JrnlID 10965_ArtID 429_Proof# 1 - 07/04/2014

J Polym Res (2014) 21:429
DOI 10.1007/s10965-014-0429-0

REVIEW PAPER

From clay to graphene for polymer nanocomposites—a survey

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Received: 6 February 2014 / Accepted: 27 March 2014

Abstract The development of aerospace and automotive industries requests lightweight, high-performance materials, and polymer nanocomposites are ideal candidates in this case, which is shown by the increasingly more publications in this research field over the past two decades. However, the performance of nanocomposite not only depend on the properties of their individual constituents, but on their morphology and surface characteristics of fillers as well. Selections of nanofillers geometries, e.g. particulate, fibrous or layered have a tremendous influence on the properties of nanocomposites and their processing methods. In this paper, we review the chronological works performed in the field of polymer nanocomposites, in particular epoxy nanocomposites reinforced with layered fillers, such as clay and graphene. Surprisingly layered fillers are commercially available and more cost-effective than nanoparticles and carbon nanofibres, and these make them to the most extensively studied fillers that can be geared toward future applications, particularly in large-scale polymer nanocomposite production.

Keywords Epoxy · Nanocomposite · Clay · Graphene

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Introduction

Developing high-performance materials and systems by cost-effective means is an everlasting topic in science and engineering. Inspired by this topic, researchers endeavour to achieve increasingly higher performances by designing, fabricating and controlling materials with possibly smallest scales. Nobel Prize laureate Richard P. Feynman once predicted that controlling the arrangement of structural units on a small scale would bring enormous improvement of properties that substances can have [1]. His vision not only serves as a foundation for all the excitement about nanomaterials, but for the success of modern science. Today, there is no doubt that the nanomaterials drive the world and affect our daily life.

Last year, the worldwide demand for nanomaterials has already reached over $4.2 billion [2]. For example, the demand for nanomaterials in Japan is expected to exceed $6.3 billion by 2025 due to the use of nanomaterials beyond their initial outlets, such as wafer polishing slurries used in semiconductor manufacturing, high-performance plastic composites, superior adhesives, transparent sunscreens, personal care products and high-end sports equipments. Figure 1 contains a detailed forecast for nanomaterials' demand in Japan in 2001–2025 including the price of nanomaterials per gross domestic product (GDP); it shows a steady annual increase.

Of all nanomaterials, polymer nanocomposites are the most well-known and have been broadly investigated for a wide range of applications, including flame-retardant panels, anti-scratch coating for surface protection, high-barrier film for packaging applications and lightweight, high-performance components used in aerospace and automotive industries [3–7]. Different to other materials such as metals and ceramics, polymers feature low manufacturing cost and high specific strength, which means less energy needed for produc-

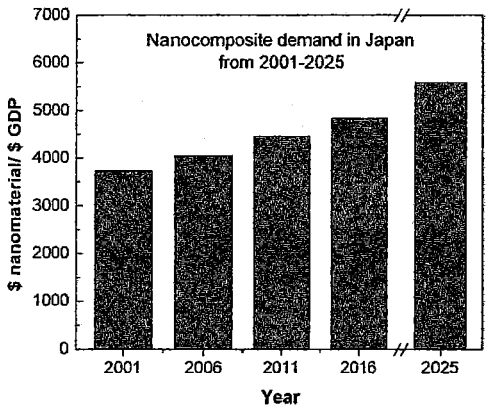


Fig. 1 Total values of the demand of nanocomposites in Japan per GDP [2]

tion and recycling. In automotive industry, polymers allow design flexibility and weight saving compared to metals. This indirectly improves fuel economy and reduces the emission of exhaust gases. For example, 100 kg of polymer can substitute 200–300 kg of traditional materials, resulting in fuel saving by 750 l over an average lifespan of a vehicle.

In spite of these advantages, the major downsides of polymers include inherently low mechanical properties and thermal stability and lack of functionality. For instance, automotive polymer parts are not allowed to deform under solar radiation and motor heat, the aerocraft parts must be able to dissipate lightning strike and a car brake pad used in dynamic loading environment must be able to dissipate heat build-up in parts. These requests promote the development of polymer composites—a combination of two or more materials has the potential to provide value-added properties absent in the neat polymers.

Polymer nanocomposites

The advent of nanotechnology leads to a reduction in the filler size of composites to nanoscale. The consequences of this reduction conceptually produce an increase in the interfacial area per volume and a reduction in the surface–surface interparticle distance. Nanocomposites produce superior performance to their peer composites, and this creates brighter prospects to polymer nanocomposites with regards to industrial applications. Figure 2 shows the discrepancy between composites and nanocomposites in terms of total particle surface area and surface–surface interparticle distance.

As the volume fraction increases, the surface–surface interparticle distance (Fig. 2a) is far more reduced in nanocomposites than composite. This means that at a similar volume fraction, the interaction between nanoparticles is much higher than that between micron-sized particles. Therefore, nanoparticles under loading are able to interact each other more effectively to restrain the matrix molecular deformation. The total surface area of nanoparticles (Fig. 2b) enhances significantly with their volume fractions when compared to composites. This is because, by being small, nanoparticles have a far higher surface area to volume ratio, therefore leading to more interaction with matrix for higher reinforcement as illustrated in Fig. 3. At very low fractions (typically 0.1–3.0 vol%), the interfacial region of nanoparticles would be sufficient to interact with matrix molecules for reinforcement or toughening of polymers [9–14]. These two structural features determine that nanocomposites possess more superior properties than composites at low filler fractions.

