Review of thermal conductivity in epoxy thermosets and composites: Mechanisms, parameters, and filler influences

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ABSTRACT

Rapid development of energy, electrical and electronic technologies has put forward higher requirements for the thermal conductivities of epoxy resins and their composites. However, the thermal conductivity of conventional epoxy resins is relatively low, which could cause major heat dissipation issues. Therefore, the thermal conductivity enhancement of epoxy resins has long been a hot research topic in both academia and industry. In recent years, many promising advances have been made at the technical and mechanistic levels. This review includes the different approaches, the thermal conduction mechanisms implied, and the main research progresses. The research and academic achievements are mainly focused on the development of intrinsically liquid crystal epoxy resins and their composites, and the addition of fillers on amorphous epoxy resins. Finally, the challenges and prospects for thermal conductive epoxy resins are provided. Notably, this review can provide a more comprehensive understanding of thermally conductive epoxy resins and a guideline for the cutting-edge development direction of thermally conductive epoxy resins.

1. Introduction

With the speedy advancement of energy, electrical and electronic technologies, the speedy build-up of heat in associated equipment and components will unavoidably cause serious threats to their stability and reliability [1]. Epoxy resins (ERs) are frequently used in energy, electrical and electronic fields due to their good mechanical properties, resistance to environmental degradation, adhesive properties, low shrinkage during curing, good chemical resistance, high electrical insulation, wear resistance, and heat resistance properties [2,3]. However, the thermal conductivity (TC) of ERs is often low, around 0.2 W/(m·K), which cannot meet the requirements of thermal conduction for energy transmission, 5G communication equipment, and electronic packaging materials [4]. Therefore, the research and development of ERs and their composites with high TC are of urgent theoretical significance and

practical application for the design and expansion of materials in the fields of energy, electrical and electronic technologies.

Generally speaking, there are two methods to enhance the TC of ERs [5]. One is to increase the intrinsic TC of ERs. The core to the synthesis of intrinsic thermally conductive polymers is to arrange the molecule in a particular direction and increase molecular rigidity. Through the molecular design method, the epoxy molecular chain with a liquid-crystal structure is synthesized to realize the orderly arrangement of mesogenic elements [6]. This method can increase the mean free path of phonon transmission and reduce the scattering of phonons in the disordered molecular chain, thereby reducing thermal resistance. Another improved method is to add a thermally conductive filler into the ERs [7–9]. The intrinsic TC of the filler, the added percentage, and their size, shape, and aspect ratio are essential to the final properties of the epoxy composite (EC). The fillers are evenly dispersed in the matrix by an external force [4]. After casting, coating, and solvent removal, the composite materials are cured under appropriate conditions.

During the past few decades, researchers [10,11] have been trying their best to design and fabricate ERs and ECs with high TC. For instance, different approaches have been addressed, such as (1)

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Abbreviations and symbols

ER	Epoxy resin
EC	Epoxy composite
DGEBA	Diglycidyl ether of bisphenol A
DGEBF	Bisphenol F epoxy resins
MFP	Mean free path
LCERs	Liquid crystal epoxy resins
LCECs	Liquid crystal epoxy composites
TC	Thermal conductivity
DDS	4,4′-Diaminodiphenyl sulfone
BLCM	Biphenyl liquid crystalline small molecule
DDM	4,4′-Methylene-bis(2-ethylaniline)
E−51	Bisphenol A epoxy resin
S-LCE	Side-chain liquid crystal epoxy
PCH	Phenylcyclohexyl
D-LCE	Discotic liquid crystal epoxy
BPH	N-benzyl pyraziniumm hexafluoroantimonate
LCER	Liquid crystal epoxy resin
M-LCE	Main-chain liquid crystal epoxy monomer
S-LCE	Side-chain liquid crystal epoxy monomer
DPDA	Diphenyl diacetylene
BP	4,4′-diglycidyloxybiphenyl
GNPs	Graphene nanoparticles
BPIB	Biphenyl and pyrene groups
Cu	Copper
Ag	Silver
Al	Aluminum
CNTs	Carbon nanotubes
CF	Carbon Fibre
BN	Boron Nitride
SiC	Silicon carbide
Al_2O_3	Aluminum oxide
PMMA	Poly (methyl methacrylate)
EEG	Exfoliated graphene
GNPs	Graphene nanoplatelets
LSGA	High-quality graphene aerogel
JPGO	Janus graphene oxide
PDA	Polydopamine
GO	Graphene oxide
AF	Alumina foam
MF	Melamine foam
AgNPs	Silver nanoparticles
ITR	Interfacial thermal resistance
CVD	Chemical vapor deposition
SiC-BNNS	Silicon carbide-boron nitride nanosheets
γ-APS	γ-aminopropyl triethoxysilane

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improving the intrinsically thermally conductive ERs [9]; (2) including novel thermally conductive fillers [12], looking for enhancing the interface interaction between epoxy matrix and thermally conductive fillers [11] on EC; (3) designing and manufacturing new unique structures and morphologies of thermally conductive fillers [13]. Despite this, only a few reviews have been published [14] about this field, particularly centered on the TC of the ER.

This review includes the different approaches, the thermal conduction mechanisms implied, and the main research progresses. The research and academic achievements are mainly focused on the development of intrinsically liquid crystal epoxy resins and their composites, the addition of fillers on amorphous epoxy composites. Finally, a future outlook in the hope of facilitating progress is provided at the end of the article.

2. Thermal conductivity of epoxy thermosets

ER, or poly(epoxides), are a significant class of thermosetting polymers created by the crosslinking between monomers, one of which must contain epoxy or oxirane groups [15]. The oxirane rings can react with different curing agents, such as amines, anhydrides, carboxylic acids, alcohols, and thiols. The curing reaction transforms the low molecular weight precursors into a three-dimensional network with infinite molecular weight [16].

The research and development of new formulations never stopped in the history of ER. Since the discovery of diglycidyl ether of bisphenol A (DGEBA) by Schlack in 1941 [17], numerous ER has been developed and commercialized. Such as petroleum-based epoxy resin (DGEBA, Bisphenol F epoxy resins (DGEBF), etc.) and biobased epoxy resin (soybean oil-based epoxy resins [18], cardanol-based epoxy resins [19], furan-based epoxy resins [20], etc.). However, most ERs intrinsically have low TC (~0.2 W/(m·K)) due to a severe phonon scattering originating from its random 3D network structure.

The TC of polymers can increase with enlarging the phonon mean free path (MFP), which is inversely proportional to the degree of phonon scattering. To maximize the MFP of phonons in polymers, or to minimize the phonon scattering, it is necessary to enhance the crystallinity and the orientation of the polymers. However, conventional ERs are amorphous polymers. The first research describing the intrinsically thermally conductive liquid crystal epoxy resins (LCERs) was proposed in 2003 by Takezawa et al. [21]. The regions of crystal-like structure and the regions of amorphous structure in LCERs are connected by chemical bonds, and the heat flow can be conducted along the ordered molecular chain direction, which effectively suppresses the scattering of phonon in the ERs, thereby greatly improving the intrinsic thermal conductivities of the ERs. Table 1 depicts the TC of various epoxy monomers, including both amorphous ERs and LCERs.

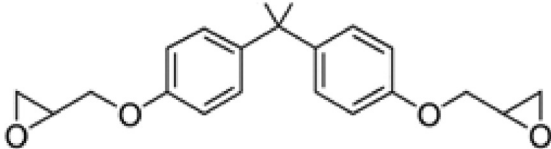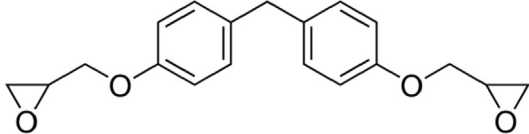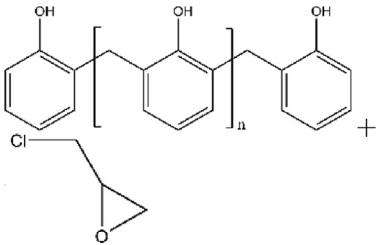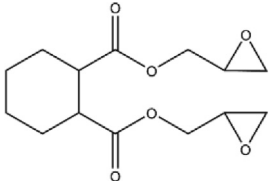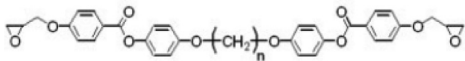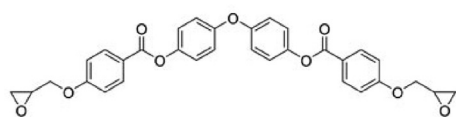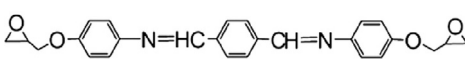## 3. Thermal conduction mechanisms

Heat transfer of cured ER is promoted by the transfer of phonon oscillations in the crystalline and non-crystalline regions. It is represented by the Debye equation [3].

$$\lambda = \left(\frac{L}{3}\right) \times Cp \times v \times l \tag{1}$$

Where L is the mean free pathway of a phonon, v is the phonon group velocity, Cp is the specific heat capacity per unit volume, and λ is the polymer's thermal conductivity [29]. L of ER is an extremely small constant due to numerous defects which defect scattering of phonons in amorphous states. Therefore, ER exhibits a quite low TC at the range of 0.15−0.35 W/(m·K).

