

Polymer Nanocomposites in Sensor Applications: A Review on Present Trends and Future Scope

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Abstract Polymers are crucial constituents of modern electronic devices. They can be used in their pristine, composite or nanocomposite forms for several domestic and industrial applications with innumerable unique possibilities. Polymer nanocomposites have gained wide theoretical interest and numerous practical applications in diverse fields of science and technology as they bestow the materials not only with virtuous processability but also with exceptional functionalities. It is evidenced that the electrical conductance of polymer nanocomposite is governed by the conductive filler networks within the polymer matrix. Hence, insignificant variation in the conductive networks can result in noteworthy variations in the output electric signal of polymer nanocomposite. Exploiting this stimuli-responsive performance of conductive networks to the physical parameters, polymer nanocomposites can be harnessed to fabricate novel sensitive sensors to detect vital physical parameters viz. strain/stress, pressure, temperature, solvent or vapor. Technical and phenomenological studies on polymer nanocomposites are still enduring. Advanced explanations are being sought but the mechanisms governing the formation of several polymer nanocomposites are still topics of debate in the material science community. Their in-depth investigation requires copious scientific work. This review analytically sketches the synthesis, microstructures, physiochemical properties and the underlying mechanisms for stimuli-responsiveness to the physical parameters of the polymer nanocomposites as well as their applications in various sensitive sensors and detectors. Thus, it became evocative for this review to focus on their processing methodologies, physiochemical physiognomies, classification and probable potentials of polymer nanocomposites. This review primarily presents the current literature survey on polymer composites and the gap areas in the study encourages the objective of the present review article. Finally, the status, perspectives and the advantages of specific polymer nanocomposites at present are summarized. The attention of this review is drawn to the present trends, challenges and future scope in this field of study. Finally, the vital concern and future challenge in utilizing the stimulus responsive behavior of polymer nanocomposites to design versatile sensors for real time applications are elaborately discussed.

Keywords Polymers; Polymer nanocomposites; Sensors; CNT; Graphene

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1. LITERATURE REVIEW

1.1 In Brief about Composites

In the past few years, composites have developed into one of the most encouraging substitutes for traditional materials in a broad realistic way in automobile, aircraft, entertainment,

railway, medical and defense R&D sectors. Two different materials are combined chemically or physically to yield a composite material, offering an anticipated set of physio-chemical properties which can be augmented to accomplish the precise prerequisite for a certain application.^[1,2] Unfortunately, the conventional materials such as metals, glass, ceramics, alloys *etc.* do not exhibit such a unique blend of applicative properties. A composite is a heteromorphous material formed by the physical or chemical amalgamation of two or more distinctive materials, having enhanced bulk properties which are absolutely different from any of its discrete components.^[3,4] Typically, composites are comprised of two different phases: matrix material and dispersed material.

1.1.1 Matrix material

Matrix material is the principal incessant fragment which grasps and chains the spasmodic dispersed or reinforced material. It enables the composites to achieve their basic profile, orientation, strength, toughness, *etc.*

1.1.2 Dispersed material

The material for dispersal is the subsidiary component reinforced into the matrix in sporadic fashion. The dispersal material delivers its unique applicative properties to augment the matrix both physically and chemically; hence, it is also known as filler or reinforced material. Typically, the material for dispersal is sturdier and tauter in comparison to the matrix material. It delivers worthy and unique thermal, physical, electrical and many applicatively significant properties to the composite.

1.2 An Introduction to Nanocomposites

In the past few decades, due to extensive research and development in the field of nanotechnology, the nanocomposites have attracted copious attention due to their exceptional design and extra-ordinary performance, which is incomparable to traditional composite materials.^[5] Due to the physical or chemical interplay taking place at nanoscale amongst the matrix material and the dispersed material, the nanocomposites demonstrate rare combination of extraordinary properties and design potentials. The term “nano” derived from Greek language designates that physical measurements are in the order of 10^{-9} m or nm, also termed as nanometric scale. As per the convention, the dimension lying within 1–100 nm are recognized as applicable for the nanoscale.

The nanocomposites are synthesized using wide variety of matrix materials like polymers, metals, alloys and ceramics. The commonly chosen fillers at the nanoscale are carbon, clays, fibers and inorganic materials. These nanocomposites are synthesized to unveil substantial electrical conductivity, high mechanical sturdiness, thermal steadiness, chemical resistance, durable elasticity, light weight, power efficiency and cost effectiveness. Before couple of decades, the name “nanocomposite” was not coined and terms like “hybrid” or “molecular composite” were in use instead.^[6] At that time, fillers were used with polymers, called as additives, to improve their mechanical, thermal and chemical stabilities.^[7] However, conventional fillers were almost micron sized and did not impart the extraordinary physical and chemical properties of nanoparticles. Presently, the research, innovations and development in the field of nanocomposites offered advanced tech-

nological prospects for real-time applications in a rapidly sprouting area of nanotechnology. With cumulative prospect of nanocomposites, these materials are advantageous in numerous capacities ranging from biodegradable packing material to information technology and non-invasive biomedical therapeutic applications.

Nanocomposite is defined as a technically tailored material comprising dissimilar constituents with disparate physical and chemical properties, which forms a discrete interface within the nanocomposite.

One of the most distinct features of the nanocomposite is that it is composed of two dissimilar material-matrix material and dispersed material, out of which at least one dimension of the dispersed material should be on nanoscale.

Nanocomposites are capable enough to create unique structures, efficient and precise instruments and hi-tech user-friendly electronic systems that have innovative properties and utilities owing to their nano and /or transitional size.

Nanocomposites are capable to regulate or influence properties on the microscopic scale.

However, the foremost contest in the field of nanotechnology and nanocomposite science is to stretch the application window of nanocomposites by recollecting their novel features while augmenting their specific physiognomies.

1.3 History of Polymer Nanocomposites

Polymer nanocomposite is composed of a matrix material and a polymer as one of the constituents, along with a dispersed material like single or multiple nanoparticles within the parent polymer matrix. Decades ago, polymer nanocomposites emerged as an alternative to conventional structural materials due to their greatly-amended electrical properties, mechanical robustness, chemical resistance and steadiness, easy and adaptable processing technique, and low cost effectiveness. Polymer nanocomposites became a thrust research area in 1940 with a precise prominence rubberized tyres. It took around half a century that polymer nanocomposites could be revived in 1990 when clay, as the dispersing material, was exfoliated into the matrix of a semi-crystalline polymer and much later into its amorphous counterparts and other matrix materials.^[8] In the past few years, polymer nanocomposites seriously impacted the existence of the traditional composite materials because of their emerging applicative potential. Polymer nanocomposites have effectively substituted conventional metals and their alloys in many fields of domestic and industrial applications, such as from aircraft industry to manufacturing of wind turbine blades, from automotive sector to sports and safety gears, and even from electronic devices to massive civil structures like dams and bridges. One of the most promising explanations frequently emphasized regarding the ascendancy of polymer nanocomposite is its “dimension reliant serviceability”. The chemical and physical properties of polymer nanocomposite change beyond a crucial size limit of dispersed nanoparticles which is significantly smaller than 100 nm as stated by Auffan *et al.*^[9] The crucial size of nanoparticles which was also correlated to the escalating upsurge in the number of atomic entities at the surface of the polymer nanocomposite to the dimension of nanoparticles was identified to be around 20–30 nm. Thus, the surface energy of nanoparticles increased

manifolds resulted in crystallographic changes that significantly affect the properties of polymer nanocomposite.

Typically, polymers are used as elastomeric and stretchy matrices which donates worthy pliability, sturdiness, plasticity, precise surface and bulk properties and other exceptional physical characteristics within the polymer nanocomposite system.^[10] The vital polymer physiognomies are transformed in combination with nanoparticles, however, this transformation is based only on the fact that, in combination with the nanoparticles, polymer physiognomies should not be disrupted. Consequently, this intensification in the accomplishment is stimulating the research in the field of nanotechnology aiming at synthesizing novel nano-materials with advanced potential applications as well as asserting the supporting underlying science. The field of polymer nanocomposites has attracted a large volume of engineers and researchers to investigate and recapitulate the status of combination of several promising nanoparticles with conventional and advanced polymers.

1.4 Mechanism Governing Polymer Nanocomposites

In deciding the properties of matter, dimensionality plays a crucial part. Nanostructure of material is the key element in the creation of innovative properties and in the nano-level regulation of the structure. Therefore, nanotechnology is a highly exhilarating field of the twenty-first century in which technological applications in the fields of semiconductors, inorganic and organic materials, energy storage, and biotechnology are expected to be fully restructured. The word “nanotechnology” can be described as the controlled processing of materials of less than 100 nm with at least one dimension. This technology aims to combine chemistry, physics, materials science and biology in order to establish new properties of materials that can be utilized to develop simple processes for the development of electronic devices, biomedical products, high-performance materials and consumer articles. It is anticipated that the commercialization of nanotechnology will fuel widespread technological growth, enhance the quality of life and benefit society around the world. Over the years, the concept of nano-composite material has greatly extended to include a wide range of systems, such as 1D, 2D, 3D and amorphous materials, fashioned from distinctly different components and mixed at the nanometric scale.

Polymer nanocomposites have been proved to be a promising multifunctional material finding their scope of usage in packing industry, sporting goods and gears, air-water-land transportation sector and also in bio-medical engineering applications. The multidimensional serviceability and capability of the polymer nanocomposites can be attained only due to their exceptionally high aspect ratio, unique combination of physical and chemical properties, and distinctive synthesis achievability. The nanoscale dimensions of polymer nanocomposites support them to confer physio-chemical exchanges by modifying the surface properties. Over the period of recent years, numerous brilliant researches as well as review articles have been popularized in the field of polymer nanocomposites. In the year 2010, Kim *et al.*^[11] published a review article to exhibit the dispersion of graphene and graphene derivatives in the polymeric matrix. The methodo-

logy adopted to synthesize graphite nanoplatelets filled polymer nanocomposites along with their emerging potentials were discussed by Ruoff *et al.*^[12] The chemical configuration and promising functionality of the polymer nanocomposite with chemically reformed graphene nanocomposite was deliberated in a review by Wu *et al.*^[13] A detailed review article published by Arun *et al.* emphasizing the conformation achieved by numerous synthesis techniques also explains the strong interaction amongst the polymeric material and graphene nano platelets.^[14] The structural and functional potentials of polymer-graphene nanocomposite was summarized by Tsukruk *et al.*^[15] Duan *et al.* highlighted the contemporary developments achieved in field of 3D polymer-graphene composite with methodologies for its synthesis methods and probable potentials.^[16] Detailed scrutiny about the technical confrontations and the prospects of graphene as a nanoscale filler in polymer composite which resulted into unique structural, thermal, mechanical and electrical properties was made by Maloney *et al.*^[17]

Recently, Kumar *et al.* underlined his viewpoint of using polymer nanocomposites and emphasized on the basic chemical sciences, which is essential to explore and excel the applied significance of polymer nanocomposites by taking the past attainments and botches into consideration.^[18] Huang *et al.* demonstrated the tailored parallel multiwalled carbon nanotube and graphene stripes in variety of polymer thin films exhibiting tunable microstructures and anisotropic conductive properties utilizing shear induced self-assembly technique.^[19–21] Hence, it can be concluded that polymer nanocomposites emerged out as an advanced multifunctional material with numerous encouraging potentials in different areas including MEMS, NEMS, electronic gadgets, mechanical instruments, power sector, ecology and environment, bio-medical applications, smart optical devices, drug delivery management, multifunctional smart coatings, solar PV, fuel cells and Li-ion batteries, sensors, biosensors, *etc.*

1.4.1 Selection of polymer matrix

There are infinitely numerous classes of monomeric, oligomeric and polymeric matrices which can be specifically regulated and tailored to unveil the properties as per the requirement of the usage.^[22] Polymers can be classified into two different categories: thermosetting polymers and thermoplastic polymers. Due to chemical alteration in thermosetting polymers, they lose their ability to be reused, remolded or recycled. However, when thermoplastic polymers are embedded by orderly oriented crystalline domains which are not chemically cross-linked, they can be processed, shaped, melted and recycled.^[23] Thermoplastic polymers, including a wide range of polymeric materials like polystyrene, poly(vinylidene fluoride) (PVF), polymethylmethacrylate (PMMA), polycarbonate, polyethylene, polysulfone *etc.*, are appropriate materials for stretchy substrates. The thermoplastic polymers such as polystyrene and PMMA are transparent, light weighted, flexible, durable and tough in nature. These flexible polymers are also promising substitutes to conventional glass substrates, metals and alloys which are rigid in nature and often unmanageable. Thermoplastics polymers are extensively popular in domestic and industrial applications due to their chemically independent macromolecules and long, linear or branched flexible molecular

chains. On the other hand, the thermosetting polymers are rigid and strongly cross-linked covalently because of their intrinsic hardness and their extraordinarily high brittleness,^[24] which are generally tougher and sturdier than thermoplastic ones and have better dimensional stability.