It is undeniable that low fractions of nanoparticles enhance a variety of properties considerably without sacrificing other desirable properties of polymer matrix. Examples include superior mechanical properties, reduction of residual stresses, lower water sensitivity, lower permeability to gases, better thermal stability, improved chemical resistance and enhanced conductivity [15–19]. In spite of these achievements, poor adhesion between inorganic nanoparticles and polymer matrix due to their inert chemical structure still remains a challenge; therefore limit their applications in industry.

Nylon-6/clay nanocomposites are the first set of polymer nanocomposites that have been commercialized by the Toyota Central Research Laboratories in Japan, which are now used as the heat-resistant timing belt covers in Toyota cars [20–22]. Since this successful achievement, many studies have been progressively conducted on the synthesis and characterization of nanocomposites, to understand the fundamentals of nanofiller interaction with polymer matrix. These studies have been extended to various types of polymer systems including thermoplastics [23–26] and thermosets [27–30], where eventually different levels of property enhancement have been more or less accomplished, depending on the nature of polymer matrix and fillers and the interaction between them.

Epoxy-based nanocomposites

Of thermosets, epoxy resins are by far the most widely used polymer in industries; typical applications include coating, structural adhesives and composites. This is due to their excellent chemical resistance against severe corrosive conditions, high thermal and mechanical properties, excellent adhesion to a wide range of materials and ease of processing. Using different curing agents (hardeners), epoxy resins can be tuned to a broad spectrum of properties and thus suit various applications. The high crosslink density of epoxy resins make them inherently brittle, which leads to instant crack propagation causing catastrophic disasters. This spurred extensive studies for toughening epoxy.

A myriad of attempts have been made to improve the fracture toughness of epoxy resins by using inorganic particles. This is proved by over 20,000 publications on epoxy/inorganic particle composites over the past 10 years as shown

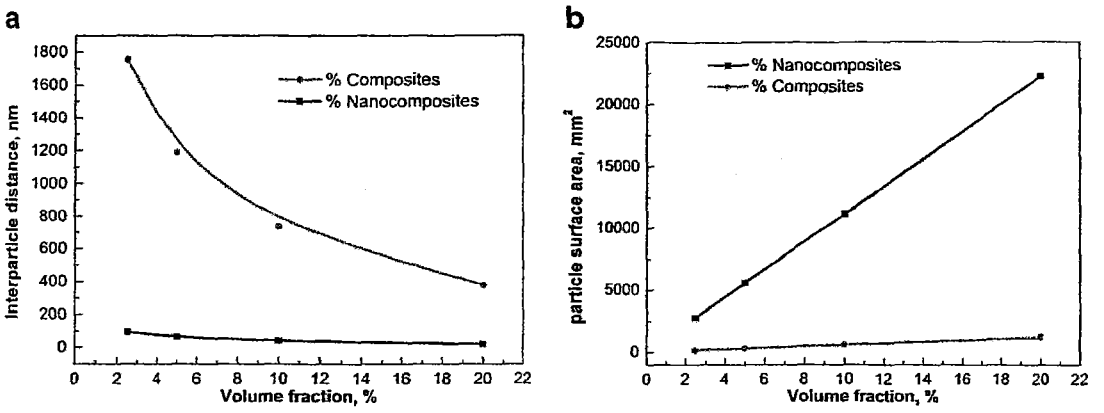


Fig. 2 Comparison of nanocomposites with composites in terms of **a** Surface–surface interparticle distance and **b** Total particle surface area in 1 mm^3 [8]

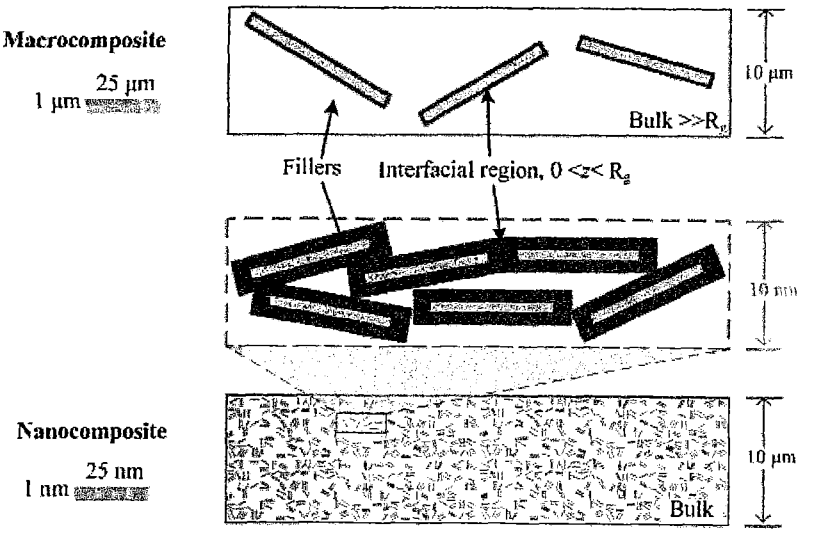
in Fig. 4. However, these toughening processes cause loss of other desirable properties such as stiffness, strength and ease of processing. For example, the use of rubber-toughened epoxy improved the fracture toughness substantially but it compromised the thermal stability, yield strength and modulus of epoxy [31, 32].