The thermal conduction mechanism is quite distinct in and filled with amorphous ERs and LCERs [30]. For amorphous ERs, the presence of a large number of defects and randomly oriented structures in the polymer chains creates a tortuous path for the propagation of vibrational waves. This random curvature and the bending sequence would seriously affect phonon transmission and promote phonon scattering [31]. Fig. 1 described the thermal conduction mechanism in the amorphous structure of a polymer. Heat

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Table 1
Thermal conductivity for epoxy monomers.

Epoxy resins	Monomer		TC(W/(m·K))	Ref
Amorphous epoxy resins	DGEBA		0.20	[22,23]
	DGEBF		0.20	[24]
	Novolac epoxy resins		0.15−0.25	[25]
	Aliphatic epoxy resins		0.16	[26]
Liquid crystal epoxy resins	TMEn (n = 4,6,8)		0.85−0.96	[21]
	Oxybis(4,1-phenylene) bis(4-(oxiran-2-ylmethoxy) benzoate)		0.29	[27]
	Terephthalylidene-bis-(4-aminophenol) diglycidylether		0.45	[28]

reaches the surface atom or monomer, and then diffuses to the neighboring atom, and the next one, and so on. Due to the tortuous paths and disordered vibrations in the polymer chains, the heat will diffuse slowly, which means that the phonon scattering is initiated by the polymer structure itself.

Crystal polymers show different heat transfer mechanisms. In highly ordered regions, an individual polymer chain traverses from one end of the crystal to the other, or highly aligned chains are extended and share the same axial orientation but are not necessarily connected head to tail. Because of the stiff covalent bonding in these areas, polymer chains can function as efficient thermal conductors in the axis direction [32]. To elucidate the heat transfer mechanism of a crystalline polymer, an analogy can be made with a Newtonian pendulum, which can be considered as a crystalline phase in the material. As shown in Fig. 2, the initial kinetic energy is rapidly transferred from one side of the ball to the other without extra irregular vibrations, as heat propagates rapidly over the lattice atoms without phonon scattering. LCERs are considered to be the mesogenic phases within both the crystalline and disordered phases. The highly ordered structure of the

crystalline phase promotes phonon transport, which contributes to TC [33]. In contrast, disordered phases with many defects contribute significantly to the so-called "thermal resistance",
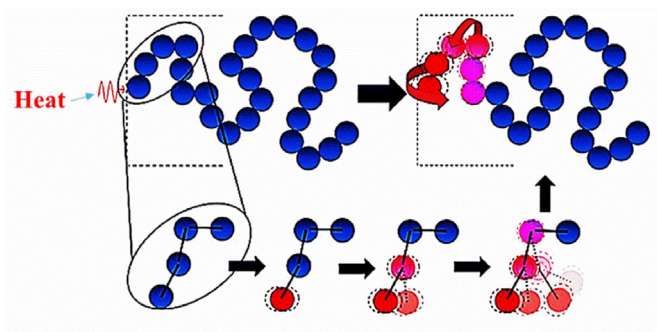

Fig. 1. Thermal conduction mechanism in an amorphous polymer [32]. Copyright 2020. Reproduced with permission from Wiley Ltd.
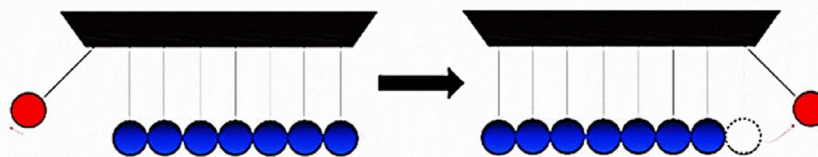
Fig. 2. Schematic comparison by the Newton pendulum of thermal conductivity in crystalline materials, and polymers [32]. Copyright 2020. Reproduced with permission from Wiley Ltd.

which causes phonon scattering and slows down heat conduction considerably.

4. Research progresses of thermally conductive epoxy resins

4.1. Thermal conductivity of liquid crystal epoxy resins and composites

LCERs are cured from liquid crystal epoxy monomers containing rigid rod-shaped mesogens, special flexible segments, and epoxy end groups. It combines the characteristics of a high order of liquid crystal and high cross-linking of the network, which can effectively improve the intrinsic thermal conductivities of the ERs. There are three main preparation methods for LCERs [34]. (1) Starting from the molecular structure of liquid crystal epoxy monomers, through the selection of types and decisions in the position of mesogens, and the harmonization of the rigid and flexible structures of liquid crystal epoxy monomers, as well as the introduction of groups with strong intermolecular force, liquid crystal epoxy monomers can be synthesized, and intrinsically thermally conductive LCERs can be prepared. (2) Starting from the structural and functional design of the curing agent or crosslinking agent, the LCERs with intrinsic TC can be prepared by introducing mesogens through the curing agent or crosslinking agent. Alternatively, the regular arrangement of epoxy monomers can be promoted according to the force between curing agents or crosslinking agents. (3) based on the synthesis of intrinsic thermally conductive LCERs, filling with fillers to further improve the TC of LCERs.

4.1.1. Design of the molecular structures of liquid crystal epoxy monomers

Research on LCERs first began in Takezawa's research group in Japan [21]. Based on the orderly structure of molecules, the liquid crystalline epoxy monomers with diphenyl benzoate groups were synthesized, and the TC of the cured epoxy exceeded 0.90 W/(m·K), which was about 5 times higher than that of the common ER (0.2 W/(m·K)). Since then, research on the creation of LCERs with relatively high intrinsic thermal conductivity has mostly concentrated on the structural design of epoxy monomers. In particular, the main-chain structure has the most important influence on the intrinsic TC of ER. Lin et al. [35] synthesized a kind of liquid crystal epoxy monomers using ketone as mesogens, and the TC of the LCER after curing was 0.34 W/(m·K). Chen et al. [27] synthesized two kinds of liquid crystal epoxy monomers containing biphenyl ether and aromatic ester cured with 4,4′-Diaminodiphenyl sulfone (DDS). The two kinds of cured resins exhibited a nematic phase, and the corresponding TC was 0.292 W/(m·K) and 0.296 W/(m·K), respectively. Giang et al. [28] designed and synthesized three kinds of methylene amine-type liquid crystal epoxy monomers, and studied the influence of the main chain structures on the performances of ER. The results showed that the ordering trend of mesogens directly affects the thermal conductivities of the materials. With higher order of the structure, the corresponding TC is higher and can reach 0.45 W/(m·K).

In addition to the main chain structures, the side-chain structures of the liquid crystal epoxy monomers also have a great impact on the TC of ERs. Gu et al. [36] synthesized one kind of side chain liquid crystal epoxy (S-LCE), which was prepared by thiol-epoxide nucleophilic ring-opening reaction and coating method (Fig. 3). S-LCE presents nematic liquid crystal from room temperature to 160 °C, and the through-plane TC and in-plane TC were 0.33 and 1.25 W/(m·K), respectively, much higher than through-plane TC (0.19 W/(m·K)) and in-plane TC (0.65 W/(m·K)) of bisphenol A epoxy resin (E−51). Goh et al. [37] synthesized three kinds of liquid crystal epoxy monomers via the substitution of phenylcyclohexyl (PCH) mesogenic moieties into the 2,5 positions of duglycidyl terephthalate. The smectic phase with a wide temperature range of 98−145 °C was observed for the eutectic mixtures of a family of stable smectic LCERs. The thermally cured LCERs at the liquid crystal phase exhibited a high TC of 0.4 W/(m·K). Gu et al. [38] designed and synthesized discotic liquid crystal epoxy (D-LCE) and P/Si flame-retardant co-curing agent (DOPO-POSS, DP) (Fig. 4). D-LCE was cured with 4,4′-diaminodiphenyl methane (DDM) and DP, to obtain intrinsic highly TC/flame retardant epoxy resins with multi-functionality. The through-plane TC and in-plane TC value of D-LCER$_{DP-10.0}$ with 10 wt% DP reached 0.34 and 1.30 W/(m·K), higher than that of E−51 (through-plane TC of 0.19 W/(m·K), in-plane TC of 0.65 W/(m·K)) The high intrinsic in-plane TC can be explained by the fact that the LCERs with regular arrangement structure are easy to form the partial crystal structures so that the heat flow is conducted in the direction of the ordered molecular chains, effectively suppressing the phonon scattering in the heat transfer process and thus greatly improving its intrinsic TC.

