polymer nanocomposites, which are expected to enable a broader range of applications. In this review, we aim to: 1). systematically summarize the understanding on the physical mechanisms that controls the thermal transport in polymers by relating those to polymer chain morphology and inter-

chain coupling; 2). highlight the rationales in the recent efforts in enhancing the thermal conductivity of nanostructured polymers and polymer nanocomposites.

The thermal conductivity of bulk polymers is usually very low, on the order of 0.1–$0.5\,\mathrm{W \cdot m^{-1} K^{-1}}$, which is due to the complex morphology of polymer chains [6]. Fig. 1(a) shows a typical structure of a polymer, which consists of crystalline domains where polymer chains are aligned periodically, and amorphous domains where the polymer chains are randomly entangled. The thermal conductivity of a polymer depends greatly on its morphology. When amorphous domains are dominant, vibrational modes in the polymer tend to be localized, resulting in a low thermal conductivity. It is therefore natural to expect that thermal conductivity can be enhanced by improving the alignment of polymer chains. Indeed many efforts have been devoted to align polymer chains to enhance the thermal conductivity, by using mechanical stretching, nanoscale templating and electrospinning. A thermal conductivity as high as $104\,\mathrm{W \cdot m^{-1} K^{-1}}$ has been achieved for polyethylene (PE) after stretching with a draw ratio of 400 for nanofibers with a diameter of 50–500 nm and lengths up to tens of millimeters [7]. The thermal conductivity was shown to be enhanced for more than 20 times in polythiophene nanofibers with a fiber diameter of about 50 nm, prepared using templated electropolymerization [8]. Inspired by these experimental efforts, molecular dynamics simulations have been conducted to understand how nanoscale structures affect the thermal conductivity. As shown in Fig. 1(b), in addition to polymer

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Nomenclature

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0D	0- dimensional	PA6	polyamide-6
1D	1- dimensional	PBX	polymer-bonded explosives
2D	2- dimensional	PC	polycarbonate
3D	three dimensional	PDA	polydopamine
Al_2O_3	aluminum oxide	PE	polyethylene
AlN	aluminum nitride	PEEK	poly(ether-ether-ketone)
BB	Bottlebrush	PEG	Poly(ethylene glycol)
BN	boron nitride	P-GC	phenyl-aminated GO and CNT hybrid fillers
BNNS	boron-nitride nanosheets	PHB	poly(3-hydroxylbutyrate)
CE	cyanate ester	PI	polyimide
CF	carbon foam	PMMA	poly(methyl methacrylate)
CNT	carbon nanotubes	PP	Polypropylene
EG	expanded graphite	PPS	polyphenylene sulfide
E-G	Cethyl-aminated graphene-oxide and CNT hybrid fillers	PS	polystyrene
EMT	effective medium theory	PVS	Poly(vinyl alcohol)
GF	graphene foam	PVDF	poly(vinylidene fluoride)
GNP	graphene nanoplate	PVP	Polyvinylpyrrolidone
GNR	graphene nanoribbons	PVPh	poly(4-vinyl phenol)
GO	graphene oxide	R-GC	raw GO and CNT hybrid fillers
GS	graphene sheet	Si_3N_4	silicon nitride
H-bond	Hydrogen bond	SiC	silicon carbide
h-BN	hexagonal boron nitride	SR	silicone rubber
HDPE	high density polyethylene	SWCNT	Single-wall CNT
MD	Molecular dynamics	UHMW-	ultrahigh molecular weight
MgO	magnesium oxide	PE	polyethylene
MWCNT	Multi-wall CNT	vdW	van der Waal
P3HT	poly(3-hexylthiophene-2,5-diyl)	ZnO	zinc oxide
PAA	Poly(acrylic acid)	P(VDF-	poly(vinylidene
		TeFE)	fluoride-trifluoroethylene)
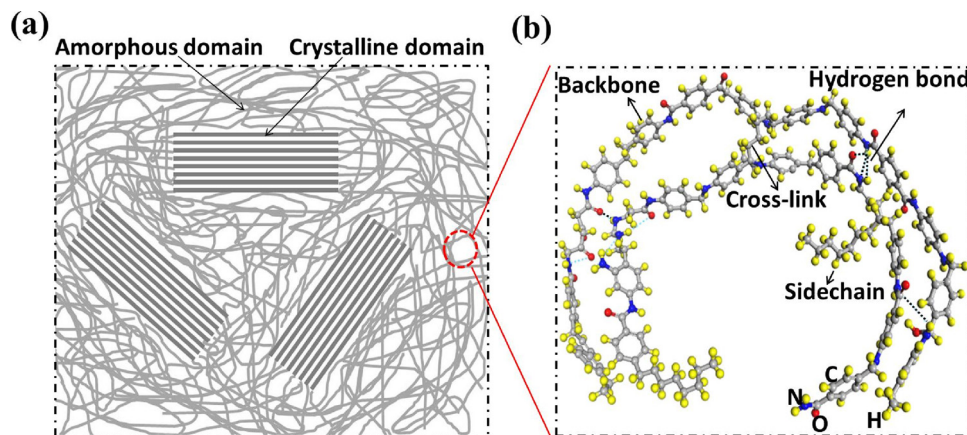
Fig. 1. Schematic diagrams of a polymer: (a) the morphology of a polymer consisting of crystalline and amorphous domains; (b) structure of a polymer chain.

chain alignment, the thermal conductivity of a polymer also depends on the structure of chains including backbone bonds and side chains, and the inter-chain coupling.

In addition to engineering the morphology of polymer chains, another common method to enhance the thermal conductivity of polymers is to blend polymers with highly thermal conductive fillers. The progress of nanotechnology over the last two decades not only provides more diverse high thermal conductivity fillers of different material types and topological shapes but also advances the understanding at the nanoscale. Fig. 2 shows a sketch of a polymer nanocomposite to illustrate the thermal transport mechanisms. In general, there are two types of polymer nanocomposites depending on whether nano-fillers form a network or not. When the filler concentration is low, no inter-filler networks could be formed, as shown in Fig. 2 (a). The thermal conductivity is essentially determined by the filler-matrix coupling, i.e,

interfacial thermal resistance, and the concentration and the geometric shapes of fillers. When the filler concentration is large enough, high conductivity fillers might form thermally conductive networks, as shown in Fig. 2(b). Although nanocomposites with filler network could possess a higher thermal conductivity than that without a network, their thermal conductivity could still be low due to the large inter-filler thermal contact resistance. Recently, three-dimensional fillers, such as carbon and graphene foams, have drawn a lot of attention. The fundamental thermal transport mechanisms and recent synthesis efforts in both types of nanocomposites are reviewed.

This review article is organized as follows. In Section 2, we introduce the experimental progress on the enhancement of thermal conductivity by aligning polymer chains, and then review the methods to further tune the thermal conductivity by engineering chain structure and inter-chain coupling, as illustrated in Fig. 3 (a). In Section 3, we