Alternatively, polymers, containing layered fillers such as clay or graphene, have demonstrated an impressive potential for development of new materials possessing high mechanical performance and new functionalities that mainly include high barrier property and thermal/electrical conductivities [33–37]. The high surface area and uniform dispersion are the two key aspects for improvement of the mechanical properties and fracture toughness.

Layered structural fillers

The fabrication type of nanofillers is quite important as it produces significant impact on the interface between fillers and matrix. The properties of nanocomposite materials not only depend on the properties of their individual constituents, but on their morphology and surface characteristics of fillers. Selections of nanofillers, such as filler shape and filler size, have a tremendous influence on the properties of nanocomposites and their processing methods.

There are three main categories of filler geometries that have been adopted in polymer nanocomposites, including particulate [38, 39], fibrous [40, 41] and layered fillers [42, 43]. Figure 5 shows how these fillers are distinguished by their respective total surface area, geometry and size. As indicated by Hussain et al. [44], any modification carried out on these three categories of filler would affect the surface area-to-volume ratio by three orders of magnitude. By assuming (i) a volume of 10 μm^3, (ii) a filler fraction of 1 vol%, (iii) an average lateral dimension, l of 1 μm, and (iv) a thickness, t or diameter, d of 1 nm, the total surface area of filler can be calculated by using the following equations,



Q2 **Fig. 3** Uniqueness in nanostructured materials

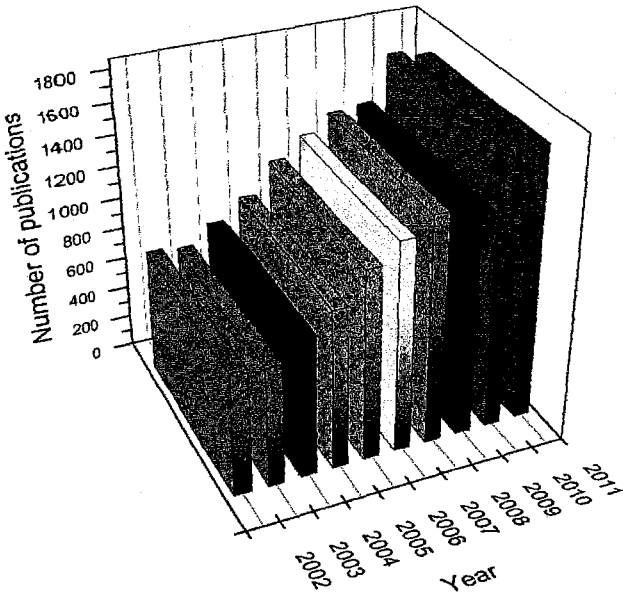


Fig. 4 Number of publications on epoxy nanocomposites in 2002–2011

$$\text{Total number of fillers, } n^* = \frac{10\ \mu m^3 \times 0.01}{\text{filler's volume, } V} \quad (1)$$

$$\text{Total surface area, } A^* = \text{filler's surface area, } A \times n^* \quad (2)$$

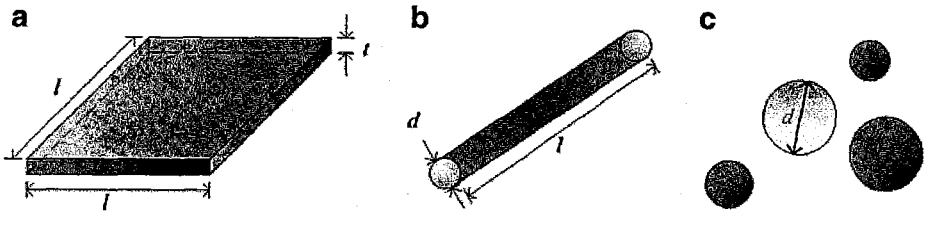
Figure 5a shows a particle of platelet-like structure, also known layered structure. Its thickness, t is less than a few nanometers and the lateral dimension, l may be in the range of several hundred nanometers to microns. Typical examples include clay and graphite, each of which will be discussed in the following chapters. The second type of geometry is fiber or tube-like structure, i.e. nanofiber and carbon nanotube. They possess elongated structure, whereas one dimension (diameter, d) is in the nanometer scale as illustrated in Fig. 5b. The third type has all three nanoscale dimensions—referred as particulate or spherical particles as shown in Fig. 5c. Silica nanoparticles are a typical example. Comparing these three geometries leads to a conclusion that the layered nanofillers have the highest specific surface area.

Moreover, of all nanofillers, clay and graphite are known for low cost in comparison with carbon nanotubes and nanospheres-like structure, as tabulated in Table 1. In spite of the low cost, their performance is comparable to or even higher than other expensive fillers. Rafiee and co-workers [48] compared graphite platelets with carbon nanotubes for their effect on the mechanical properties of polymers; the tensile strength and fracture toughness were enhanced by 40 % and 53 %, respectively by the platelets, as compared to 14 % and 20 % improvement by multi-walled carbon nanotubes. The authors suggested that the enhancement related to the high specific surface area and the two-dimensional geometry of the platelets.