4.1.2. Design and preparation of curing agent or crosslinking agent

At present, there are few studies on the preparation of intrinsically thermally conductive LCERs through the design of epoxy curing agents. However, there are some research works to improve the intrinsic TC of LCERs by promoting the regular arrangement of liquid crystal epoxy monomers through the force between curing agents or cross-linking hardeners, increasing the intermolecular forces. Islam et al. [39] propose replacing the traditional amine crosslinker (DDS) with a cationic initiator (N-benzyl pyraziniumm hexafluoroantimonate, BPH) (Fig. 5). LCER was achieved to give a value ~141% (0.48 W/(m·K)) higher than that of the amorphous amine-cured LCER. This is because the ordered liquid crystal microstructure can be preserved after curing thanks to the cationic initiators' linear fixation of the epoxy groups on the mesogens in a regular configuration. Gu et al. [40] synthesized a biphenyl liquid crystalline small molecule (BLCM) containing flexible units using E−51 as the matrix, DDM as a curing agent, and the BLCM as a co-curing agent, and EPs were cured by casting method. The results showed the inter-stacking of biphenyl mesogens promoted the formation of locally ordered regions in the LCER, resulting in higher TC. When the mass fraction of the BLCM was 60% of E−51 (LCER3), the TC of LCER3 was 0.42 W/(m·K), which was 2.1 times that of neat ER cured with DDM. This structured liquid crystal structure
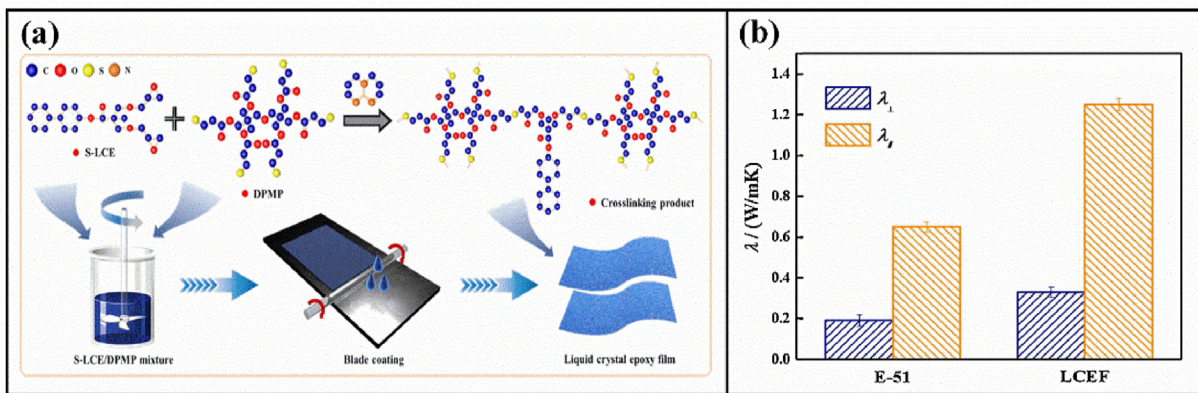
Fig. 3. (a) Schematic diagram for fabrication of LCER, (b) The TC of E−51 and LCEF [36]. Copyright 2021. Reproduced with permission from Elsevier.
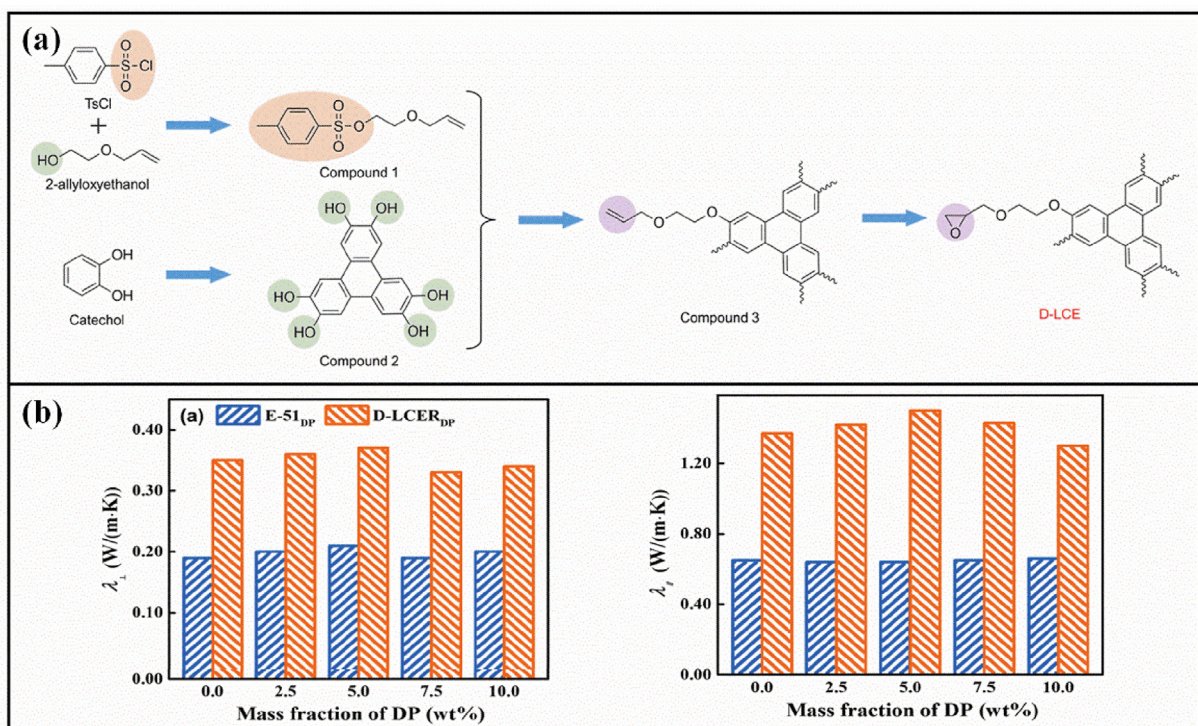

Fig. 4. (a) Schematic diagram of synthetic route for D-LCE, (b) The TC of E−51$_{DP}$ and D-LCER$_{DP}$ [38]. Copyright 2021. Reproduced with permission from John Wiley and Sons.

decreased phonon scattering during heat transfer and greatly raised the inherent TC of ER.

As can be observed, the above design ideas or processing techniques rely on the alignment and orientation of molecular chains to create quasi-crystals and partially regular crystals to reduce phonon scattering. Hossain et al. [41] studied the other important factors for the enhancement of TC in LCERs such as intermolecular interaction, fine-turning of the polymer chain structure, and interchain conjugation. The diphenyl diacetylene (DPDA) mesogen was designed and used to assemble a highly ordered lamellar microstructure and create interchain π-conjugation networks via topochemical polymerization of well-organized diacetylenes (Fig. 6). The TC of cured DPDA resins with a highly organized lamellar structure (~0.43 W/(m·K)) was 194% compared to a commercial ER (~0.22 W/(m·K)). Through post-topochemical polymerization of diacetylenes, which results in π-conjugation and

interchain π-π stacking, the TC was further improved up to 227% (~0.50 W/(m·K)). Cahill et al. [42] prepared four ER, which were cured using one commercial diepoxide and four diamine hardeners with an anthraquinone structure. The TC of these four epoxy resins showed a positive correlation with the density, at higher density, higher TC. The TC of the highest density of epoxy resin reached 0.52 W/(m·K), which is ~2.5 times that of common resins.