It should be mentioned that physical and chemical properties of polymers are dependent not only on their conformational structures but also on their structural morphologies, processing methodologies and the involved experimental conditions. One of the most advantageous facts associated with using thermoplastic polymers is that the physiochemical properties of subsequent polymer composite can be tailored by regulating the molecular properties of the polymer such as chain length and molecular weight.

Currently, out of all the wide varieties of polymeric matrices for the progressive research and development activities, elastomers, thermoplastics and thermosets, thermoplastics are found to be one of the most promising candidates due to their unique physiochemical properties which can be tailored as per the requirement for various applications. Although significant efforts have been made for synthesizing advanced polymer matrices, exertions are also made to improve the physical, mechanical and electrochemical behaviors of the polymer nanocomposites by introducing nanoscale dispersants. The dispersion of nanofillers in polymer matrices noticeably enhances the structural sturdiness of the polymer nanocomposites and also augments the surplus functionalities including thermal steadiness, mechanical robustness and electrical conduction properties. Merits of using thermoplastic polymers as integral component of polymer nanocomposites are summarized as follows: low density, resistance to corrosive chemicals, exceptional mechanical robustness and durability, simple fabrication technique, flexibility, economical usage, stiffness and ductility and tranquil manufacturing (Table 1).

1.4.2. Filler reinforcement

Generally, polymer nanocomposites are synthesized either with organic or inorganic filler materials as fibers, laminates, clays or

particles. Formerly, fillers were used with pristine polymers to reduce the cost of polymers. On the contrary, in due course of time, reinforced materials became the integral part of the polymer industry to transform and enhance the physiochemical properties of the parent polymer by converting it into polymer nanocomposites for various applications in domestic and industrial sectors. A few of the reinforced materials like glass fibers, kaolin, wollastonite, clay minerals, talc, chalk, carbonaceous fillers, mica, dolomite, precipitated silica and metal nanoparticles are used traditionally to develop polymer nanocomposite systems.^[25] Out of them all, several traditional reinforced materials such as talc, glass fiber, chalk, mica and dolomite particles are in the micron scale range. Nevertheless, these micron-sized, traditional reinforced materials are required to be loaded in higher volumes even for negligible property augmentations, which also resulted in serious complexities during the fabrication and processing of the polymer nanocomposite systems. The most common subjects of concern with micro-sized reinforced materials in polymer nanocomposites show disadvantages of interfacial and molecular defects or disorderliness, reduced amenability, poor interfacial interaction, brittle interfacial adhesion, quality deprivation and upsurged processing and manufacturing cost. In due course of time nanoscale reinforced materials have attained a profound popularity and importance in the area of polymer nanocomposites. The nano-sized reinforced materials possessing 1 wt%–5 wt% attains the comparable underpinning as 10 wt%–30 wt% of micro-sized reinforced materials, suggesting the nanoscale reinforced materials and nanoparticles have budded as promising reinforced fillers which can significantly enhance the surface area manifolds and interfacial and molecular interactions even at minimal filler volumes.

According to their structural dimensions, the nanoscale reinforced materials can be broadly divided into unidimensional nanoscale reinforced materials including nanowires and nanotubes, bidimensional nanoscale reinforced materials such as graphene and nanoclays^[26] and 3D nanoscale reinforced

Table 1 Advantages and disadvantages of thermoplastics and thermoset used as matrix in polymer nanocomposites.

Type of polymer	Advantages	Disadvantages
Thermoplastics	Extremely recyclable Exceptionally adhesive to metals Easy rework and fast processing Resistant to corrosion & chemical abrasions during application processing No curing required Minimal impact of environmental humidity and other harsh environments Superb impact resistance Remoldable and reshapable Flexibility and elongation of the coating film Electrical insulation Chip resistance Aesthetically-superior finishes	Restricted-service temperature performance Form weaker adhesive bonds Soften when reheated Expensive than thermosets
Thermosets	It resists deformation Resistant against high temperature Mechanically hard and rigid Excellent aesthetics finishes High mechanical sturdiness Cost-effective Excellent dimensional stability Reactive with various surfaces/substrates Thermosets form stronger durable chemical bonds	Extreme handling inconvenience Non-recyclable Complex to surface finish Cannot be remolded or reshaped Poor thermal conductivity for housing replacements. The rigidity of the material may lead to product failure when subjected to high vibration applications Required greater control and monitoring Curing required and permanent clamping needed which can cause mechanical stresses

materials including cubical and spherical nanoparticles. Indeed, metal and carbonaceous filler nanoparticles exhibit unpredicted physiochemical properties that delivers enhanced electrical conduction, thermal steadiness, catalytic action, mechanical robustness and plasmonic properties. However, the reinforcement of metal nanoparticles in the polymeric matrices is an enormous perplexing task due to the water repellent nature of metal nanoparticles and the limitations of involving organic ligands. The dispersal of metallic oxide nanoparticles elucidates multifunctionalities such as excellent process capability in an aqueous medium and high mechanical steadiness in comparison to other nanoparticles, therefore, the assimilation of these metal nanoparticles in polymer matrices is still very encouraging. Hence, functionalization as well as grafting of metal nanoparticles with several harmonious ligands and functional groups have been gaining significant pace in nanocomposite research and development.

Carbon and its derivatives can be used as reinforced materials. In the past few years, carbon-derived nanoparticles are one kind of the most promising reinforced materials in the field of nanotechnology which have clutched the consideration of many engineers and scientists because of their exceptional mechanical, thermal, opto-electronic and electrical properties.^[27] The crystalline state of carbonaceous nanoparticles assisted in transformation of physiochemical behavior of the polymer nanocomposites in a significant manner. The carbonaceous reinforced materials such as single and multiwalled carbon nanotubes, expanded graphite, fullerene and graphene demonstrated remarkable properties owing to their high aspect ratio. These nanomaterials have been comprehensively synthesized, investigated and explained over the past couple of decades. Researchers have extensively highlighted the amalgamation of carbon based nanofillers in polymeric matrices. An early review that recapitulates the investigated outcomes of graphene-polymer based nanocomposites was published by Chee *et al.*^[28] Kullia *et al.* made significant contributions to the efficient amalgamation of a variety of polymers with graphene.^[29] The physiochemical characteristics of graphene and its oxides as reinforced nanoparticles were elaborately deliberated by Campton *et al.*^[30] Huang *et al.* concentrated on the fabrication of devices as promising outcomes through polymer-graphene nanocomposites.^[31] Young *et al.* reviewed the methodologies, synthesis, and characterization of the graphene-polymer nanocomposites.^[32] Bhattacharya *et al.* conferred the configuration and likely scientific and advanced potentials of polymer nanocomposites synthesized by chemical functionalization technique.^[33] Yang *et al.* contributed his foremost consideration by assessing layer-by-layer assemblage of graphene thin sheets in polymer nanocomposites.^[34] A current review converging on the incorporation of both carbon nanotubes and graphene nanofillers dispersed in the polymer matrix was published by Sun *et al.*^[35] Cheng *et al.* has reported an adaptable methodology to synthesize thermoplastic polymer/graphene nanocomposite with outstanding thermal conductivity.^[36] Very recently, nanographitic platelets (NGPs) emerged out as low-cost substitutes to carbon nanotubes and carbon nanofibres due to their exceptional physiochemical and mechanothermal properties analogous to CNTs and natural copiousness of their

precursor graphite. NGPs, as carbonaceous reinforced nanomaterials, have attracted intensive attention by the research community owing to their reduced compactness, high aspect ratio, exceptional mechanical properties, outstanding thermal steadiness, decent chemical resistance and adjustable electrical properties. NGPs are very economical substitutes for CNTs with superior characteristics. Poly(lactic)nanographite platelets nanocomposites synthesized by Narimissa *et al.* brought improved electrical, thermal and mechanical properties with increasing NGPs contents.^[37] Elham *et al.* synthesized functionalization-assisted polymer-grafted nanographitic platelets for biomedical applications.^[38] The brilliant thermomechanical and electromagnetism properties of NGPs have been briefly deliberated by Han *et al.*^[39] All carbon-derived reinforced nanomaterials are discussed as follows.

Graphite, as a reinforced material, comprises several layers of graphene with the thickness of a few hundreds of nanometers affixed together by feeble van der Waals forces. The competency of graphite as reinforced material is restricted, since the maximum number of the graphene layers in the piles are incapable to efficiently intermingle with the polymer matrix during the physical or chemical synthesis of polymer composite. For the past few decades, several exertions have been made to desquamate graphite to its parent constituents. For the first time, Fernandez *et al.* extracted millimeter-sized graphene layers with nearly 5 nm thickness through micromechanical desquamation.^[40] However, it was not until 2004 that Novoselov *et al.*^[41] quarantined distinct graphene sheets by recurrently smiting of graphite crystal with a scotch tape to its limit. This gradually yielded a magnificent conception of two-dimensional material, proved to be the milestone in the commencement of efficacious synthesis and processing of single layer graphene. Presently, the desquamation of graphite chips in bulk is the most prevalent technique utilized for the corpus fabrication of graphene layers.

One of the most important derivatives of graphite, graphene, as a reinforced material, is a 2D monolayer with sp^2 hybridized carbon atoms arranged in a honey comb lattice structure. Its sp^2 -hybridized framework is the fundamental building block for variety of carbon allotropes.^[42] Furthermore, the carbon atoms are enfolded into 0D fullerene, trundled into 1D nanotubes or 3D graphite by piling up the graphene layers one on top of the other. The thoroughgoing proliferation in the aspect ratio of these graphene nanosized sheets is due to its two-dimensional conformation. Graphene as reinforced material have grabbed research consideration due to its extraordinary electromechanical properties such as Young's modulus of 1 TPa, mechanical sturdiness of 130 GPa, high electric conductivity of $6 \times 10^{-5} \text{ S}\cdot\text{m}^{-1}$, high specific area of $2600 \text{ m}^2\cdot\text{g}^{-1}$, appreciable thermal conductivity of $5.1 \times 10^3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and high gaseous impenetrability.^[43] Advancing from its properties, these materials are auspicious candidates as promising reinforced materials in polymeric matrices.