Progress in epoxy/clay nanocomposites

The first set of epoxy/clay nanocomposites was explored in 1994 by Lan and Pinnavia [49]. By compounding modified clay with elastomeric epoxy [50], they discovered that a surfactant containing hydroxyl groups promoted the intercalation of epoxy into the layer spacing and thus helped the exfoliation of layers.

The major challenge in the development of layered polymer nanocomposites is how to achieve a complete exfoliation of silicate layers and their uniform dispersion in matrix. According to Kornmann et al. [51, 52], a key to achieve exfoliation is to design and conduct a higher rate of polymerization between the layers than that of polymerization outside galleries. This was later supported by a research by Lan et al. which showed that chemical reactions in the intergallery can drive the layers to delaminate [53]. Of the many strategies developed to fabricate epoxy/clay nanocomposites, the most important ones are highlighted as below.



$A = 2l^2 + 4lt$
$V = l^2t$
Specific surface for a given volume = 2.0×10^6 m^{-1}

$A = \pi d^2/2 + \pi dl$
$V = \pi d^2 l/4$
Specific surface for given volume = 3.1×10^4 m^{-1}

$A = \pi d^2$
$V = \pi d^3/6$
Specific surface for given volume = 3.1×10^1 m^{-1}

Fig. 5 Geometry and specific surface area of nanoparticles

t1.1 **Table 1** Cost comparison on commonly used nanofillers [45–47]

t1.2 Types of nanofillers	Cost
t1.3 Graphite	$ 2 to $ 5 per kilograms
t1.4 Clays	$ 2 to $ 5 per kilograms
t1.5 Carbon nanofibres	$ 95 to $ 1,500 per kilograms
t1.6 Single-walled carbon nanotubes	$ 170,000 per kilograms
t1.7 Multiple walled carbon nanotubes	$ 8,000 per kilograms
t1.8 Nanosilica	$ 8.50 per kilograms

In 1995, Pinnavaia et al. [54] reported the exfoliated nanocomposites formed by clay modified with primary and secondary onium ions, whereas those modified with tertiary and quaternary onium ions retained the intercalated structure. Meanwhile, Zilg et al. [55, 56] dissolved alkylamine with HCl solution to modify clay; using a similar approach as Pinnavaia et al. [54], different alkyl chain length was employed in their study, ranging from butyl (C4) to hexyl (C6), octyl (C8), decyl (C10), dodecyl (C12), hexadecyl (C16), and octadecyl (C18). They found a different result where merely intercalated nanocomposites was observed, although the interlayer distance increased significantly when the alkyl chain length is over six carbon atoms.

In 2001, Chin et al. [57] compounded epoxy with a C18 alkyl ammonium-modified clay. Intercalated structure was formed when equivalent molar or higher amount of hardener was used; by contrast, exfoliation was achieved when less amount or no curing agent was used. Nearly at the same time, Kornmann et al. [58] stated that when organoclay was combined with an epoxy resin, the mixture would initially form intercalated structure. Further combination of the mixture with a hardener can produce exfoliation, but the exfoliation degree is dependent on the reactivity of the hardener. Figure 6 shows that a lower reactivity produced a greater level of exfoliation, and more exfoliation was obtained when a higher temperature of curing is used for the same curing agent, which is in agreement with Chin et al. [57]. All these studies proved that curing helps to promote exfoliation.

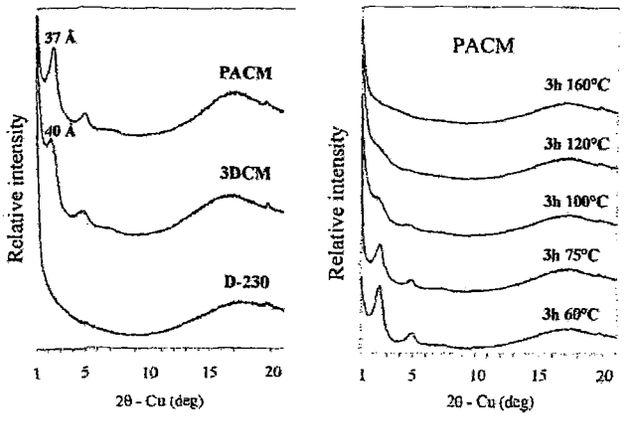


Fig. 6 XRD patterns for different epoxy systems and curing temperatures [58]

Later in 2003, Yasmin et al. [59] presented an interesting method to exfoliate clay layers in epoxy, by combining the epoxy/clay mixture with an anhydride curing agent and an accelerator. They found that exfoliation was achieved with the clay fractions lower than 8 wt% but higher fractions resulted in the restacking and agglomeration of layers. A similar method was presented by Zhang et al. [60] in 2004 who used an alkyl ammonium salt to exchange for inorganic cations in clay, followed by compounding with epoxy and curing by an anhydride hardener.

It is noteworthy that Ma et al. [61] achieved the disordered exfoliation of clay layers in epoxy, by modifying clay surface with a diamine hardener—one amine group grafted with clay layer by ion exchange and another subsequently reacted with epoxy during curing as illustrated in Fig. 7. However, no mechanical properties and toughness were reported, which was due to no sufficient manpower and facilities available.