4.1.3. Thermal conductivity of liquid crystal epoxy composites

Based on the preparation and synthesis of intrinsically thermally conductive LCERs, many researchers have further improved their TC by filling thermally conductive fillers. A new idea for preparing high TC ECs involves combining of intrinsic thermally conductive ER with thermally conductive fillers, which can obtain high TC with less filler content and effectively reduce the disadvantages caused by the introduction of too much filler.
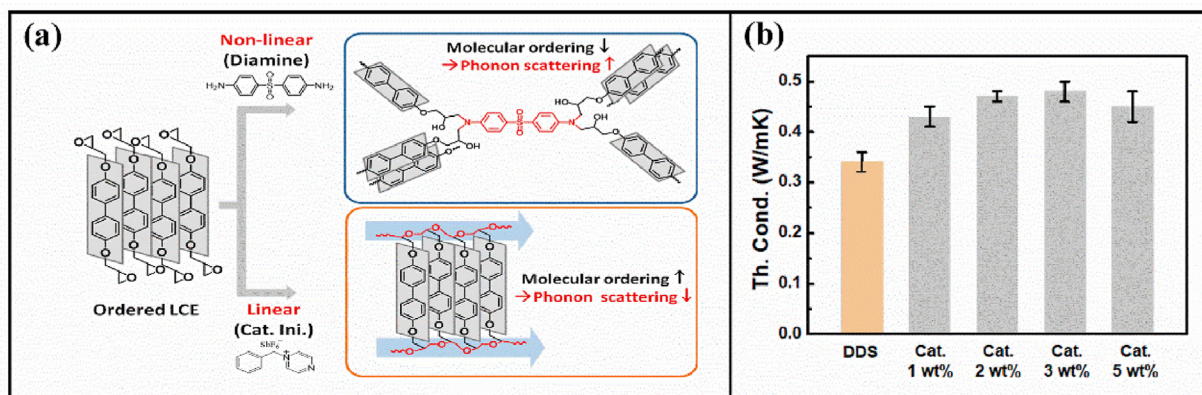
Fig. 5. (a) Schematic illustration of the different microstructures of LCER cured using DDS and BPH respectively, and (b) The TC of LCER$_{DDS}$ and LCER$_{BPH}$ [39]. Copyright 2018. Reproduced with permission from the American Chemical Society.

Gu et al. [43] synthesized a type of LCER based on a biphenyl mesomorphic unit and then corresponded intrinsic highly thermally conductive LCER and the BN/LCER composites. The LCER exhibited a high TC of 0.51 W/(m·K) due to the localized nematic liquid crystal order (Fig. 7 (a)), which directs the phonon propagation along the direction of the liquid crystal domain, thus effectively suppressing the phonon scattering from the material (Fig. 7 (b)). The BN/LCER composites had a much higher TC, 1.02 W/(m·K), with 30 wt % BN (Fig. 7 (c)), which was twice as much as that of the DGEBA composite at the same BN percentage.

Yeo et al. [44] systematically investigated various ERs containing alumina fillers. They discovered that getting high TC required an ordered microstructure and large fillers with spherical shapes rather than irregular ones. The TC of the 4,4′-diglycidyloxybiphenyl (BP) epoxy was about 30% higher than that of DGEBA having the same type of fillers. The highest TC among the BP composites with 80 wt % content of alumina (spherical shape and 70 μm size) was 6.66 W/(m·K).

Yeom et al. [45] manufactured biphenyl-based LCECs containing graphene nanoplatelets (GNPs). To improve the filler-matrix interaction, a compatibilizer containing biphenyl and pyrene groups (BPIB) was synthesized and incorporated into the composites (Fig. 8 (a)). It was found that the aggregation of GNPs in the LCECs matrix could be greatly reduced by using BPIB due to its bridging effect (Fig. 8 (b)). By varying the size, thickness, and dispersion of GNPs, the authors reported unprecedentedly high TC (44.9 W/(m·K)) at low filler content (13.6 vol %) (Fig. 8 (c)). Similar

work has been carried out by Li et al. [46]. Polyethylene glycol (PEG) is introduced to the interface of biphenyl-based LCECs/graphene composite. The highest TC of the composite can reach 10.17 W/(m·K). The presence of PEG facilitates the dispersion of fillers in the epoxy matrix, meanwhile, significantly reducing the interface thermal resistance between fillers and matrix.

4.2. Thermal conductivity of amorphous epoxy composites

Thermally conductive fillers are one of the most important factors in the TC of amorphous ERs [1]. There are three common types of thermally conductive fillers: metal-based fillers [47], carbon-based fillers [48−51], and ceramic fillers [52,53]. Table 2 shows the TC of these fillers. EC with metallic-based fillers and carbon-based fillers are mainly used in heat transfer and dissipation areas where electrical insulation is not required, such as heat exchangers [49]. Thermally conductive Ceramic filled EC is widely used in areas needing electrical insulation, such as printed circuit boards [54]. The loading, size and shape, surface morphology (isotropic or anisotropic), etc. of the thermally conductive fillers have great influences on the TC of the ECs. It is worth noting that the anisotropic of the fillers causes the ECs to have both through-plane TC and in-plane TC. Above all, an in-depth understanding of the physical and chemical performances of the thermally conductive fillers is important for the preparation of high-quality thermally conductive EC.
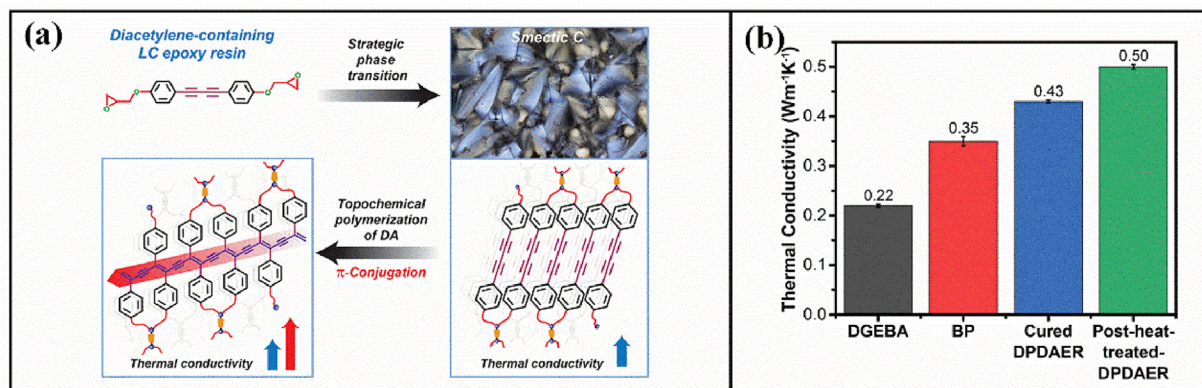

Fig. 6. (a) Strategic phase control of diacetylene-containing LCER for efficient π-conjugation network formation and π−π stacking, and (b) The TC of LCER [41]. Copyright 2022. Reproduced with permission from the American Chemical Society.
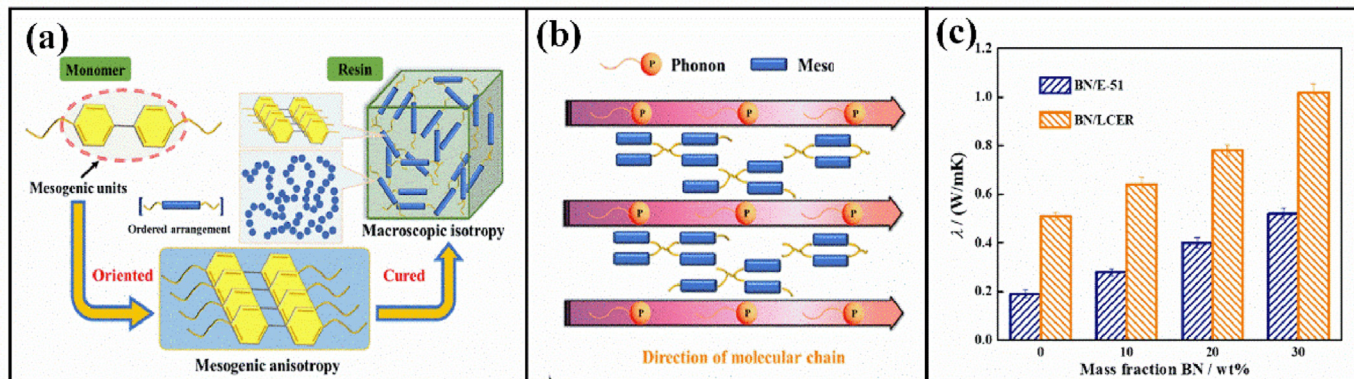
Fig. 7. (a) Schematic illustration of microscopic anisotropy and macroscopic isotropy of a biphenyl LCEN, (b) regulated phonon transport through ordered LC domains, and (c) The TC of BN/E−51 and BN/LCER [43]. Copyright 2020. Reproduced with permission from Elsevier.
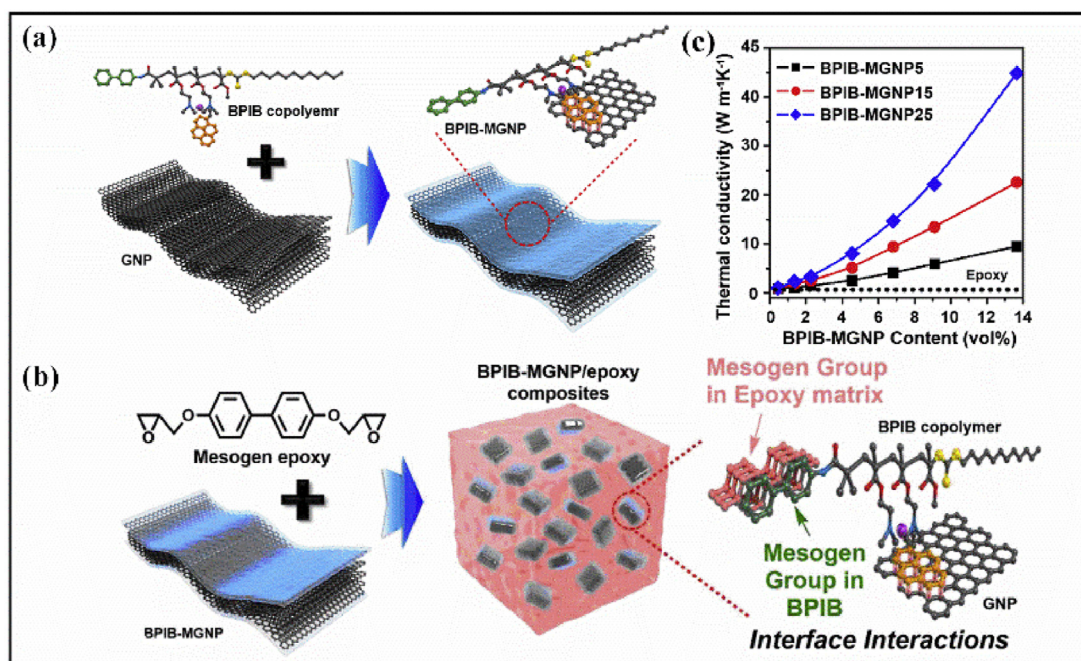