Furthermore, carbon nanotubes (CNTs) have attained eminence because of their exceptional structures and extraordinary physical and chemical properties. CNT has a hexagonal framework comprising sp^2 -hybridized carbon

atoms. CNTs are hollow cylindrical structures with a fullerene molecule crowning at each of its end. CNT is named based on the number of homocentric coaxial cylinders included in its geometry such as single-walled (SWNT) or multi-walled carbon nanotubes (MWNT).^[44] At the interface of a co-continuous immiscible polymer blend, Zhu *et al.* detailedly described the superior conductive polymer composite design with precisely controlled carbon nanotubes through a balance of π - π and dipole-dipole interactions to achieve conductive composites with ultra-low percolation thresholds.^[45,46] Natural sunlight-actuated memory materials with reversible shape shift and self-healing properties based on carbon nanotubes filled with conductive polymer composites have been demonstrated by Chen *et al.*^[47]

Carbon nanotubes exhibit exceptional tensile modulus of 1 TPa and tensile strength of 50–150 GPa. Strengthened interfacial bonding is indispensable for complete exploitation of the physio mechanical properties of a reinforcing material such as CNTs within the polymeric matrix. The existence of feeble interface region may lead to de-bonding along the interfacial region. The weak van der Waals forces and electrostatic interactions existing in the reinforcing material are responsible for the accumulation of nanotubes which may lead to thin fibrous structures. These aggregated nanotube fibres can skid, when loaded owing to their weak linkage in polymer matrix disturbing the elasticity of the entire polymer composite. In few cases, CNTs may act as pressure concentrated sites in the polymer matrix which may condense the mechanical properties of the parent polymer matrix. Moreover, the fabrication of CNTs is an expensive affair, thus economic fabrication of CNTs is still a challenging task.

The CNFs possess different diameters varying from few to hundreds of nanometers and dimensions ranging from less than micrometers to few millimeters. The CNFs reveal cylindrical or conical structures with hollow cores of single or double graphitic sheets.^[48]

Nanographite platelets are synthesized by the desquamation of graphite shavings. The compaction of desquamated graphite chips results in the materialization of nanographite platelets with high suppleness and lubrication. The nanographite platelet is composed of small heaps of graphene sheets. The heaped sheets of nanographite platelets with distance of around 0.34 nm among its successive layers are attached altogether by weak van der Waals forces.^[49] As graphite is eolotropic, nanographite platelets exhibit exceptional electrical, mechanical and thermal properties, similar to those of graphene monolayer. The nanographite platelets may form composites having independent phases with a polymer, so surface alteration/functionalization of nanographite platelet is mandatory. The brilliant mechanical amendment of 208–650 GPa and around several thousands of S/m substantial augmentation of electrical conductivity is accomplished by composite using nanographite platelet as material for dispersion in the polymer matrix.^[50] In comparison to the two-dimensional layered reinforce nanomaterials, nanographite platelet shows upsurged thermal consistency, outstanding electrical conductivity and low mass compactness. Nanographite platelet demonstrated outstanding specific surface area of about 2630–2965 m²·g⁻¹. Nanographite platelets have engrossed the consideration of material scientists and re-

searchers due to their affordable price, as the raw material to produce nanographite platelet is graphite mineral, which can be excessively manufactured at a very nominal cost. Nanographite platelets with exceptional physiochemical and thermomechanical properties are treated as low cost substitutes to other carbonaceous reinforced materials. In 1990, Drzal *et al.* recommended nanographite platelet as more apposite reinforce material for the synthesis of EVA polymer nanocomposites than CNTs.^[51] Brinson *et al.* also reported that nanographite platelets are more appropriate reinforce materials in polymer nanocomposites as compared to clay and CNT, because of their remarkable thermal consistency, mechanical sturdiness and electrical conduction.^[52] Lately, Xu *et al.* deliberated the distinctive properties of nanographite platelets which makes them a cross functional carbonaceous reinforced material.^[53]

1.5 Selection of Polymer Matrix and Reinforced Material

Over the past few years, there has been a mounting attentiveness in synthesizing polymer nanocomposites with a sensible and smart selection of polymer matrices and reinforced material conformation according to the requirement of the application. The methodologies for synthesizing semiconducting polymer nanocomposite by utilizing insulating polymer matrix and conducting reinforced nanomaterials as promising candidates for advanced electronic and sensing devices as well as multifunctional materials for structural applications are highlighted in this review.

A novel polymer nanocomposite is synthesized by transforming the properties of thermoplastic polymer and reinforced material, completely modifying the inherent bulk properties along with the modification of the chemical conformation of the parent materials.

In order to be a promising candidate for advanced micro-electronic and structural applications, polymer nanocomposite should demonstrate the properties like amended thermal constancy, improved temperature of crystallization, amended mechanical sturdiness and amended dimensional steadiness.

The methodology adopted by the polymer nanocomposite (insulated polymer/conductive reinforced nanomaterial) transform the electrical, mechano-thermal properties of the whole composite. Chen *et al.* proposed balancing the electrical and mechanical properties of immiscible polymer blends filled with carbon black with a double percolation structure.^[54]

1.5.1 Transformation in electrical properties

Conductive reinforced nanomaterials are homogeneously dispersed in an insulating polymer matrix to synthesize a semiconducting polymer nanocomposite as demonstrated schematically in Fig. 1. The insulating polymer matrix reveals electrical conductivity higher than 10⁻¹² S/cm whereas conductive reinforced nanomaterials show an electrical conductivity of about 10 S/cm. The synthesis of polymer nanocomposite using both the polymer matrix-conducting filler materials is truly a promising asset for many biomedical, optoelectronic, sensing and advanced engineering applications. The mechanism governing the electrical conduction behavior of the polymer nanocomposites is investigated on the basis of percolation theory. According to percolation theory, there is a

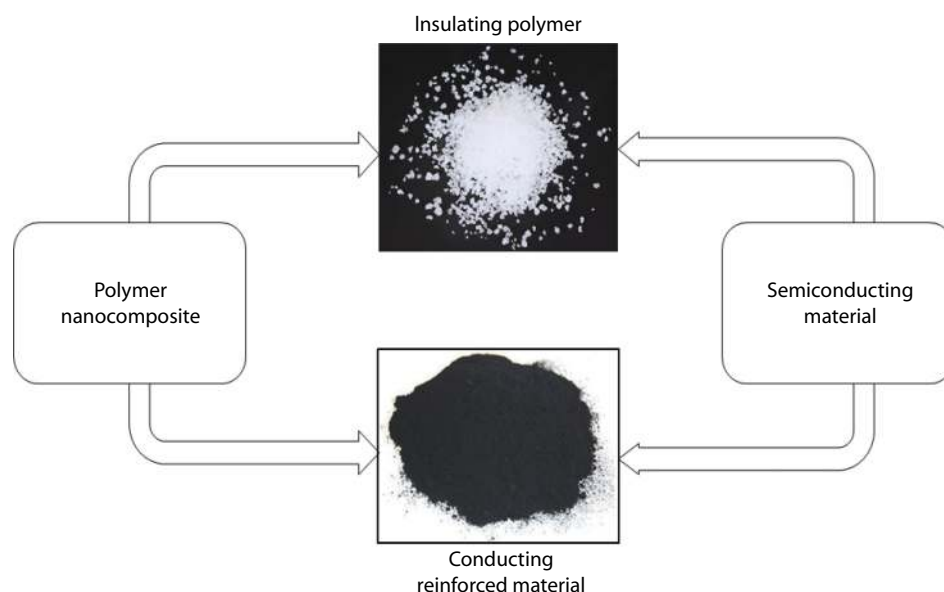


Fig. 1 Polymer nanocomposite system suitably selected for electronic applications.

certain concentration of fillers called the critical concentration or percolation threshold, at which a conduction path in the polymer composite material is created, turning the insulating polymer material into a conductor. As the volume of the conductive filler is raised, a non-conductive-to-conductive changeover is encountered by the polymer composite. Apart from being electrically transmitting, these polymer nanocomposites also demonstrate mechanical sturdiness and flexibility.

1.5.2 Transformation in mechanical properties

The tailorable mechanical sturdiness and stiffness of the polymer nanocomposites are governed by the extent of interaction between the conductive reinforced nanomaterial and the non-conductive polymer matrix. The extraordinary aspect ratio supports the proliferation in the mechanical sturdiness of the polymer nanocomposite. Configuration of the reinforced nanomaterial in polymer matrix stimulates the strong inter-particle bonds among the reinforced nanomaterial and the polymer matrix so that whenever an external stress is applied to the polymer nanocomposite, is relocated to the reinforced nanomaterial, permitting them to swallow maximum of the applied load. The exceptional complex framework among the insulating polymer matrix and conducting reinforced nanomaterial collectively makes a sturdy and supple material called polymer nanocomposite. Additionally, the polymer matrix adds solidity and shape to the polymer nanocomposites.

1.5.3 Transformation in thermal properties

The thermal steadiness of polymeric material with conducting reinforced nanomaterial rely on numerous aspects like the content of reinforced nanomaterial in the polymer matrix, their aspect ratio, extent of reinforcement and interfacial interactions with the polymer matrix. The thermal solidity of the polymer nanocomposite is improved than that of the parent polymer, because of the resilient interaction existing between the polymer matrices and conducting reinforced nanomaterial which confines the mobilization of polymeric chains and adjournment the degradation. The schematic portraying the

selection of filler nanomaterials for desired properties of polymer-nanocomposite is represented in Fig. 2.

1.6 Cutting-edge Developments in Field of Polymer Nanocomposites

Polymer nanocomposite is a budding contender for application in various fields of science and technology, due to the remarkable physiognomies and exceptional physiochemical properties of both polymer matrix and conducting reinforced materials. In recent years, efforts have been made to transform the physiochemical properties of the polymer composites to efficiently broadened its advanced implementation. The unique characteristics of polymer nanocomposites rely primarily on two strategies (i) modifying the chemical conformation of the polymer and (ii) regulating the assimilation of the conducting reinforced material. The promising potentials of the polymer nanocomposites depend mainly on the localized chemistry of the polymer composite, mobility of the long polymer chains, degree of crystallinity and curing methodology. Polymer nanocomposites predominantly find their applications in several domestic and industrial sectors including automotive manufacturing, encapsulation for solar cells, rechargeable batteries and super capacitors, conductive inks and paints, aerospace and opto-electronic engineering, wearable electronics and biomedical applications. Till date, significant and exhaustive research innovations have been executed with wide variety of polymer-carbon-based nanocomposites to explore their potentials in innumerable fields.^[55] The imperative characteristics of carbon-based nanocomposite materials are upgraded, such as mechanical, thermal, electrical, gas-barrier, engorgement, and flame retardant properties. Polymer nanocomposites have their own specific thought-provoking arena which provide the opportunity of sprouting diverse scientific veins for material scientists and engineers, with forthcoming potentials in miscellaneous industrial segments like energy generation and its storage (solar photovoltaics, batteries, super capacitors, fuel cells etc.), medicine (bio-compatible materials, efficient drug delivery, scanning and imaging etc.), smart functional coatings

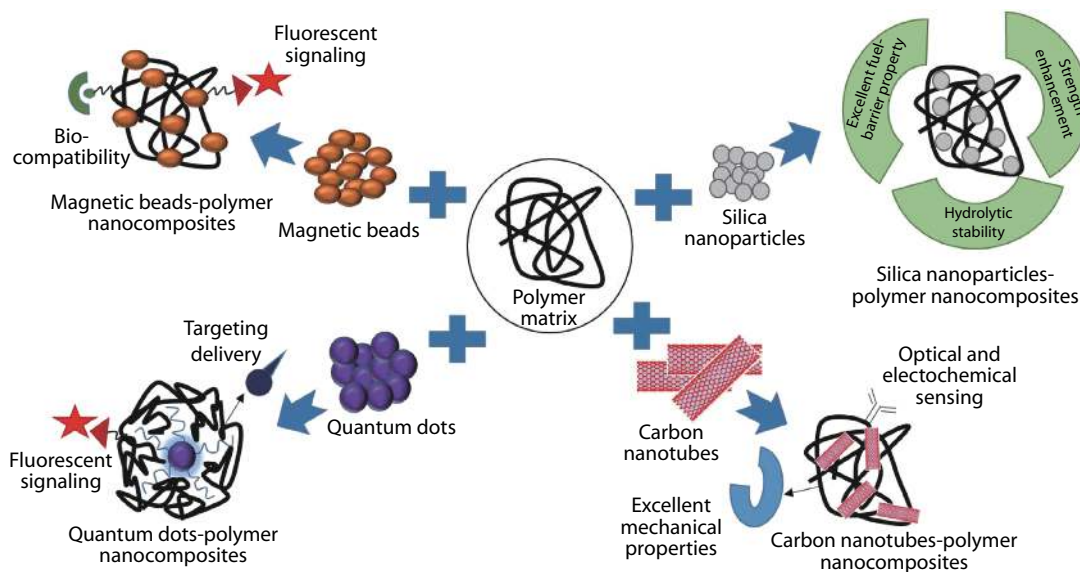


Fig. 2 The selection of filler nanomaterials for the target properties. The choice of particular nanofiller exerts considerable impact over properties of the polymer nanocomposites. For instance, magnetic beads-polymeric nanocomposites offer fluorescent signaling, whereas carbon nanotubes-polymeric nanocomposites offer excellent mechanical stability. Similarly, silica-polymeric nanocomposites exhibit excellent fuel-barrier property and hydrolytic stability, whereas QDs-polymeric nanocomposites offer excellent fluorescent signaling and targeted drug delivery. (Reprinted with permission from Ref. [179], Copyright (2018) Elsevier Ltd.).

and paints, fire safety and environment (fire resistance, membranes etc.).^[56] Sahu *et al.* detected health hazardous toxic metal ions like Cu^{2+} and Hg^{2+} , utilizing nanogold and nanosilver imprinted PVA nanocomposite thin films^[57,58] as demonstrated in Figs. 3 and 4, respectively.