A slurry compounding method was developed for nanocomposites of nylon/clay [22] and recently for epoxy/clay [62, 63]. The basic idea is to first increase the clay interlayer spacing through polymerization or suspension in water/solvents and then intercalate the matrix polymer into this enlarged spacing. Ma et al. actually used this method to achieve exfoliation of clay in polymers [64, 65].

Later in 2008, Wang et al. [66] adopted an epoxide-containing surfactant to modify clay, such as reactive flame retardant (RPC), Glycidyloxypropyltrimethoxy silane (GPMS) and then compounded with epoxy resins; the epoxide groups reacted with hardeners to produce links between layers and matrix, promoting the exfoliation of layers (refer Fig. 8). More recently, a similar study by Park et al. [67] used a silane coupling agent to carry out a similar process.

Exfoliated structure is generally believed to produce higher increment in the modulus, fracture toughness and glass transition temperatures of epoxy resins than intercalated structures. Table 2 tabulates a summary of the mechanical properties of epoxy/clay nanocomposites. Obviously, it can be seen that stiffness (Young's modulus) increases when reinforced by clay, and the increment is more obvious for a softer matrix. Unlike the stiffness, the tensile strength shows different trends: it increases in some systems but reduces in others. This is explained as the following: (1) improvement of tensile strength by clay is often occurred in an elastomeric matrix [66, 74], while in a stiff matrix, it showed reduction [68, 69]; (2) weak interface formed between layers and matrix [70] would behave as defects in tensile testing; (3) incomplete degassing causes voids which reduces tensile strength

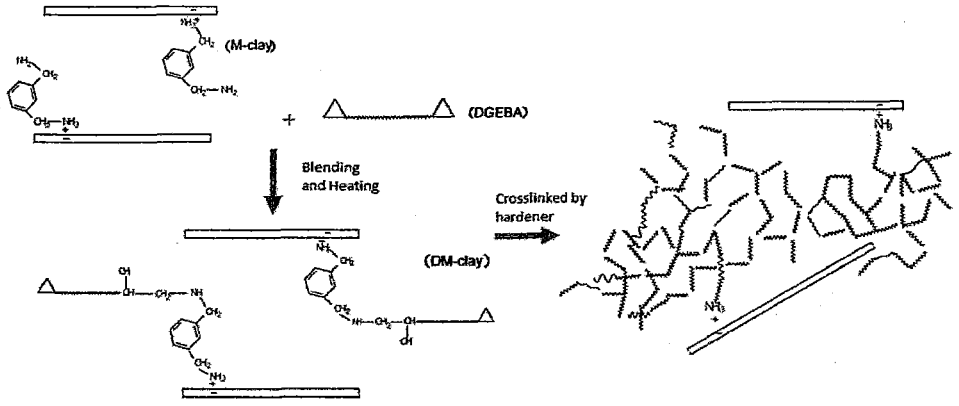


Fig. 7 Reaction mechanisms using diamine hardener [61]

[59]. Meanwhile, the fracture toughness values K_{Ic} increased substantially for nanocomposites compare to pristine resin. By contrast, the glass transition temperature, T_g shows inconsistency results. This probably caused by: (1) inappropriate ratio of epoxy to hardener, (2) variations of curing condition, such as temperature and time and (3) excess surfactants left by modification.

Progress in epoxy/graphene nanocomposites

Graphene is well-known for its stiffness 1 TPa, intrinsic strength 130 MPa and higher electrical/thermal conductivities than copper [75, 76]. One of the major means to harvest these striking properties is to compound graphene with polymers—the development of polymer/graphene nanocomposites. Historically, graphene became well-known when Nobel prize winners, Prof. A.K. Geim and Prof. K. S. Novoselov fabricated graphene by using a sticky tape to peel off graphene layer–by–layer from graphite [77–79].

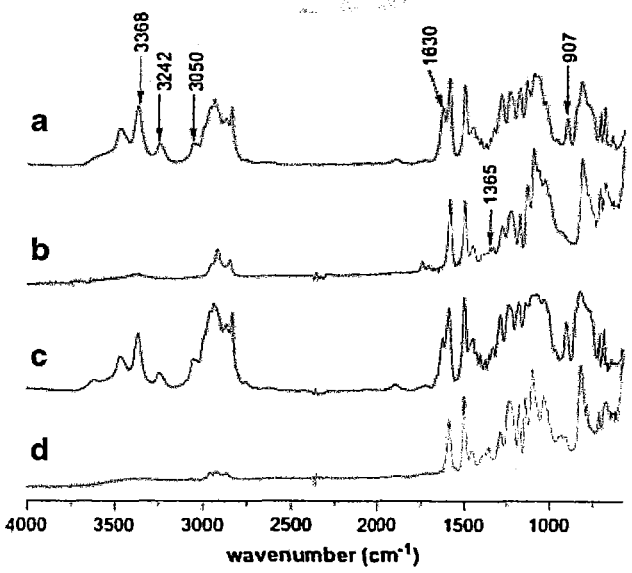


Fig. 8 FT-IR spectra of ERPC **a** Before curing **b** After curing and EGPMS **c** Before curing **d** After curing [66]

Since this breakthrough, increasingly more researchers have started graphene research. Although both epoxy and graphene are based on carbon, it is a great challenge to develop epoxy/graphene nanocomposites, because of two limiting factors: (i) costly fabrication of graphene oxide by oxidation and reduction and (ii) lack of functional groups on graphene surface for interface modification of polymer nanocomposites [80, 81]. Below is a brief review on the development of epoxy/graphene nanocomposite.