Fig. 8. (a) Schematic depiction for the synthesis of BPIB and BPIB-MGNP, (b))Schematic illustration of BPIB-MGNP/epoxy composite, and (c) The TC of BPIB-MGNP/epoxy composite [45]. Copyright 2020. Reproduced with permission from Elsevier.

4.2.1. Metal-based fillers

Metal-based fillers such as copper [57,58], silver [59,60], aluminum [61], etc. could be effective in increasing the TC of composites compared to the pure ER. However, adding metallic fillers into ERs will also cause a substantial increase in the electrical conductivity of the composites and/or a reduction in the dielectric breakdown voltage (such as Table 3). Bach et al. [62] coated the surface of poly (methyl methacrylate) (PMMA) microbeads with copper nanoparticles to form Cu@PMMA by electroless-plating to prepare thermally conductive filler and then prepared thermally conductive Cu@PMMA/ECs (Fig. 9). When the filler concentration was 50 wt%, the TC of Cu@PMMA/ECs reached 3.38 W/(m·K), over 14 times compared to the neat ER, and the volume resistivity was reduced 11 orders of magnitude ($1.9 \lozenge 10^4$ Ω cm). Kwon et al. [63] used planetary ball milling to synthesize a hybrid powder consisting of electrochemically exfoliated graphene(EEG) and surface-passivated aluminum particles(Al@EEG) (Fig. 10(a)). The EC with 35 wt % Al@EEG (8:2) hybrid showed high TC (1.43 W/(m·K))

Table 2
TC of various fillers at room temperature.

Samples	Thermal conductivity fillers	TC (W/mK)	Ref.
Metal-based fillers	Copper(Cu)	398	[55]
	Silver (Ag)	427	[13]
	Aluminum(Al)	247	[55]
Carbon-based fillers	Carbon nanotubes (CNTs)	1000−4000	[49,56]
	Carbon Fibre(CF)	400−1000	[13]
	Graphene	2000−6000	[56]
	Graphite	100−400	[13,49]
Ceramic fillers	Boron Nitride (BN)	30−600	[1]
	Silicon carbide (SiC)	90−390	[54]
	Aluminum oxide (Al_2O_3)	35	[1]

(Fig. 10(b)) and excellent electrical insulation (10^{14} Ω cm). Uniform distribution of exfoliated individual EEG sheet on Al surfaces in the Al@EEG (8:2), which prevent direct contact between EEG sheets and broke the electrically conductive path. Meanwhile, free EEG

Table 3
The TC and electrical conductivity of the ECs with metal-based fillers.

| Metal-Based fillers	Filler and loading	TC(W/(m·K))	Enhancement	Volume resistivity($\Omega\cdot$cm)	Electrical conductivity (S/cm)	Refs.
Copper (Cu)	50 wt% Cu@poly(methyl methacrylate) (PMMA) microbeads/epoxy	3.38	14 times	$1.9\lozenge 10^4$	/	[62]
	29.34 vol% Cu-carbon felt (CFelt)/epoxy	30.69	110	/	$7.49\lozenge 10^4$	[57]
	3.1 vol % polydopamine-coated copper nanowires (CuNWs)/epoxy	2.87	14 times	$\rangle 10^{14}$	/	[58]
Silver (Ag)	20 wt% tellurium (Te)/molybdenum disulfide (MoS$_2$)/Ag/epoxy	in-plane thermal conductivity 10.4	4160%	/	/	[59]
	35% Ag-deposited alumina sphere/epoxy	Out-plane TC 1.304	624%	$5\lozenge 10^{10}$	/	[64]
	8.2 wt% MXene/Ag nanowires (AgNWs)/epoxy	2.34	1014%	/	$1.532\lozenge 10^5$	[60]
Aluminum	48 vol% Al/epoxy	1.47	/	/	$3.1\lozenge 10^{-6}$ at 10^6 Hz	[61]
	35 wt% Al@ electrochemically exfoliated graphene (EEG)/epoxy	1.43	499%	$\rangle 10^{14}$	/	[63]
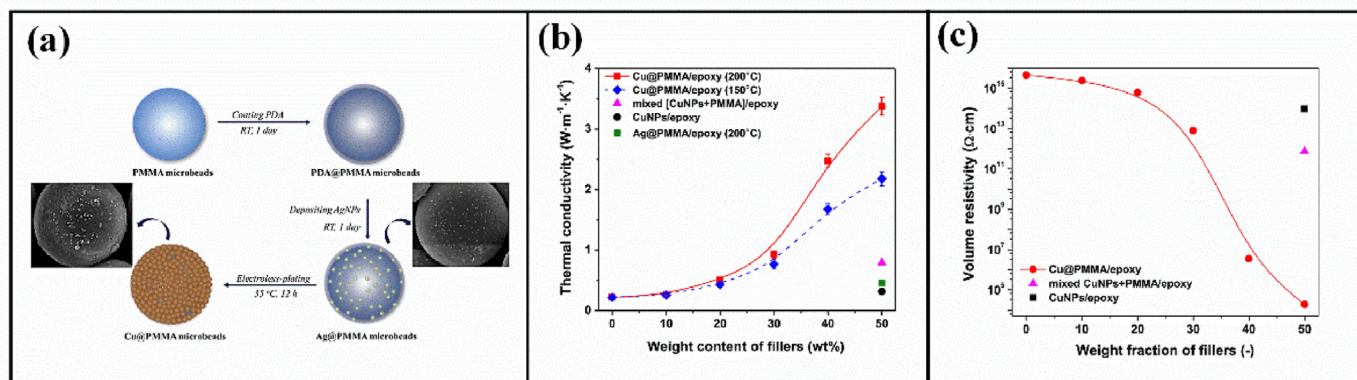
Fig. 9. (a) Schematic illustration for fabrication of Cu@PMMA microbeads, (b) The TC of Cu@PMMA/epoxy composites, (c) Volume resistivities of Cu@PMMA/epoxy composites [62]. Copyright 2019. Reproduced with permission from Elsevier.
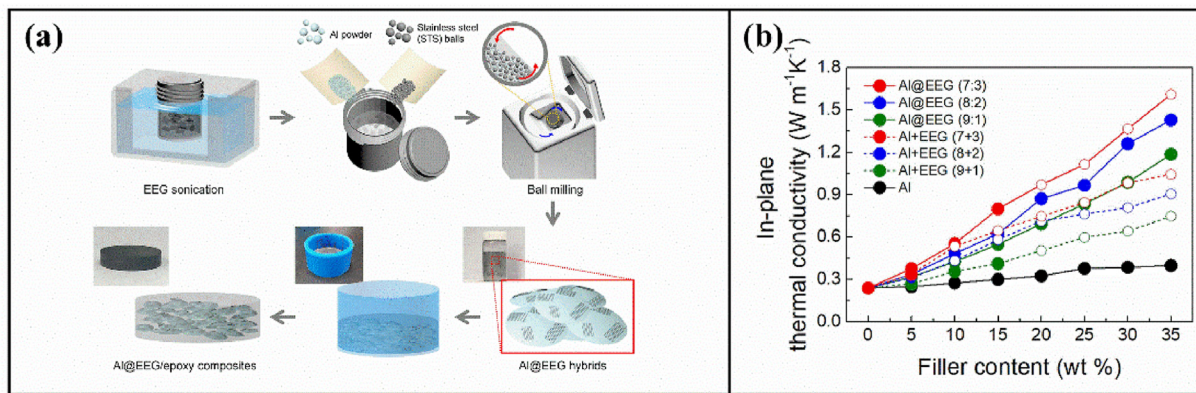
Fig. 10. (a) Schematic illustration of the procedure used to prepare Al@EEG/epoxy composites, and (b) TC of Al@EEG/epoxy composites [63]. Copyright 2022. Reproduced with permission from Elsevier.