With the addition of chemical properties, thoughtful consideration of the physical properties of carbon nanocomposites is a strategic aspect in acquisition of truncated thermal expansion, extraordinary modulus and mechanical strength. These amended characteristic features tune them as impending composite materials which discover their potential in futuristic applications, such as flexible and foldable displays, OLEDs, high efficiency solar cells, printable electronics and gas sensors. In applications related to aerospace expeditions where precisely significant mechanical sturdiness and exceptional electrical conductivity are decisive, the carbon-based reinforced materials can demonstrate foremost meritorious behavior, even with low volume fractions, and the physio-chemical properties of the polymer nanocomposite are significantly affected. The implementations of carbon-based polymer nanocomposites are still growing rapidly owing to their cost effectiveness and simple methodology for synthesis.^[59] Consequently, further expansions have been speeding up in research and development field of polymer nanocomposites. As replacements for fossil fuel-based materials, renewable polymer nanocomposites have attracted considerable research attention because they are sustainable and biodegradable, as discussed by Sun *et al.*^[60] Smita *et al.* gave a brief review on graphene-based polymer nanocomposites for various applications.^[61] The diverse applications of polymer-nano-composite are demonstrated in Fig. 5.

This review article emphasizes primarily the use of polymer nanocomposites for gas/vapor sensing and structural applica-

tions.

1.7 Sensors

Sensors are precise electronic devices which can detect the physical and chemical parameters qualitatively as well as quantitatively by evaluating the input electronic signal. The signal processing part of the sensor includes several modules that perform the following tasks: analysis of the target, signal analysis and processing, sampling, data collection and processing. Whenever brought in the vicinity of the analyte, the sensing material of the sensor produces changes in physical or chemical characteristics of the sensing material, and these changes are then transformed to readable electrical signals.^[62] Indeed, chemical sensors are essential electronic devices that detects the concentration or quantity of a given analyte by transmuting the change determined in the physical or chemical properties of the sensing material into a readable signal.

A chemical sensor classically contains two fundamental modules: receptor and transducer. Some sensors may include a separator or membrane. The receptor presented in the sensor transforms the received information in the form of energy that can be evaluated by transducer.

1.7.1 Typical designing of a chemical sensor

Receptor. The receptor accomplishes its persistence in most of the chemical sensors through a thin sensitive material portion which comes in direct interaction with the analyte molecules and also plays a crucial role in the chemical equilibrium along with the analyte. The receptor responds selectively towards a specific substance or a group of substances, where the word “molecule recognition” describes its behavior. The most important processes involved in the chemical sensor are ion exchange, formation of charge transfer complexes, physical or chemical adsorption, and

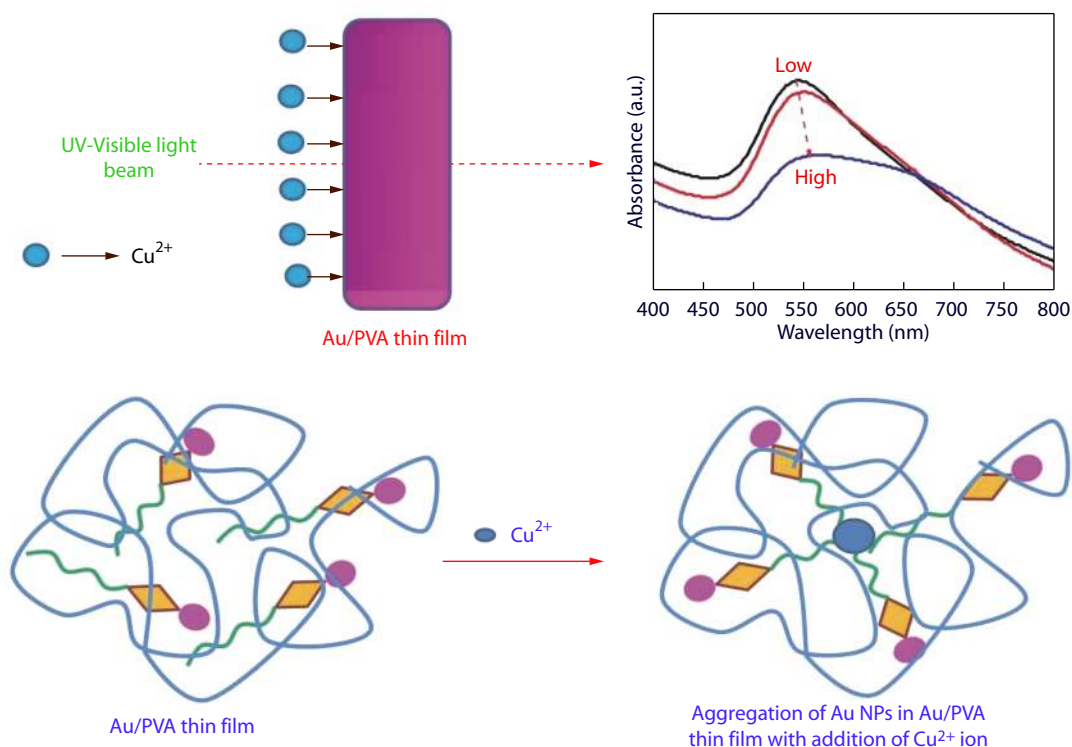


Fig. 3 Schematic representation of sensing of Cu^{2+} ion by Au/PVA nanocomposite hybrid films (Reprinted with permission from Ref. [57]. Copyright (2019) John Wiley and Sons Ltd.).

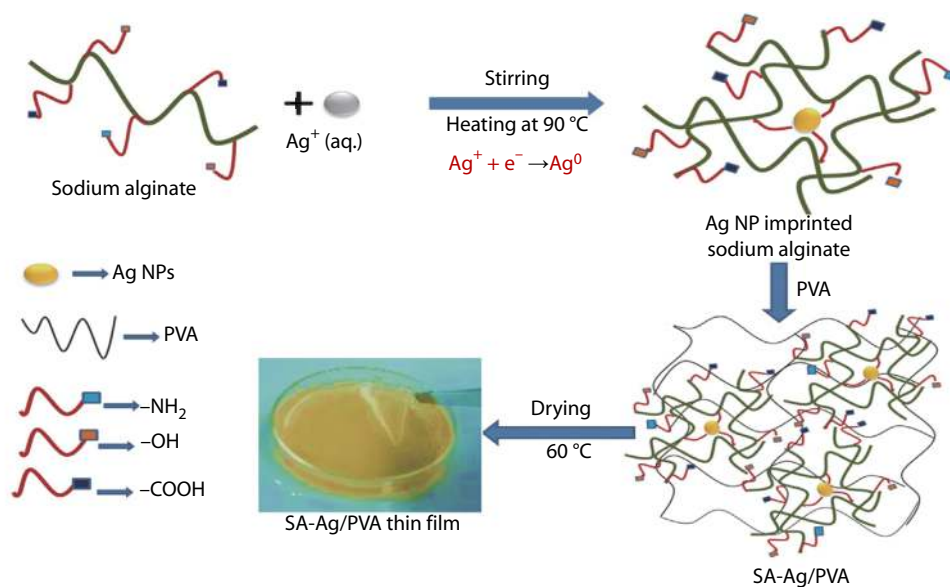


Fig. 4 Preparative scheme of SA-Ag/PVA nanocomposite thin films. (Reprinted with permission from Ref. [58], Copyright (2017) Elsevier Ltd.).

solid-liquid interaction.

Transducer. In recent period of time, the signal processing in chemical sensors performed exclusively through electronic instrumentation techniques. Hence, the existence of transducer in every sensing device becomes crucial to transform the definite value of concentration and non-electric parameters into resistance, voltage or current. Currently, some of the

sensors improve their sensing module along with the amalgamation of a supplementary receptor module. However, the receptor operation in other traditional sensors is exhibited as an integral function of the transducer.

1.7.2 Classification of sensors

Sensors are classified into numerous types depending on the

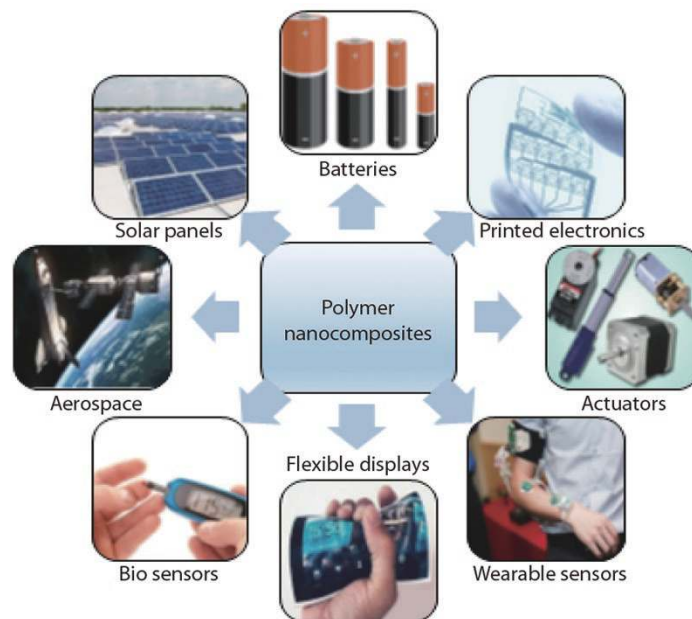


Fig. 5 Recent advances of polymer nanocomposites.

working principle of its transducer.

Optical sensor. The optical sensor precisely transforms the change observed in optical properties in the form of reflectance, absorbance, luminescence, fluorescence, light scattering *etc.* into an indispensable diagnostic and readable signal. The optical sensor measures the intensity of the light absorbed, scattered and emitted by any chemical reaction taking place within the analyte subsequently leading to absorbance and fluorescence phenomenon.

Electrochemical sensor. The electrochemical sensor has the competence of transforming the electrochemical interaction between analyte molecule and the sensing electrode into the valuable signal. The sensor consists of two or more electrode systems, out of which the appropriate electrode system has the proficiency to get oxidized or reduced.

For example, (i) potentiometric sensor: the sensing electrode or material measures the potential against a reference electrode, (ii) amperometric sensor: the sensing electrode or material measures the current in ac or dc mode, (iii) conductometric sensor: the sensing electrode or material measures the conductance or resistance.