The review started from epoxy/graphite nanocomposites, since graphene is just a single graphite layer of minimum thickness (as shown in Fig. 9). Research on epoxy/graphite composites was established 25 years ago, but most of these focused on utilising graphite fibers in the production of conventional composites [82–84].

Through thermal expansion and/or ultrasonication, graphite oxide or graphite intercalation compounds can produce platelets of 5–500 nm in thickness, which is named graphite nanoplatelets (GNP). However, depending on the production method used, the thickness and lateral dimensions of platelets could vary widely as great as 10 nm and 15 μm, respectively [85, 86]. It is emphasized that GNPs have emerged as an important candidate in polymer nanocomposites because of its capacity for large-scale production. Although it is a component of stacked monolayer graphene sheets, its low cost and lightweight cultivate GNPs as alternative to metal- and other carbon-based fillers [87].

Research on epoxy/GNP nanocomposite started in 2004 by Yasmin and Daniel [88]. They prepared 2.5–5 wt% nanocomposites by adopting ~250 nm thick GNP; the composites showed slightly higher thermal stability and increased char concentration in comparison with neat epoxy, but there was reduction in coefficient of thermal expansion and no significant enhancement in mechanical properties. Later in 2006, Asma Yasmin et al. [89] compared the effect of processing

t2.1 **Table 2** Comparison of previous studies on mechanical properties of epoxy/clay nanocomposites

t2.2 Reference	Filler fraction	Percentage property improvement from neat epoxy to its layered nanocomposites			
t2.3		Young modulus (GPa)	Tensile strength (MPa)	K_{Ic} (MPa·m$^{1/2}$)	T_g (°C)
t2.4 Zilg et al. [55]	10 wt%	41 %	−39.5 %	35.8 %	−21.2 %
t2.5 Yasmin et al. [59]	10 wt%	66.7 %	−60.3 %	N/A	N/A
t2.6 Wang et al. [63]	5 wt%	40 %	−25.7 %	80 %	−11 %
t2.7 Wang et al. [66]	5 wt%	40 %	−56.6 %	N.A	−1.4 %
t2.8 Frohlich et al. [68]	10 wt%	5.6 %	−39.2 %	68.7 %	−3 %
t2.9 Zerda and Lesser [69]	12.5 wt%	14.3 %	−30 %	44.4 %	N/A
t2.10 Kornmann et al. [70]	10 wt%	54 %	−36 %	N/A	N/A
t2.11 Wang et al. [71]	3 wt%	12 %	−16.5 %	56.4 %	−6.8 %
t2.12 Triantafillidis et al. [72]	3 wt%	24 %	N/A	N/A	−7 %
t2.13 Zaman et al. [73]	1.3 wt%	16.5 %	−8 %	14.4 %	+6.3 %

methods (e.g. direct mixing, sonication mixing, shear mixing, combined sonication and shear mixing) to observe which one dispersed better GNP in epoxy, and the composite prepared by ultrasonication showed proportional increase in modulus and slightly higher fracture toughness.

By contrast, Lu et al. [90] obtained a low electrical conductivity percolation threshold at 0.015 vol%, which unfortunately was achieved at the expense of mechanical properties of epoxy. This low percolation threshold could be explained by the large lateral dimension of GNP and the reduction of mechanical properties caused by: (1) weak interfacial interaction between GNP and epoxy and (2) the existence of aggregated GNP.

Surface modification of GNP was conducted by Li et al. [91] who exposed GNP to ultraviolet/ozone; this treatment enhanced the interfacial bonding between matrix and fillers, by creating functional groups on the surface of GNP, although the chemical reaction involved has not been identified. In Fig. 10, platelets of less than 4 nm in thickness produce much more total surface area than other thicker platelets. Since these thin platelets approximate the properties of graphene, they are name graphene platelets (GnPs).

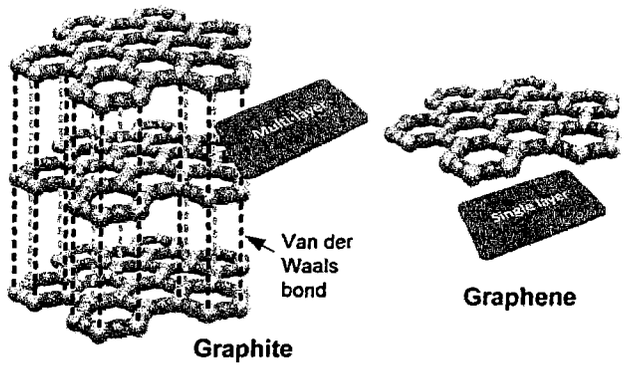


Fig. 9 Atomic structure of graphite and graphene

For GnPs-based nanocomposites, a low thickness value is vital because (i) low thickness implies a maximum possibility to retain the striking in-place properties of graphene by reducing the negative effect of its poor through-plane functional and mechanical properties, and (ii) the total number of GnPs and their total surface area in a given volume reduce markedly with increase in thickness as depicted in Fig. 10. Table 3 tabulates a typical thickness of graphene derivates.