acted as a bridge between Al@EEG hybrid grains for effective phonon delivery, further improving TC. Ren et al. [64] deposited silver on the surface of sphere alumina to form silver nanoparticle "bridges" to reduce the interfacial thermal resistance between fillers. The results show that the out-of-plane TC of the spherical alumina composite is increased to 1.304 W/(m·K), which is 624% higher than that of pure ER (Fig. 11).

4.2.2. Carbon-based fillers

Carbon-based filters, including carbon nanotubes (CNTs) [65–67], carbon fiber [68], graphite [69], graphene [70–74], etc.,

have appeared to be the best promising fillers, coupling high TC and lightweight. A list of various ECs with carbon fillers used for TC enhancements is shown in Table 4. Prolong et al. [75] fabricated EC with different GNS contents and investigated the TC of GNS/epoxy reaching 300% at 10 wt % GNPs loading compared to the pure ER. On the other hand, GNS was also added to the epoxy adhesives to increase their TC [76]. In this case, the incorporation of 8 and 10 wt % GNS reinforcement caused a TC enhancement of ~206 and ~306%, respectively.

All-graphitized graphene aerogels with a highly aligned graphene network were created by Zhong-Zhen Yu [70] using

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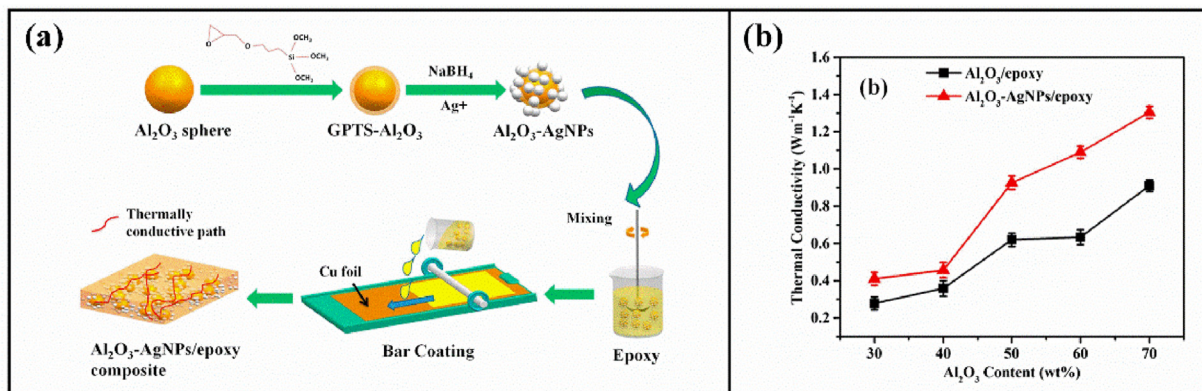
Fig. 11. (a) Flow chart of the preparation of Al$_2$O$_3$-AgNPs/epoxy composite, and (b) The TC of Al$_2$O$_3$/epoxy composite and Al$_2$O$_3$-AgNPs/epoxy composite [64]. Copyright 2018. Reproduced with permission from Elsevier.

Table 4
TC of ECs of carbon-based fillers.

Filler and loading	TC (W/(m·K))	Enhancement	Refs.
8 wt% multi-walled carbon nanotubes with imidazolium amine-terminated ionic liquids (AIL-MWCNTs)/epoxy	0.625	211%	[65]
0.5 wt% the multi-walled carbon nanotubes anchored montmorillonite hybrid (MWCNTs-Mt)/epoxy	/	161%	[67]
60 wt% functionalized Al$_2$O$_3$/3 wt% MWCNTs/8 wt%SiO$_2$ nanoparticles/epoxy	1.73	/	[66]
13 vol% 3D and vertically aligned carbon fibers (3D-CFs)/epoxy	2.84	14 times	[68]
10 wt% GNPs/epoxy	/	3times	[78]
0.75 vol% all-graphitized graphene aerogels/epoxy	6.57	37 times	[70]
2.3% 3D lamellar-structured graphene aerogels/epoxy	Through-plane 20	9915%	[71]
1 wt% 3D-graphene microspheres/epoxy	Out of plane TC 0.96	437%	[72]
0.93 wt% asymmetrically polydopamine-functionalized Janus graphene oxide/epoxy	in-plane TC 5.6	35 times	[73]
20.2 wt% siloxane cross-linked graphene framework (SGF)/epoxy	54.2	270 times	[74]

graphene oxide hydrogels as a precursor. An EC with only 0.75 vol% of high-quality graphene exhibits an excellent vertical TC of 6.57 W/ (m·K), which is more than 37 times higher than that of the neat ER, and one of the highest through-plane TC of polymer composites at similar loadings of carbon nanofillers. This group fabricated a lamellar-structured high-quality graphene aerogel (LSGA)(Fig. 12) [71] with superior TC capacity obtained because of its continuous network, densely stacked graphene lamellae, and large graphene sizes. The LSGA/ECs exhibit different TC along three directions, and in-plane TC can be as high as ~20.0 W/(m·K) at a low graphene content of 2.3 vol%. A three-dimensional linked graphene micro-sphere (Fig. 13) was created via a liquid nitrogen-driven assembly method, according to Zeng [72]. The composites produced have

excellent heat transfer enhancement efficiency of up to 431% per 1 wt% loading, leading to the maximum though-plane TC of 0.96 W/ (m·K). This rise is attributable to the graphene microspheres' well-organized three-dimensional network, which creates an efficient heat conduction path within the ER.

Wang et al. [77] examined the enhancement of the thermal transport across the interface between graphene and epoxy in graphene/epoxy nanocomposites. The heat resistance between the graphene and epoxy surfaces could be decreased by covalent and noncovalent functionalization. Butyl was found to reduce interfa-cial heat resistance better than carboxyl and hydroxyl among the various covalent functional groups. The interfacial thermal resis-tance is not affected by the carbon isotope doping in graphene.
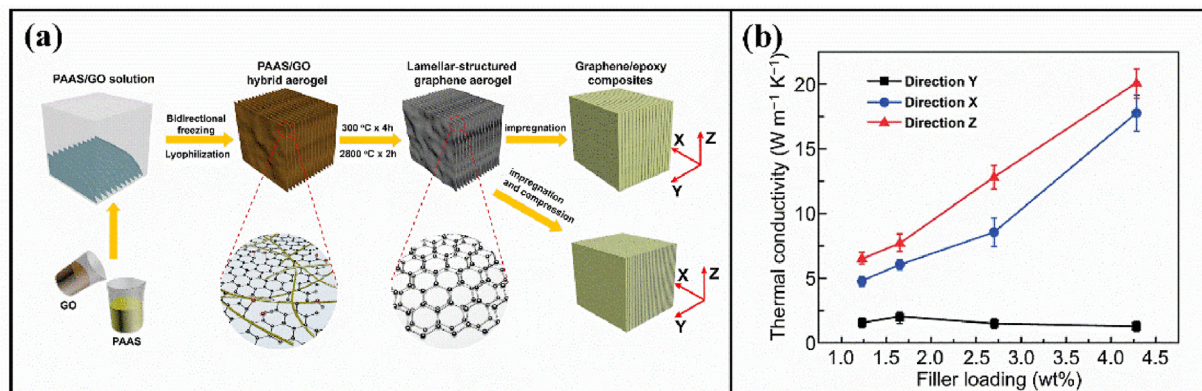