Mass sensitive sensor. Mass sensitive or receptive sensors are primarily used for gases and liquids. The basic working principle of this sensor is the change in the mass results in a change of a property. The accretion of analyte results in mass change.

For instance, (i) piezoelectric sensors: the sensing electrode or material detects the modification in frequency of the quartz oscillator plate triggered by the physical adsorption of a mass of the analyte. (ii) Surface acoustic wave sensors: the sensing electrode or material detects the modification in the propagation velocity of a generated acoustical wave which is influenced by the deposition of a certain mass of the analyte.

Electrical sensor. Electrical sensor detects the electrical signals generated by the transformation in the electrical proper-

ties owing to the interaction of the sensing material with the analyte. For example, chemiresistive sensors including the sensing electrode or material detect the analyte by monitoring the change in the resistance of the sensing electrode or material due to its interaction with the analyte.^[63]

Out of the numerous types of available sensors, chemiresistive sensors have gathered significant popularity and great attention in the scientific communities over the past few decades due to its cost effectiveness, comparatively simple design and fabrication technique, convenient methodology and procedures involved with novel concept and working mechanisms.

The review article explains and elaborates the promising potentials of the synthesized polymer nanocomposites as chemiresistive sensors.

1.7.3 Chemiresistive sensors

The chemiresistive sensors are the most popular sensors technologically developed for their utilization in various fields of domestic and industrial applications, toxic and health hazardous vapors and gas detection, defense applications, indoor/outdoor air-quality monitoring, household safety and security, self-diagnostics, food quality control, environmental and structural quality monitoring *etc.* In its ideal form, chemiresistive sensor is highly selective towards the specific analyte for which it has been fabricated. The synthesis and usage of suitably tailored sensing material enriches the selectivity of the chemiresistive sensors. There are several reports available in literature demonstrating thousands of technically engineered materials as chemiresistive sensors. Several categories of materials used as sensing materials in chemiresistive sensors are classified in Fig. 6.

Cataloguing of sensing materials used in chemiresistive sensors are as follows.

Chemiresistive sensors based on metal-oxides. Metal-oxides based chemiresistive sensors have been extensively de-

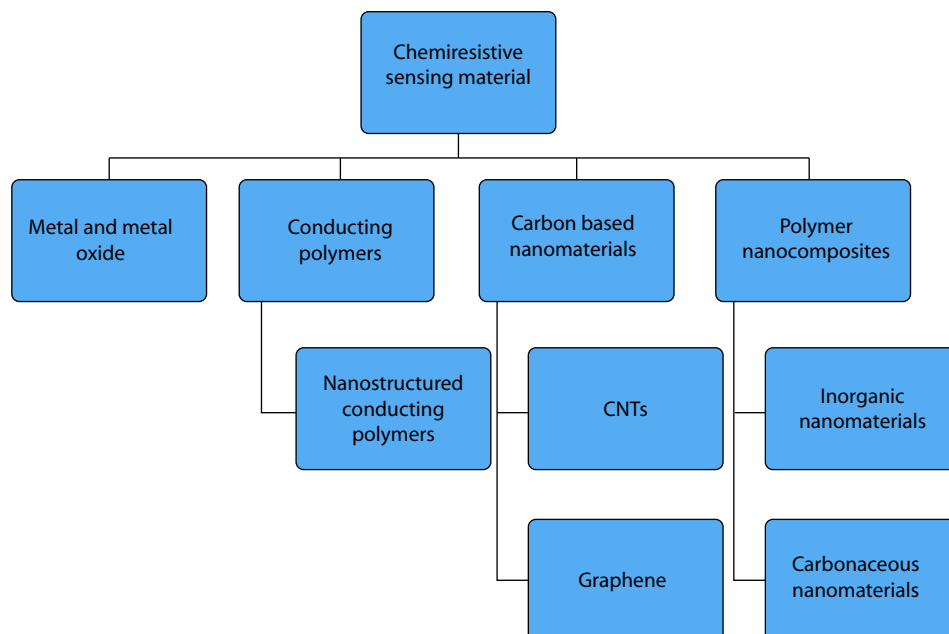


Fig. 6 Classification of chemiresistive sensing materials.

veloped and utilized for toxic vapors/gas detection because of their easy fabrication and broad applicability.^[64] Conversely, the noticeable shortcoming associated with the metal-oxide sensor is characteristic operation at an elevated temperature of around 350–400 °C, which necessitates high demands of power intake resulting in the multifarious computing system.

Chemiresistive sensors based on conducting polymers. Conducting polymers are imperative category of polymers demonstrating excellent electrical properties, which are used as sensing materials for sensors by researchers and engineers. Conducting polymers such as polyaniline (PANI), polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT) have been extensively used as sensing materials. The interrelatedness of the analyte with the conducting polymer results in alteration in the resistance of the polymer material. The detection mechanism is based on the change of resistance because of either swelling of polymer matrix or addition of dopants to the polymers. In recent time, the research interest of sensing materials has changed from primeval conducting polymers to conducting polymer nanocomposites. Kaner *et al.* synthesized PANI-nanofiber-based sensor and demonstrated better performance over the conventional PANI-based sensors.^[65] However, the demerits of using conducting polymer-based sensors which constrained their worldwide development are their poor mechanical sturdiness and high sensitivity to environmental moisture, which still remains a monotonous problem of material research.

Chemiresistive sensors based on carbon nanomaterials. Carbonaceous nanomaterials like graphene, CNTs, SWCNTs, MWCNTs, CNFs and NGPs *etc.* exhibit advanced thermoelectrical properties.^[66] These carbonaceous nanomaterials have been used as dopants to detect various molecules. Carbonaceous nanomaterial-based sensors were synthesized and fabricated as miniaturized, low-power, high-density nano-

sensor arrays. Nevertheless, the mass production of carbonaceous nanomaterials restricts their usage as active sensor materials because of the difficult association with these materials to be integrated into electronic circuits.

Chemiresistive sensors based on polymer nanocomposites. In the meantime, the successful synthesis and fabrication of polymer nanocomposites has been initiated, and its improved physiochemical properties have provoked prevalent research attentiveness for sensing applications. The polymer nanocomposites are composed of variety of carbon-based reinforced nanomaterials in the polymer matrix. Carbon-based polymer nanocomposite as a sensing material forms an auspicious expanse of investigation amongst chemiresistive gas sensors.^[67] The specificity of the polymer nanocomposite-based chemiresistive sensor is assured by the chemical conformations of the polymer composites that can effortlessly be achieved by altering structural geometry. The polymer nanocomposite-based sensor when exposed to analyte molecules exhibits inordinate inflection of electrical parameters such as capacitance and resistance because of broader zone of interaction. In order to successfully execute the applications of polymer nanocomposites as sensors, numerous strategies and approaches have been explored to assimilate nanotechnology into handheld and user-friendly electronic devices. The characteristic properties have been technologically developed and engineered which transformed the nanocomposites into high-performance materials for sensor applications with extraordinary features. The noteworthy specifications such as significant adsorbing capability, enormous aspect ratio, ease synthesis and fabrication technique, minimally possible detection limit, improvised mechanical sturdiness, fast response and recovery times, fluently applied on device surfaces as a thin adherent membrane, battery operated power efficient sensors, direct conversion of physiochemical properties of nanocomposites into a measurable

electrical signal, miniaturized, portable and user friendly sensor device, and detection of toxic and health hazardous gas at room temperature, make polymer nanocomposite a promising applicant for sensor applications.

Due to the growing interest in the field of carbonaceous reinforced materials, carbon-based polymer nanocomposite is one kind of the most promising materials for sensor applications. Grozdanov *et al.* detailedly reviewed about the investigations on polymer nanocomposites as potential material for sensor applications.^[68] Ant *et al.* fabricated PPy-SWCNT nanocomposite as a sensing material for NO_x vapor detection, which demonstrated better sensitivity than its precursors.^[69] PANI-graphene nanocomposite sensors have attained eminence due to outstanding sensitivity for hydrogen gas. Similarly, Al-Mashat *et al.* developed a PANI-graphene-based polymer nanocomposite as sensing material for toluene vapor detection.^[70] Recently, Yu *et al.* underlined the processing technology and sensing applications of polymer-graphene-based nanocomposites.^[71] He also engrossed on the merits and key challenges in using polymer-graphene composite system as a sensing material. Zhu *et al.* studied the stretchable and transparent strain sensor behaviors of conductive polymer composites filled with various dimensional conductive fillers and on sandwich composite structures such as PDMS/CNTs/PDMS comprising an ultra-thin conductive CNT layer.^[72,73] Omar *et al.* investigated experimental evaluation of the efficiency of the surface plasmon resonance sensor based on sensitive thin films of hyper-branched polymer nanocomposite^[74] as shown in Fig. 7.

1.8 Multifunctional Materials for Structural Applications

Presently, the aerospace industries have started an innovative epoch of emerging high-performance materials. The evolution of novel and technologically advanced structural materials in this sector principally rely upon the mechanical properties such as sturdiness, rigidity and mutilation forbearance under diverse environmental circumstances in terms of pressure,

temperature, pulsation, shudder, acoustic disturbances *etc.*^[75] Polyimides and epoxy resins are the two predominantly used polymers that have fascinated mounting attention for aerospace industry related applications. A polymer composed of imide monomers is polyimide (PI). PIs have been used in industry since 1955. With their high wear and tear resistance, additives, radiation and high temperatures, PIs have various potential applications in roles requiring durable organic materials, such as high-temperature fuel cells, displays and multiple military roles.^[76] The exceptionality of PIs is owing to their impressive chemical resistance, attractive thermal steadiness and outstanding retention of mechanical properties at elevated temperatures. However, these materials strive with certain disadvantages such as complexity in fabrication, hygroscopic behavior and degradation in highly oxidative environment around low earth orbit (LEO).^[77] Moreover, the conventional commercially available PI sheets customarily experience deprived optical transmittance originated from the budding of charge transfer complexes (CTC) in their highly conjugated molecular structures.^[78]

Till date, copious attempts have been made to eradicate the problems faced by embryonic polymeric material with the assimilation of reinforced material which can add on apposite properties to the material.^[79] The chemical structures of these resulting polymer nanocomposites comprise two or more dissimilar ingredients occasioning the evolution of a novel material with enriched performance characteristics and properties than each individual ingredient. The development of these novel multidimensional materials plays a substantial role in the extension of advanced high-performance materials for structural applications. The escalating scientific anxieties have steered the creation of high performance and high quality multifunctional polymer nanocomposites with excellent thermal stability, exceptional mechanical strength and extraordinary electrical conductivity. These nanocomposites can be used in aerospace area which requires high operational range of temperatures, like those experienced in com-

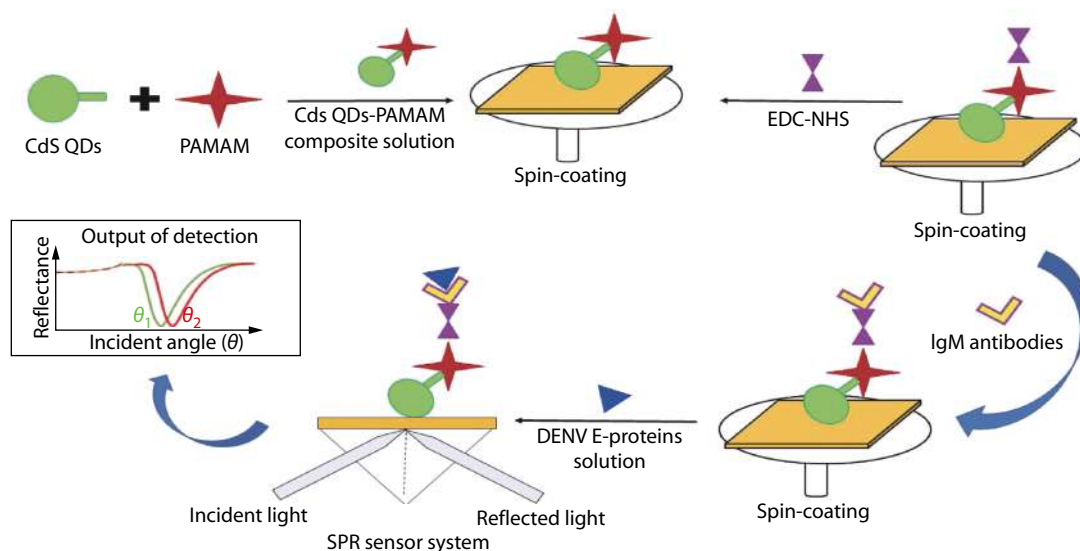


Fig. 7 Steps in development of Au/CdS QDs-PAMAM/IgM sensor film. (Reprinted with permission from Ref. [74], Copyright (2020) Elsevier Ltd.).

pressor of the aircraft engine and other components like duct, feedline and fan casing *etc.*^[80,81] Precisely, the polymer nanocomposites can also be used for manufacturing of wings of an aircraft, as the design consideration is to make it stronger, flexible, robust and durable. Moreover, the tailorable electrical conductivity of the polymer nanocomposites could be integrated into an aircraft wing for protection against lightning strike.