Recently, the thermal expansion of graphite oxide produced GnPs of ~2 nm in thickness by Yu et al. [92]; at 25 vol%, GnPs improved the epoxy thermal conductivity by 3,000 %. Later in the following year, by studying a three-phase nanocomposites based on epoxy, GnPs and single-walled carbon nanotube (SWNT) [93], they proposed that a further phonon transfer can be established when the contact area between flexible SWNTs and planar GnPs is extended via van der Waals attraction.

Rafiee et al. [94] found that GnPs synthesised from the rapid heating (>2,000 °C/min) of graphite oxide performed better than SWNTs and MWNTs; a weight fraction of just

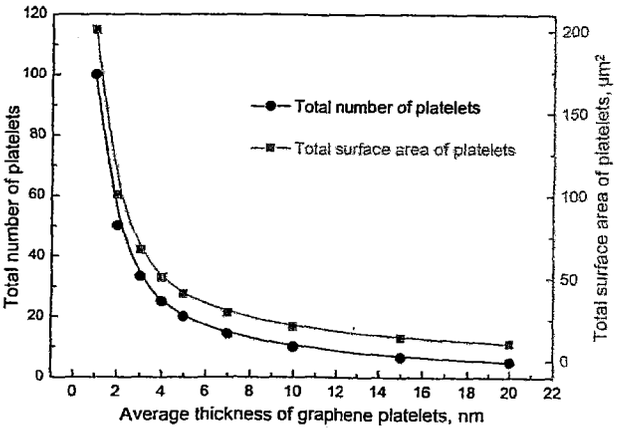


Fig. 10 The number of graphene platelets and their total surface area at 1 vol% GnPs

t3.1 **Table 3** Typical thickness of graphene derivations [85, 86]

t3.2 Graphene derivations	Abbreviation	Thickness
t3.3 Graphite	–	0.4–60 μm
t3.4 Expanded graphite	EG	100–400 nm
t3.5 Graphite nanoplatelets	GNP	5–100 nm
t3.6 Graphene platelets	GnP	0.34–5 nm

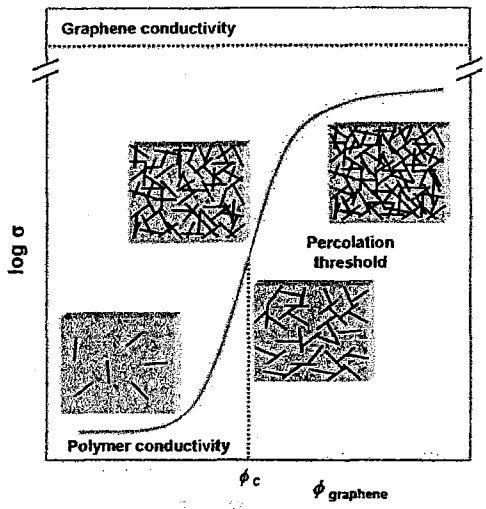


Fig. 11 Schematic model for conductive nanocomposites, where $\varnothing_c$ represents the critical concentration at the percolation threshold [101]

0.1 % of GnPs increased the critical buckling load by ~52 %, outperforming identical weight fractions of SWNTs and MWNTs. Coincidently in another study, it was found again that GnPs offered more significant improvements of mechanical properties and fracture toughness than SWNTs and MWNTs [48]. Table 4 tabulates the mechanical properties and electrical conductivity of epoxy/graphene nanocomposites, including Young's modulus, tensile strength, fracture toughness, glass transition temperatures and electrical percolation threshold.

It is noticed that the graphene fraction used to toughen epoxy was lower than silicate layers. This advantage definitely makes graphene the next generation of layered filler for polymer nanocomposites that feature high specific strength for applications in aerospace, automotive and wind power industries. Compounding graphene with epoxy results in higher improvement in stiffness and fracture toughness than nanotubes [48]. This is because: (i) a planar graphene sheet possesses considerably more contact surface area with polymer than carbon nanotubes; the top and bottom surface of graphene sheet can be in close contact with polymer chain, while the interior of carbon nanotubes cannot be reached by polymer chains, (2) the two-dimensional geometry of graphene sheet is far more effective in producing crack deflection than 1-D nanotubes; when it encounters a crack, the sheet forces the crack to tilt and twist, and this process helps to absorb energy to prevent the propagation of a crack. In Table 4, tensile strength and glass transition temperature show inconsistent results, which have the same explanation to the previous clay-toughened epoxy. For the electrical conductivity percolation threshold, the lowest value observed was at 0.5 wt% (~0.25 vol%). This low percolation threshold was achieved due to highly percolated pathways produced by graphene sheets for electron transfer as illustrated in Fig. 11, therefore making the composite electrically conductive.