Fig. 12. (a) Schematic illustration of the fabrication of an LSGA and its epoxy composites, and (b) The TC of LSGA/epoxy composites [71]. Copyright 2020. Reproduced with permission from Springer Nature.
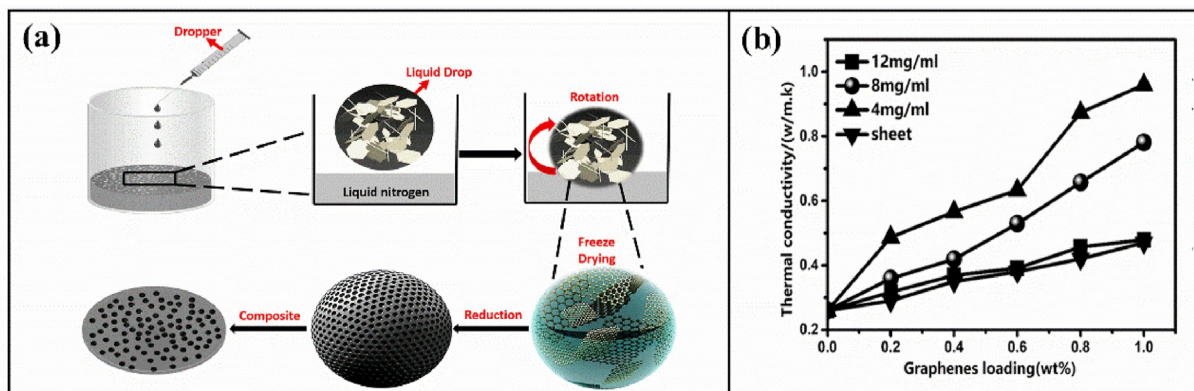
Fig. 13. (a) Schematic diagram of the preparation of graphene oxide microspheres/epoxy resin composites, and (b) The TC of graphene oxide microspheres/epoxy resin composites [72]. Copyright 2019. Reproduced with permission from Elsevier.

However, it can be slightly decreased by substituting acetylenic connections for the graphene's sp^2 bonds. Dong [73] prepared thermally conductive epoxy nanocomposites based on an asymmetrically polydopamine-functionalized Janus graphene oxide (JPGO) scaffold. The in-plane TC increased almost 35 times (~5.6 W/(m·K)) when the content of JPGO is 0.93 wt%. JPGO has a PDA coating on one face of nanosheets. The GO faces of JPGO in contact with each other decrease the internal resistance. The JPGO scaffold structure ensures that phonons transport efficiently through GO/GO interfaces, leading to high TC properties. Bao et al. [74] prepared a siloxane cross-linked graphene framework (SGF). The SGF/EC containing 20.2 wt% graphene exhibits an in-plane TC of 54.2 W/(m·K), which is about twice higher than that of GF/ER without siloxane and 270 times higher than neat ER. Here, siloxane molecular bridges not only resulted in the formation of a network of siloxane between adjacent graphene sheets via covalent bonding but also grafted the free amino groups on the surface of the graphene. These amino groups further reacted with ER, forming molecular chains and strengthening the interface reaction between SGF and matrix. Phonon can transfer through these molecular chains, and the thermal resistance of the composite was thus reduced.

Adding carbon fillers into epoxy is a promising approach to increasing the TC of ECs. The key points for TC improvement are content, dispersion, and alignment of fillers and the interfacial interaction between the fillers and matrix. The distinct thermal properties of the filler and matrix lead to a temperature jump at the interface and the associated interfacial thermal resistance.

4.2.3. Ceramic fillers

Ceramic fillers have been widely studied for thermally conductive and electrically insulating composites due to their inherent properties. They lack free electrons, and heat transfer is predominantly through phonons. Most ceramic fillers, such as silicon carbide (SiC) [79—81], Aluminum oxide (Al$_2$O$_3$) [82], and boron nitride (BN) have high TC as their strong interatomic bonds and crystal structure can significantly reduce phonon scattering. A list of various ECs with ceramic fillers used for TC enhancements is shown in Table 5. Sun et al. [83] reported SiC nanowire (SiCNW) networks that are vertically aligned and linked as effective fillers for polymer composites that result in dramatically improved TC. The composite obtained by infiltrating SiCNW networks into ER, at a relatively low SiCNW loading of 2.17 vol %, represents a high through-plane TC (1.67 W/(m·K)) compared to the pure matrix, which is equivalent to a significant enhancement of 406.6% per 1 vol % loading. The outstanding thermal performance is thought to be mostly due to

the well-organized SiCNW network, which can serve as a macroscopic expressway for phonon transport.

Thermally conductive and insulating thermal interface materials made of ER and Al@ Al$_2$O$_3$ with a core-shell structure are reported by Zeng et al. [84]. At 60 wt% filler content, the composites had a TC of 0.92 W/(m·K), which is 4.2 times more than that of resin. The creation of dense nanoscale insulating Al$_2$O$_3$ shells from the oxidation of aluminum particles effectively prevents electron transmission, increasing the composites' electrical resistivity and puncture voltage. The polymer composites loaded with Al@Al$_2$O$_3$ particles exhibit exceptional thermomechanical performance and high TC. Traditional polymer composites filled with Al$_2$O$_3$ powders present limited enhancement in TC even at a high loading due to thermal resistance on the filler/filler and filler/matrix interfaces. Yu et al. [85] added a contiguous 3D network of alumina foam (AF) filled with different diameters of Al$_2$O$_3$ microparticles to the ER, and the AF/Al$_2$O$_3$/EC exhibited a high TC of 4.1 W/(m·K) and a significant TC enhancement of 2097%. AF reduces the agglomeration of particles, and the Al$_2$O$_3$ fills the pores and voids of the AF and serves as bridges, and connects the adjacent strut walls to provide additional

Table 5
TC of ECs with ceramic fillers.

Ceramic fillers	Filler and loading	TC (W/(m·K))		
		Through-plane TC	In-plane TC	Refs.
SiC	3.71 vol% vertically aligned (VA) 3D-structure SiC sheet/epoxy	14.32	/	[79]
	3.91 vol% SiC nanowires/epoxy	0.43		[80]
	6.52 vol% 3D-SiC aerofoam/epoxy	10.26		[81]
	2.17 vol% SiC nanowire (SiCNW)/epoxy	1.67	1.45	[83]
Al$_2$O$_3$	36.5 vol% Al$_2$O$_3$/epoxy	3.17		[82]
	60 wt% Al@ Al$_2$O$_3$/epoxy	0.92		[84]
	Alumina foam(AF)/5 μm Al$_2$O$_3$/ 40 μm Al$_2$O$_3$/epoxy	4.1		[85]
BN	65.6 vol% BNMB/epoxy	5.08	17.61	[87]
	15 vol% 3D BN/epoxy	3.87	4.02	[86]
	90 wt% BN nanosheets (BNNSs)/ epoxy	2.6(25 °C) 3.5(200 °C)	6.6(25 °C) 8.4(200 °C)	[88]
	15 vol% BNNS/epoxy	6.07		[89]
	23 wt% tannic acid modified BN/C network/epoxy	1.524		[90]
	1.1 vol% 3D melamine foams@BNNSs/epoxy	0.6		[91]
	55.85 vol % 3D-BN/epoxy	3.53		[92]
	20 wt% BNNS@ silver nanoparticles (AgNPs)/epoxy	1.13		[93]

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heat conductive pathways. It indicates a synergistic effect between Al_2O_3 microparticles and 3D AF in the TC improvement.