The weightlessness and cost effectiveness are the supplementary motivating factors for the improvement of existing and synthesis of advanced novel polymer nanocomposites in aerospace industries, which will result in light weight aircraft and cost reduction due to the abolition of the expensive metallic entangles as well as eradicating the time associated with integrating the metallic entangles into the structure. A schematic representation of the brief outlay displaying classification of nanocomposites and their improved properties is shown in Fig. 8.

1.9 Polymer Nanocomposites for Sensors over Conventional Composites

Compared to other functional composites, polymer nanocomposites have been proved to be the most promising and preferred nanomaterials, which have attracted substantial interest of researchers in different fields of science and technology due to their remarkable performances to advance engineering applications such as outstanding thermal, mechanical and electrical properties. Polymer nanocomposites have been thoroughly studied since they were discovered as a nanomaterial. Their extraordinary properties have made them favorable in many areas, including the energy field, defense equipments, sport goods manufacturing, automotive industry, supercapacitors and sensors. These multi-dimensional applications are actually focused on flexible processing methods, ultra-high strength, light weight, and strong longevity based on polymer nanocomposites. Moreover, polymer nanocomposites are of high electrical conductivity and can be used as

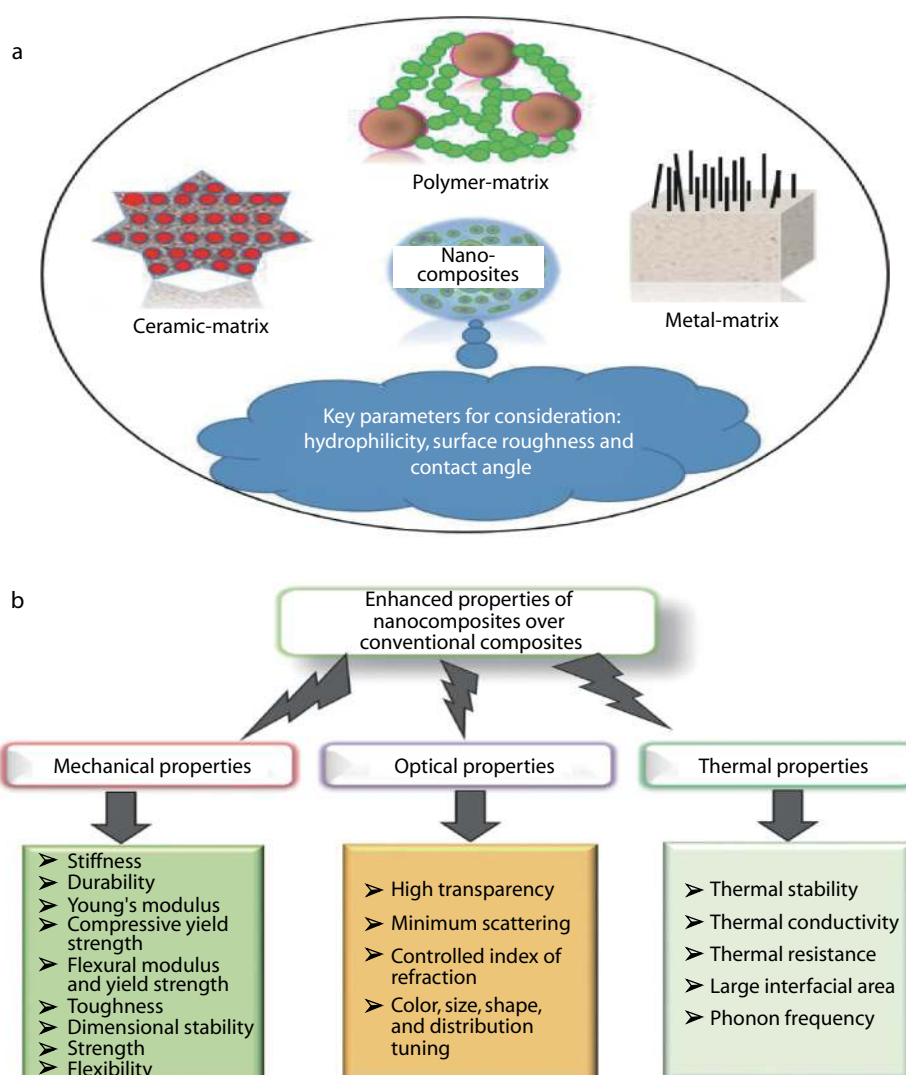


Fig. 8 Classification of nanocomposites and their improved properties: (a) grouping of nanocomposites into three basic categories (involving ceramic matrix, polymer matrix, and metal matrix nanocomposites) and (b) their excellent (mechanical, optical, and thermal) properties over conventional composites. (Reprinted with permission from Ref. [179], Copyright (2018) Elsevier Ltd.)

electrostatic discharge (ESD) and electromagnetic interference shielding materials (EMI). However, the viability of a nanofiller to produce the nanocomposite polymer depends primarily on its homogeneous dispersion without losing its integrity within the polymer matrix. Another advantage of these nanocomposites over other traditional composites is that they can be manufactured using easy and precise production methods, such as injection molding, compression molding, molding of vacuum bags, contact molding and molding of resin transfer. Therefore, polymeric nanocomposites are positioned as acceptable options to resolve the inherent constraints placed by microcomposites and monoliths while posing preparation challenges related to the control of elemental composition and stoichiometry in the nanocluster method.

As stated above, polymer nanocomposites are a new class of advanced composite materials that have received considerable attention at both research and commercial levels. The dimensions of the nanofillers incorporated in these materials are only up to a few nanometers, which gives an ultra-large interfacial specific area to the nano-element and polymer matrix. Consequently, polymer nanocomposites show major improvements in strength, thermal stability, etc., without losing their inherent characteristics, such as stiffness or optical clarity. Nanofillers typically interact with the matrix *via* weak intermolecular forces. In certain situations, however, the interaction occurs *via* chemical bonds. One of the most significant aspects of the synthesis of polymer nanocomposites is the homogenous dispersion of the nanofiller within the polymer matrix. In general, it is difficult to disperse nanofillers homogeneously in a polymer matrix because the nanoparticles have a high degree of surface energy that facilitates their agglomeration.^[82] In addition, the incompatibility between hydrophilic nanoparticles and polymers with hydrophobic chains limits the integration of inorganic nanoparticles, resulting in poor surface interaction. Nanoparticles, with the improved tensile strength and optoelectronic properties, are easy to process with organic polymers, and therefore, a large number of MEMS, NEMS and microelectronic devices are developed using organic polymers and nanoparticles in a hybrid configuration. Polymer nanocomposites are used in electronics and nanoelectrical devices because of their unique properties, such as light weight, large surface area and high aspect ratio, flexible transport properties, chemical specificities, easy accessibility, low price, easy processing and scalable production.^[83] Conducting polymer nanowires are ultrasensitive to trace-level biological analytes and can be used as chemical nanosensors due to their tunable conductivity, resilience, and chemical diversity.^[84,85]

1.9.1 Considerations for developing polymer nanocomposites

A number of main factors make effects on the role played by nanoparticles as reinforcement fillers in the polymer matrix because of the contrast in structure, interaction and properties between various components in polymer nanocomposites. For example: (i) fillers should have excellent mechanical properties such as strength and Young's modulus; (ii) they should have high aspect ratio and high surface area to allow interaction with the polymer; and (iii) they should be well distributed and agglomeration should be avoided. The high surface energy of the nanofiller and, consequently, its high tendency to agglomeration

is one of the most vital concerns, implying difficulties in controlling the interface of the matrix-nanofiller, the dispersion, and the distribution of the nanoparticles. It is extremely important to disperse nanoparticles in the matrix to the point that a polymer coats the individual particle. The increased dispersion helps to achieve efficient load transfer to the network of nanofillers, resulting in a more consistent stress distribution. These critical issues have a profound effect on the macroscopic properties and certainly on the polymer nanocomposites' responsiveness to external stimuli in sensing applications. Different synthesis methods of nanocomposite materials have been proposed to date, as well as various surface modification methods of nanofillers, aimed at achieving a better distribution of the nanofiller in the polymer matrix.

This topic also requires further focus, however, as achieving its homogeneous dispersion in the polymer matrix remains a challenge due to the intrinsic properties of nanoparticles. By increasing the interfacial area between the filler and the matrix, the mismatch between the nanoparticle and polymer properties is mitigated, contributing to improved endurance. The creation of new materials with more uniform properties and more reproducible synthesis processes can be achieved through studies, aimed at discovering strategies for the best dispersion of nanoparticles both in solutions and in the polymer matrix. Indeed, control over all of those crucial and demanding issues would give these materials an even greater impetus to evolve and provide clarity about their scaling potential. Furthermore, it should be noted that this quest for new methodologies for the synthesis and modification of polymer matrices and fillers must be closely linked to new technological solutions relating to 3D printing, as there is an increasing demand for sensitive nanocomposites to obtain new technological advancements through printing techniques. Because of the importance of nanofiller-matrix interfaces in polymer nanocomposites, selected surface modification is often needed in accordance with the specific objectives and characteristics of the specific polymer system. The general concept is based on the theory providing an ultra-large interfacial area between the polymer matrices and nanoscale fillers. However, the interfacial region is not the only important factor affecting the properties of nanocomposite polymers, and the interfacial interaction is also important for the determination of nanocomposite properties. Proper surface modification is therefore necessary, and thus polymer nanocomposites with tailored properties can be obtained for various engineering applications.

Alignment of the filler in the matrix is necessary but not crucial. It makes the composite anisotropic, while modulus and mechanical strength are maximized by alignment. Bonding between the filler and the polymer is required to enable the external stress applied to the composite to be transferred to the nanofillers, enabling them to bear most of the load applied. Therefore, to improve their dispersibility, nanoparticles are often functionalized allowing their interaction with polymers. In addition to the above criteria, the cost of nanomaterial is also a concern to be addressed. In this section, only brief discussions are given on the basics of nanoparticles and nanoscale filler-polymer interfaces. Some related research articles published for further information and in-depth analysis of these concerns could be referred.^[86–88] Detailed discussions

of the dispersion and alignment of carbon nanotubes in polymer matrices can be found in many studies.^[89,90] In further sections, several factors affecting the efficacy of high performance polymer nanocomposites along with the probable remedies are elaborately discussed.