Prospect of applications

Research on polymer nanocomposites has been intensifying since 2002 (Fig. 4). Two landmark studies include: (1)

t4.1 **Table 4** Comparison of previous studies on various properties of epoxy/graphene nanocomposites

t4.2 Reference	Filler fraction	Percentage property improvement from neat epoxy to its layered nanocomposites				Electrical percolation threshold
t4.3		Young modulus	Tensile strength	K_{Ic}	T_g	
t4.4 Yasmin and Daniel [88]	5 wt%	25 %	8.8 %	N/A	+2.1 %	N/A
t4.5 Jana and Zhong [95]	5 wt%	13 %	45.2 %	27.8 %	N/A	N/A
t4.6 Li et al. [91]	2 wt%	13 %	−24.5 %	N/A	+3.1 %	1 wt%
t4.7 Yasmin et al. [89]	1 wt%	15 %	−6 %	N/A	N/A	N/A
t4.8 Liang et al. [96]	N/A	N/A	N/A	N/A	N/A	0.5 vol%
t4.9 Miller et al. [97]	1 wt%	52 %	30.5 %	−11.0 %	−2.9 %	0.5 wt%
t4.10 Rafiee et al. [48]	0.1 wt%	31 %	41.8 %	53 %	N/A	N/A
t4.11 Ganguli et al. [98]	8 wt%	N/A	N/A	N/A	+7 %	8 wt%
t4.12 Zaman et al. [99]	4 wt% (2 vol%)	22 %	17 %	93 %	+12.4 %	N/A
t4.13 Zaman et al. [100]	1 wt% (0.5 vol%)	27 %	23 %	123 %	+14.6 %	0.25 vol%

t5.1 **Table 5** Potential applications of nanolayers and graphene in industry [102–106]

	Fillers	Area	Application
t5.2			
t5.3	Nanoclays	Aerospace and aviation	Cryogenic storage systems
t5.4		Automotive	Making timing belt cover, engine covers, structural seat backs and fuel system components
t5.5		Flame retardants	Use as coating systems to reduce flammability in computer and monitor housings
t5.6		Packaging	Food, drink and beverage packaging
t5.7	Graphene	Aerospace and aviation	Provide electrostatic discharge and electromagnetic interference shielding components as well as weight saving
t5.8		Automotive	Benefit to the electric vehicles to offset adding weight of their batteries
t5.9			Electrostatic spray painting in the body parts
t5.10			Next generation Li-ion battery and fuel cell bipolar
t5.11		Sporting goods	Baseball bats, rackets and hockey sticks
t5.12		Electronics	Transparent electrodes, LCD screen and integrated circuits

development of nylon/clay nanocomposites by Toyota research group [21], where the improvements of thermal and mechanical properties were accomplished at 4.2 wt% clay loading, and (2) research on a free standing, single-layer graphene sheet by scientists at the University of Manchester [77].

Now with highly improved properties and ease of manufacturing, the polymer nanocomposites would be expected to substitute more conventional composites. Indeed, these improvements obtained at low filler content make polymer nanocomposites ideal candidates for applications in high-performance structural composites, such as those used in production of aircraft, automotive, marine, spacecraft composites and sporting goods. Table 5 shows some of the potential applications of layered polymer nanocomposites. Liqun Zhang et al. have achieved the commercial production of rubber/clay nanocomposites (i) in Hainan Province of China for fabricating the tyre tread used in heavy trucks and the cover layer of conveyor belts with high chipping- and chunking-resistance and (ii) in Jilin Province of China for manufacturing the inner tyre layers of low permeability. In fact, the automotive and aerospace industries are investigating layered polymer nanocomposites as a potential candidate of structural materials for the 21st century [3]. Nevertheless, the commercial impact of nanocomposites is still not overwhelming, in spite of the extensive interest and high performance from research. This is because major discoveries normally take several decades to reach large commercial scale due to the cost and performance variables [32]. That is why in future research, facile fabrication is always considered to produce a combination of excellence in performance and cost-effectiveness in manufacturing.

Potential applications of layered epoxy nanocomposites include electronic packaging, coating, adhesives, sport equipment and advanced composites. These nanocomposites are solutions to future automotive applications, for instance gas tanks, interior and exterior panels, and aircraft applications such as high performance components and flame retardant panels. Some of them are already commercially employed, such as in golf clubs, tennis racket and hockey stick. A NASA report described epoxy nanocomposites as a potential candidate for cryogenic storage application [107]. These nanocomposites show more commercial prominence in advanced composites, since weight reduction is believed to be the primary driving factor to this application.

Functionalities, such as electrical and thermal conductivity provide advantages to utilization of epoxy nanocomposites. In aerospace applications, electrically conductive composites are crucial to mitigate electrical charge in space vehicles in the charged space environment. On the other hand, thermal conductivity is important to dissipate tremendous heat build-up in elastomeric products, such as vehicle track pads, which are used in dynamic loading environment. This improvement is not only able to improve the service life of thermoset polymer, but reduces the impact of thermosetting waste on the environment.

Conclusion

Over the last two decades, polymer nanocomposites have been remaining the focus of research and development in materials science and engineering. The demand for polymer nanocomposites increases every year due to the industrial leaning for high-performance composite materials used in applications such as aircrafts, spacecrafts, automobiles and military and sports facilities. Although some of these nanocomposites have already been commercialized in industries, there are a number of challenges needed to be addressed in polymer nanocomposites, including effective toughening or reinforcement and provision of functionality. In this paper, we have presented a brief review of the recent works and properties enhancement in epoxy nanocomposites reinforced with

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layer structured fillers, such as clay and graphene. We anticipate seeing more research activities in this lively field and in fact, we believe that there is always a room for improvement, e.g. the interface of polymer nanocomposites, and this research area is full of challenges, given the complexity of interface which involves extensive cross-disciplinary research.

Acknowledgments IZ thanks MOHE (Ministry of Higher Education Malaysia) and University Tun Hussein Onn Malaysia for the award of scholarship. Special thanks to University of South Australia for providing facilities for this research.

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