The alignment of the atom and their interaction affect the efficiency of the heat transfer dramatically. For example, due to BN's special crystal structure, it shows anisotropic TC with ~600 W/(m·K) in the in-plane direction and ~30 W/(m·K) in the through-plane direction [86,87]. BN is difficult to realize that BN-filled composites with high TC in the through-plane direction. Tang et al. [88] successfully constructed a series of BN/epoxy composites filled with ultra-high BN content (65–95 wt%) by mechanical-balling pre-reaction process and general pressure molding methods. This compact structure provides efficient phonon transport pathways along a dense network of interconnected BN, resulting in BN/ECs with the highest in-plane TC. In addition, the slightly interlaced layers of BN between the neatly arranged layers of BN in the composite also play an important role in improving the through-plane TC of the BN/ECs. Bai et al. [89] prepared a high thermally conductive BNNS/EC, by building a nacre-mimetic 3D TC network within an epoxy resin matrix, realized by a unique bidirectional freezing technique. Su [90] fabricated a unique 3D interconnected tannic acid-modified BN and C network (M-BN/C), while the corresponding EC was manufactured with the easy-to-operate vacuum-assisted impregnation. Wu et al. [91] reported the fabrication of 3D BNNS networks (MF@BNNS) supported by melamine foam (MF) via multilayer assembly using BNNS as building blocks. The resultant 3D MF@BNNS supports were further encapsulated by ER to obtain the EC. Wu et al. [92] designed a 3D-BN framework by decomposing the sacrificial material. Then, highly thermally conductive 3D-BN/ECs were obtained by infiltrating ER into the BN framework. The thermal resistance was greatly reduced due to the formation of continuous heat transfer pathways in the BN framework and the reduction of the matrix-filler interfaces. Shi et al. [93] prepared edge-contaminated BNNS (BNNS−NH₂) by solid-state ball milling of h-BN using urea as a grinding aid (in Table 5). In addition, AgNPs were reduced in situ and deposited on the planes of BNNS-NH₂. BNNS@AgNPs/ECs were prepared by mixing and curing EP with BNNS@AgNPs nanoparticles. BNNS nanosheets will be interconnected by melting and coalescing of AgNPs attached to their surfaces, which will act as heat transfer junctions to reduce the thermal contact resistance between BNNS. The construction of continuous filler networks provides a new and promising route to improve the TC of composites. The fillers are specially designed to form continuous channels, which are like the "expressway" for phonon transmission [86]. Consequently, the TC of composites was significantly improved.

4.3. Microstructure control of TC epoxy composites

4.3.1. Effect of the microstructure on thermal transfer

One effective approach to enhance the TC of ER is the incorporation of TC fillers. Various types of fillers, such as metal-based, carbon-based, and ceramic fillers have been discussed. Many of these fillers exhibit immensely anisotropic TC due to their anisotropic structures. For example, 2D graphene and BN sheets demonstrate remarkable in-plane TC of 6000 and 600 W/(m·K), respectively [94,95]. While their through-plane TC is two orders of magnitude lower. To fully leverage their high in-plane TC, the design of aligned structures because necessary. however, fully translating their exceptional TC to composites remains a formidable task. This is because conventional processing routes, such as direct solution mixing and melt compounding, are unsuitable for forming percolated networks of TC fillers, even with homogeneous dispersion leading to huge thermal resistance at the filler-matrix interfaces and thus unsatisfactory TC of composites, typically below 5 W/(m·K). Various external forces can be employed to develop ordered pathways for efficient thermal conduction, such as

magnetic field, electrical fields, tape casting, and freeze-casting, and are described in detail by Mehra et al. [96].

Contrary to uniform dispersion strategies, by employing diverse rational assembly techniques, such as in situ chemical vapor deposition (CVD) growth [97], sol-gel method [98], self-assembly [99], and template method [100,101], 3D conductive networks are constructed, facilitating the orderly aggregation and assembly of TC fillers. Their pre-constructed filler networks ensure the inherent percolation of nanofillers when incorporated into composites. Consequently, phonons can efficiently travel through the interconnected networks without significant scattering at the filler-matrix interfaces, thereby maximizing the improvement in TC in composites, even with minimal filler loading. Yang et al. [102] and Zhang et al. [103] provided a critical overview of recent advancements in 3D assembly techniques for TC fillers.

4.3.2. Effect of the interface on thermal transfer

The epoxy resin by itself only has a TC of 0.2 W/(m·K) [15], and the thermal transfer is mainly dependent on the fillers and interfacial thermal resistance (ITR) [104]. Therefore, thermal interface resistance is an important factor that limits the TC of ECs. In general, the thermal interface resistance can be divided into two parts: matrix-filler interfaces and filler-filler interfaces [105]. Reducing either or both types of ITR can effectively improve the TC of ECs.

Current strategies for reducing ITR can be summarized as in-situ growth of hetero-structured TC fillers [106], surface functionalization of TC fillers [107], ordered alignment of TC fillers [108], and bridging of TC fillers [109]. Among them, the in-situ growth of hetero-structured TC fillers is only effective for reducing filler-filler interfaces, and the other three strategies are effective for reducing both the matrix-filler interfaces and filler-filler interfaces.

Han et al. [110] synthesized silicon carbide-boron nitride nanosheets (SiC-BNNS) hetero-structure TC fillers by sol-gel and in-situ growth method and the SiC-BNNS/ECs were then prepared. When the amount of SiC-BNNS is 20 wt%, the TC of the SiC-BNNS/ECs (0.89 W/(m·K)) was 1.7 times of SiC/BNNS/ECs (0.52 W/(m·K)) with the same amount of fillers, which proved that the SiC-BNNS hetero-structured TC fillers are beneficial for enhancing the contact and interaction between the fillers, and simultaneously improving the interfaces.

Yu et al. [111] treated Al_2O_3 nanoparticles with γ-aminopropyl triethoxysilane (γ-APS) to introduce amine groups on the surface of the particles, and then grafting of the hyperbranched aromatic polyamide started from the modified surface to obtain a thin polymer layer on the Al_2O_3 surface. The results presented that there are a 69% enhancement in TC for ECs with treated Al_2O_3 fillers and only a 21% enhancement in TC for ECs with untreated particles at the same fillers content. The authors attributed this to the formation of strong covalent bonding between Al_2O_3 particles and the epoxy matrix, which led to a heat flow network and reduced interfacial thermal resistance. Various surface modifiers have been studied to modify filler surfaces to decrease interfacial thermal resistance and enhance the dispersion of filler, including surfactants, coupling agents, functional polymers, etc.

Zeng et al. [100] reported a novel composite consisting of a 3D BN network infiltrated with an epoxy, which exhibited a high TC of 2.85 W/(m·K) at a relatively low BN content (9.29 vol%). This TC was 181% higher than that of the composite with randomly dispersed BN nanosheets. The 3D BN architecture provides improved heat conduction decreasing the interfacial thermal resistance among the BN sheets.

Wang et al. [112] prepared Ag/MXene/ECs. The TC of the Ag/MXene/ECs was 72.7 W/(m·K), which was 24.7% higher than that of Ag/ECs. This is due to that MXene acted as a bridge between dispersed Ag particles in the composites, thereby reducing the ITR.

5. Summary and conclusions

We have presented the different approaches, the thermal conduction mechanisms implied, and the main research progresses. The research and academic achievements are mainly focused on the development of intrinsically LCERs and their composites, the addition of fillers on amorphous ECs. Based on these researches, we can formulate several key messages.

(1) The TC of ECs holds particular significance, especially when considering low filler contents. At low filler contents, ER act as a thermal barrier and become a rate-limiter in the heat transfer channel. Increasing the TC of ER can help increase the TC of composites. Liquid crystal ordering and orientation in LCERs may be a possible approach to achieve high TC at low filler content.

(2) The addition of thermally conductive fillers is essential to achieve high TC. The filler type, filling amount, filler size, and shape have a great influence on the TC of ECs. High TC can be achieved with amorphous ECs at high filler loadings, when the fillers are in contact with each other and form thermally conductive pathways.

(3) The orientation of anisotropic fillers can lead to composites with anisotropic TC. The filler orientation should be avoided or enhanced according to the specific application requirements.

6. Future outlooks

While substantial advances have been reached in the TC of epoxy thermosets and composites, there are still some challenges necessary to break through in the future, motivated by the significance of this topic.

(1) ER, as a continuous phase, determines the overall performance of the EC. Therefore, precise design of epoxy molecular structures (e.g. mesogenic units and aliphatic chains) or modification of ER with specific functional groups (e.g. flame retardant groups, epoxy vitrimers) can provide composites with better TC, higher flame retardancy, self-healing ability, etc. This is a very meaningful future direction.

(2) The TC improvements of ECs based on fillers mainly depend on three major factors: intrinsic properties of fillers, their dispersion and orientation, and the interaction between fillers and matrix. How to improve the interaction between fillers and epoxy matrix, and the orientation of filler in epoxy needs to be further studied.

(3) The less expensive fillers such as Al$_2$O$_3$, AIN, and BN are available commercial products, their composites have great potential for TC application. It is important to develop high TC composites containing low-cost thermally conductive fillers and scale up their production through the joint efforts of academia and industry.

Declaration of competing interest

There is no conflict of interest.

Acknowledgments

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