1.9.2 Interaction at interfacial boundaries

A polymer nanocomposite is termed as a material with multiple discrete phases with a distinct interphase. The interface is the region starting at the commencement of the filler content at which the properties are different from those of the bulk fillers and ending at the point in the polymer matrix at which the properties become similar to those of the bulk polymers. The Nobel Laureate Prof. Feynman once prophesied that the colossal enhancement in the properties of the material can be controlled by the arrangement of structural units on a smaller scale.^[91] His visualization paved the path leading to success of modern science as the foundation for synthesizing novel nanomaterials. To comprehend the chemical structures and physiochemical properties of the polymer matrix and nanoscale reinforced materials, the interface region needs to be premeditated meticulously.

The interface region needs to be regulated and augmented as per the requirement of the properties intended for applications. The key feature in the development of polymer nanocomposites is the interface between the reinforced material and the polymer. When the length is reduced from micrometer to nanometer scale, the role of the interface becomes more vital in defining the properties of nanomaterials from being phase subjugated to interface subjugated. The property of the interfacial region is dissimilar from those of the bulk polymer matrix and reinforced material.^[92] For example, if the polymer nanocomposite containing 1 wt% by of monodispersed 10 nm nanoparticles as filler is studied, even if the thickness of the interfacial region is only 2 nm, the volume fraction of this interfacial region can be as high as

20%. The nanoscaled size of the reinforced particles leads to an extraordinary large interfacial area in the composites. Experimental investigations have exposed that with a insignificant quantity of the reinforced material, significant modification in the sturdiness, toughness and strain can be accomplished. Furthermore, improved electrical, mechanical, thermal and functional properties of polymer nanocomposite can be attained by aggregating the aspect ratio. When there is a slight increase in the loading level of the reinforced nanomaterial, the volume fraction of the nanocomposite as a whole becomes even more substantial.

The interfacial region governs the potentials of the polymer nanocomposites in two key ways: (1) the disparity in the chemistry (*e.g.* typical crosslinking density and crystalline morphology) of this region can noticeably alter the properties of the bulk composites, and (2) the modifications in the mobility (*e.g.* changes in the relaxation time spectra) have a strong influence on the mechanical and dielectric properties of the bulk composites. Schematic representation of interfacial regions displaying polymer composites from micrometer to nanometer scale is shown in Fig. 9.

These metaphors are customarily circumscribed only to those materials which comprise reinforcing nanoparticles with different lengths engrained in the polymer matrix. The interaction among the polymer and the reinforced nanoparticles are categorized on the basis of matrix nature, matrix origin, presence and alignment of the particles of the reinforced material, reinforcement and architecture of the reinforced material *etc.* On the contrary, these remunerations can be attained only if the reinforced materials are uniformly distributed without agglomeration in the polymer matrix. Researchers believe that the interaction between the reinforced material and the interface polymer matrix plays a crucial role in improving the properties of the whole polymer nanocomposite.^[93] It is likely to predict as well as synthesize polymer

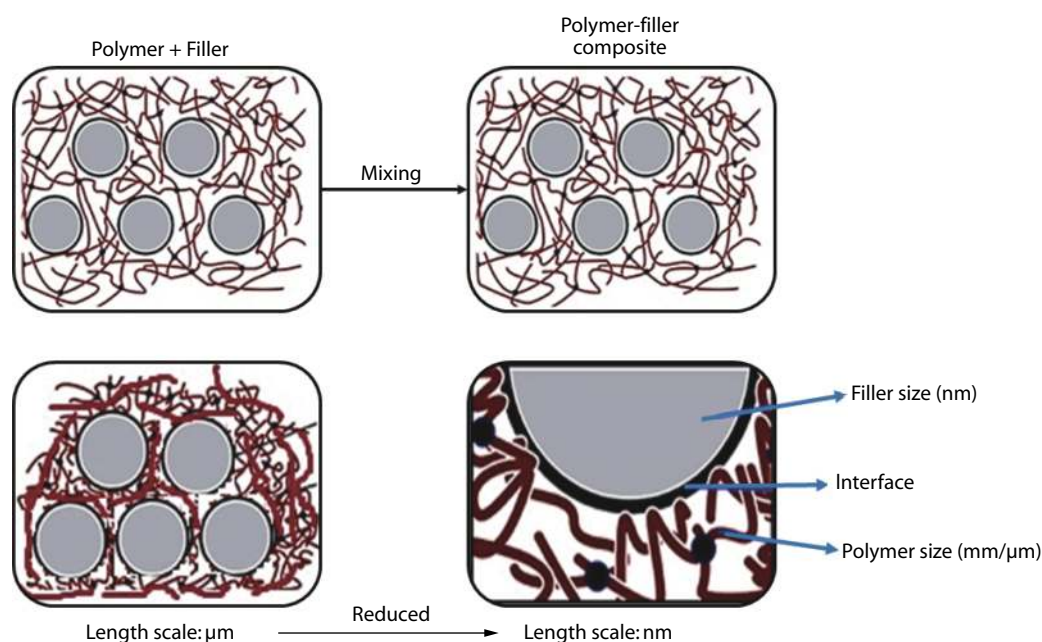


Fig. 9 Schematic representation of Interfacial regions displaying polymer composites from micrometer to nanometer scale.

nanocomposites with desired properties and performance by thoroughly understanding the physiognomies of the interfacial area. Until now, efforts have been made for the development of polymer nanocomposites according to the envisioned applications. Several recent reports exhibited the enhancement in the properties of the entire polymer nanocomposites owing to the strong interfacial interaction.^[94,95] The interphase properties should be tuned to boost performance of the polymer nanocomposite by enhancing the inherent properties of both the polymer matrix and the strengthened nanomaterial. In addition, the predominant failure mode in filler reinforced polymers is the interphase associated with debonding between the polymer matrix and the reinforced material, and its identification and even healing are especially preferred. Schematic representation of interphase formed between polymer matrix and dispersed nanoparticles is shown in Fig. 10.

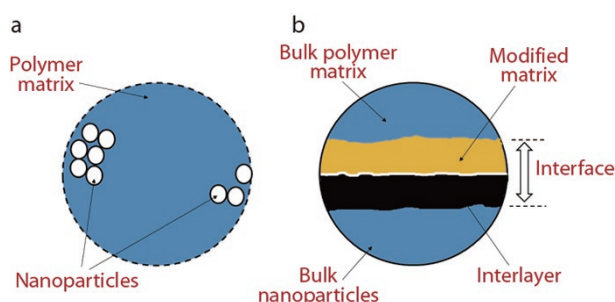


Fig. 10 Schematic representation of interphase between polymer matrix and dispersed nanoparticles

The interphase between the reinforced material and the polymer governs the properties to enhance the stress transfer between the polymer matrix and reinforced material and also to provide the interphase with advanced serviceable properties as shown in Fig. 11. Typically, the coarseness of the surface is advantageous in enhancing the frictional constituent of adhesion. When the cracks are evolved at the interfacial region, it is enforced to follow a zig-zag route due to the local hitches created by reinforced material nanoparticles. It is evident that the failure of polymer matrix-filler nanocomposite involves high energy dissipation when following the zig-zag cracked path than that of the planar route. The advantageous effects as mentioned can be triggered from the reinforced material *via* coating, accumulation, and functionality. It was found that diminutive functionality can be attained through an easy modification of the interphase region instead of the bulk. Sharma *et al.* published a review on the carbon fibers-based composites which studied interphase modification approaches using the reinforced nanomaterials.^[96] A comprehensive survey addressing the effect of nanofillers at the interphase reported by Karger *et al.*^[97] suggested that nanofillers play a key role in implementing the novel properties of nanocomposites *via* appropriate processing strategies, resulting in controlled particle size distribution, uniform dispersion and stronger interfacial interactions.

1.9.3 Dispersion of nanomaterial in polymer nanocomposites

One of the main aspects of the synthesis and improvement of

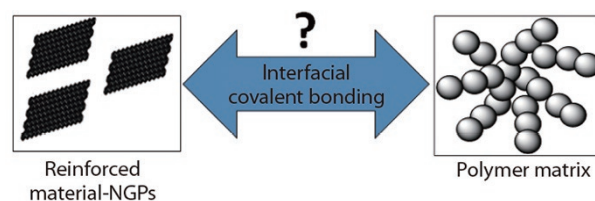


Fig. 11 The interphase between the nanofiller and the polymer matrix governs the physiochemical properties.

high performance polymer nanocomposites is the perfect and homogeneous dispersion of the nanomaterial in the polymer matrix. In the polymeric matrix, the dispersion of inorganic reinforced materials is mainly subjected to internal shear stress intimidated by glutinous encumbrance on the reinforced materials. Carbon-based reinforced materials are passive in nature; they have a propensity to agglomerate, resulting in weak dispersion thereby obstructing the complete prospective of the synthesized nanocomposites. Regrettably, scientists and researchers have reported the poor dispersion of the reinforced materials in the polymer matrix. Carbon nanotube-based polymer nanocomposites prepared by Salve *et al.* exhibited pitiable dispersion which resulted in a weak interaction between the polymer and reinforced material.^[98] Zhang *et al.* demonstrated the influence of dispersion on the thermomechanical properties such as storage modulus and thermal consistency of the PP-clay nanocomposites.^[99] Similar to other carbonaceous reinforced materials, NGPs are expected to restack due to its layered structure. NGPs shows poor wettability, high surface area to volume ratio and inert nature towards polymer matrix. The reinforced materials form steadied bundles due to the weak van der waal forces of interaction. The foremost challenge in synthesis of polymer nanocomposites is the homogeneous dispersion of reinforced materials in the polymer matrix and the improvement of polymer-filler interfacial interaction for augmenting the properties of the entire polymer nanocomposite.

There has been a number of approaches reported for the preparation of homogeneous dispersion of the carbon-based reinforced materials within the polymer matrices.^[100] The reported methodologies indicate certain shortcomings, for example, surfactants and ligands should be used in functionalization, but these methods comprise complex molecules which are very expensive. Some investigation studies also depicted the use of physical dispersion methods such as ultrasonic mixing and mixing using shear forces, however, they could not efficiently disperse reinforced materials in the polymer matrix. Presently, the perfect dispersion of nanoparticles in the polymer matrix relies strongly on chemical functionalization procedures. Even though, the chemical functionalization of nanoparticles effectively improves the reinforced material dispersion, the processes recognized are complex which forms chemically active additives that can vitiate the integral properties of the polymer nanocomposites.

1.9.4 Filler shape

Smart and hybrid polymer nanocomposites that use mixtures of wide variety of polymers and fillers have drawn increased attention in recent years. Obviously, not only the contribution of individual fillers, but also their interactions or the synergistic

effects are attributed to the improvement of the composites resulting from the mixture of various fillers. However, there is still no systematic understanding of the relative strengths and limitations amongst various types of fillers, except for individual contributions. So far, most of the experimental investigations performed have concentrated on a single material framework. The effects of interfacial properties on composite properties were studied by Needleman *et al.*,^[101] for instance, but only for carbon nanotube-based composites. The impacts of volume fraction and filler aspect ratio were studied by Safaei *et al.*,^[102] but only on graphene nanoplatelets composites. Liu and Brinson^[103] have examined the relative efficiencies of reinforcement between nanotube and nanoplatelet fillers, but based only on composites elastic properties. In addition, interfacial intensity that plays a vital role in the overall performance of the composite was not taken into account. In particular, the studies carried out shed some light on a specific material system or property, but did not provide a detailed image of the reinforcement contributions of various types of nanofillers with different geometries and interfacial properties. If the nanofiller is increased to a critical value (*i.e.* percolation threshold), a nanofiller conductive network is formed, which causes a transition from non-conductivity to conductivity.^[104] The conductive properties are predominantly focused on the spatial distribution and structure of the polymer matrix nanofiller.^[105] From the point of view of the application, it is very important to decrease the spatial distribution and structure of the polymer matrix nanofiller. Therefore, how to monitor the formation of the percolation network at low filler concentration is the critical concern. Some researches^[106–108] have currently given an overview of the conductive properties of polymer nanocomposites, which concentrate on the methods of regulating the structure of the conductive network and understanding the relationship between the experimental parameters and the structure of the filler network. The formation of the nanofiller conductive network, for instance, depends on the interaction of the polymer-fillers, which affects the electrical conductivity of polymer nanocomposite.^[109,110] Substantial aspect ratio nanofillers can help to shape the conductive network and reduce the threshold of percolation.

In order to analyze the electrical conductivity behavior of polymer nanocomposites, computer simulation offers another viable choice. Using a 3D-Monte Carlo model, an exponential relationship between the nanofiller aspect ratio and the percolation threshold is revealed: the greater the aspect ratio, the lower the threshold.^[111] By adopting the simulation of molecular dynamics, the tightly connected nanorod network is formed at high polymer-nanorod interaction, which can significantly boost the electrical conductivity. The effects of different carbon nanotubes dispersion states, such as uniformly distributed, aligned, and agglomerated, on the electrical conductivity of polymer nanocomposites were analyzed, demonstrating that high electrical conductivity results from partial aggregation and aligned carbon nanotubes.^[112] Furthermore, the effect of fiber waviness on electrical conductivity has been investigated, suggesting that the percolation threshold appears to be increased by the wavy fiber.^[113,114] The addition of carbon black into carbon nanotubes composites will reduce the concentration of carbon nanotubes necessary to

transform conductivity, indicating their synergistic impact on the development of the conductive network.^[115] It is stated that the anisotropy of the electrical conductivity of aligned carbon nanotube/polymer composites is mainly influenced by the mean conductive pathway density of carbon nanotubes, which depends on the structure of the carbon nanotubes alignment.^[116] The effective interaction between silver nanoparticles in the epoxy matrix can be tuned by adding non-conductive silica nanoparticles. Therefore, it prevents the agglomeration of silver nanoparticles, which increases electrical conductivity.^[117] The conductive stability first decreases under the tensile deformation and then increases with the increasing concentration of fillers and the minimum corresponds to the threshold of percolation.^[118] A subtle shift in the topological structure of the conductive network can be due to the decrease in electrical conductivity.^[119]

1.9.5 Filler alignment

The electrical conductivity of polymer nanocomposites is significantly improved at very low volume fractions of the nanofillers due to its high aspect ratio. Highly anisotropic fillers, such as carbon nanotubes and graphene nanoplatelets, appear to get aligned due to the shear forces active during various processing processes in the polymer melt. The attractive van der Waals interactions among the fillers often prefer filler alignment. The percolation activity of polymer nanocomposite system is greatly impacted as the alignment of the filler increases. With increasing alignment, the interconnectivity of the fillers is negatively influenced, leading to an increase in the threshold of percolation. In addition, filler alignment induces anisotropy in the macroscopic electrical conductivity of nanocomposite. Such directional dependence on the macroscopic scale may be of utmost significance for particular technological applications where the material acts only as a conductor in the desired direction.

In most percolation-based studies of polymer nanocomposites, an isotropic distribution of filler orientations is assumed, *i.e.*, fillers have no preferential orientation^[120–122] and the effect of primary filler attributes, such as aspect ratio on the percolation threshold, is studied. However, some researchers have addressed the effect of other filler characteristics, such as filler orientation, polydispersity of filler scale, and spatial clustering of fillers. In this review, we explain the effect of alignment on the percolation behavior of the nanofiller.

Aided with a model based on mapping of the continuum percolation on to a percolation problem on a Bethe lattice, the effects of different filler attributes on the percolation behavior were also explored.^[123–131] The projections of this model are in semi-quantitative agreement with the generalized convergence percolation theory^[132–136] and Monte Carlo (MC) simulations^[137–140] based on the integral equation. Studies on aligned rod-like filler systems using the Bethe lattice-based model correctly predict that the percolation threshold increases with increasing alignment of the filler.^[128,141,142] For rod-like fillers, a strong dependency on the variance in the nematic order parameter $\langle S \rangle$ (a measure of filler alignment) is also expected.^[142] In addition to filler alignment, the lattice-based model has also been used to consider the effects of filler aspect ratio, filler size polydispersity^[123,128,129] filler mixture^[130] and clustering.^[124,125]

The tunneling interaction between the fillers is usually believed to be isotropic in tunneling-percolation based simulation and analytical studies, *i.e.*, the tunneling conductance is a function of only the distance between the fillers but not of the relative orientation. The effect of anisotropy on the efficient electrical conductivity of the tunnel conductance (accounting for the relative orientation of fillers) was investigated using effective medium approximation by Nigro and Grimaldi^[136] in a nanorods system. It was found that tunneling anisotropy greatly influences the electrical conductivity at volume fractions above the percolation threshold for a system of aligned fillers. The percolation threshold itself, however, was not found to be a strong function of the anisotropy of the tunneling. Therefore, since one is concerned specifically with the percolation threshold and not the electrical conductivity in the post-percolation regime, neglecting the tunneling anisotropy in modeling may indeed be justified. In several studies based on Monte Carlo simulations, the influence of filler alignment has been investigated. In 2D aspect, rod-like carbon nanotubes are modelled in a square domain using percolation of sticks.^[143–145] The angular distribution of the sticks in the isotropic case is changed from the uniform distribution between $[0, \pi]$ to represent the orientation of the filler. In 3D, by adjusting the distribution of the angle between the filler axis and a defined direction, the filler alignment is controlled.^[139,140] Given the axial symmetry of the filler used, only one angle is necessary to define the alignment. If the alignment is determined along the z-axis, the polar angle created by the axis of the filler is θ . The alignment is quantified using the nematic order parameter,

$$\langle S \rangle = \frac{1}{2} \langle 3\cos^2\theta - 1 \rangle \quad (1)$$

in which the angular brackets represent the average ensemble of all fillers in the domain. Thus, $\langle S \rangle = 0$ for isotropic angular orientations and $\langle S \rangle = 1$ for completely aligned fillers. Simulations and experiments have shown that the percolation threshold in the direction of filler alignment often increases as the filler alignment increases, *i.e.*, $\langle S \rangle$ increases from 0 to 1. The decreasing connectivity of the fillers with increasing alignment is due to this action.

To reflect behavior of carbon nanotubes, Silva *et al.*^[146] used similar tunneling-percolation model with impenetrable cylinders. With increasing axial alignment, their Monte Carlo simulations display a monotonic decrease in electrical conductivity. Rahatekar *et al.*^[140] stated a similar conclusion, but with a different approach to modeling the nanofiber composite with an orientational order. To investigate and analyze the influence of fiber orientation on electric conductivity, White *et al.*^[139] used penetrable rod-shaped fillers. Their findings show that a critical orientation S_c exists for a given volume fraction and aspect ratio of the fillers, above which the electrical conductivity greatly decreases. The orientation distribution function (ODF) is selected to be a Gaussian distribution in $\cos\theta$, where the polar angle of the filler axis is θ , in some Monte Carlo simulation-based studies on the impact of filler alignment.^[139,146] Also, only the impact of the mean parameter of the nematic order $\langle S \rangle$ is analysed. In these Monte Carlo simulation-based studies, the impact of the second moment $\langle S^2 \rangle$ on a fixed $\langle S \rangle$ that is also expected to affect the electric behavior of nanocomposites^[142] is not explored.

Little attention has been paid to studying the effect of filler alignment for disk-like fillers by simulations compared to those focusing on alignment of rod-like fillers. Analytical models, however, may provide estimates of the impact of filler alignment that become specific at the limit of broad aspect ratios. The Bethe lattice-based continuum percolation model^[123,141] was used to analyse the impact of filler alignment on the percolation threshold of disklike fillers.^[129] Other analytical models can also account for the effect of alignment by adding anisotropic ODFs instead of an isotropic one, such as the excluded volume approach^[147] and generalized connected percolation theory.^[132–135] In this review, our aim is to highlight the impact of filler alignment on percolation properties of nanofillers which has been very rarely investigated using Monte Carlo simulation model and scarcely reported as described above for rod-like and disk-like fillers with varying degrees of alignment.

A highly safe family of versatile sodium-ion batteries (SIBs) based on a $\text{Na}_{0.44}\text{MnO}_2$ cathode, a nano-sized $\text{NaTi}_2(\text{PO}_4)_3$ @C anode, and various Na^+ -containing aqueous electrolytes was proposed by Guo *et al.* The resulting aqueous SIBs in belt and fiber type exhibit high volumetric energy and power density, high flexibility, and long life and can therefore be safely used in wearable electronic devices.^[148] Chen *et al.* showed a Ti wire substrate modified on the surface with perpendicularly aligned titanium nanotubes and horizontally aligned multi-walled carbon nanotube sheets in the integrated "energy fiber" device as two electrodes.^[149] The simple synthesis of carbon nanotube/polydiacetylene nanocomposite fibers, which react quickly and reversibly to electrical current, is recorded by Peng *et al.*, with the resulting color change that can be easily observed by the naked eye. These composite fibres often react chromatically to a wide range of other stimuli. For example, with negligible elongation, they exhibit rapid and reversible stress-induced chromatism. These electrochromatic nanocomposite fibres may have various applications in sensing.^[150]

1.9.6 Efficient and effective processing techniques

The efficient and effective processing techniques leads to organized particle size dispersal, homogeneous dispersion and fruitful interfacial interaction which are the vital parameters to integrate the novel properties within the polymer nanocomposite. The interfacial interaction at the interface and uniform homogeneous dispersion of the reinforced nanomaterials in the polymer matrix can be attained and tuned only through the "effective processing technique" utilized for the synthesis of the polymer nanocomposite. Polymer nanocomposites form a broad spectrum which leads to pronounced attentiveness in the fabrication of different polymer composite systems.

Various methodologies to synthesize polymer nanocomposites as reported in copious published literature are discussed below.

Melt mixing technique. The dispersion of reinforced nanomaterials in the polymer matrix enhances the viscosity of the polymer matrix manifolds producing homogeneous dispersed commercial polymer nanocomposites.^[151] Melt mixing method is usually adopted by poorly viscous thermosetting polymer matrices *e.g.* epoxy resin *etc.*

High shear mixing technique. The high shear mixing technique involves the mixing of nanoparticles within the polymer matrix using high-shear forces to homogeneously disperse the reinforced nanomaterials in the polymer matrix.^[152] These shear forces are not high enough to disperse the reinforced nanomaterials effectively in the polymer matrix as it agglomerates so often.

Melt processing technique. Melt processing technique is the most popular technique among most of the industries and manufacturing units because of the ease in processing, economic practicability and speedy processing of large volumes of materials. The rate of fabrication of polymer nanocomposites is high by this processing technique, which mix nanoparticles with polymer matrix using a single or twin-screw extruder. The high shear rate attained by shifting the screw configuration provides an enhanced and homogeneous dispersion. On the contrary, the treatment of polymer composite with high shear not only degrades the properties of both polymer and reinforced nanomaterials but also disrupts the high aspect ratio.

Solvent processing technique. Solvent processing technique is another procedure of producing polymer nanocomposites. As per its name, it includes the dispersion of both reinforced nanomaterials and polymer in an appropriate solvent before casting and evaporating the volatile solvent during ultrasonication at high frequencies. Both the thermoplastic and thermosetting polymer matrices along with the carbon based reinforced nanomaterials are processed using this technique for better homogeneous dispersion. This is one of the simplest and reproducible processing techniques providing an excellent dispersion of the nanoparticles within the polymer matrix. It works appreciably with small sample sizes.^[153,154] Polymer nanocomposites with functionalized graphene and polymer matrices including PMMA, PVA, PP, PS, Epoxy, PANI, and PU have been synthesized using solvent processing technique. Several solvents, ranging from the aqueous to organic solvents can be used effectively in this technique. However, this technique not only necessitates the solubility of the polymer in one or the other solvent but also creates repercussions with complete removal of the solvent during drying. The polymer nanocomposite films produced by solvent processing technique is not certainly scalable.

In situ polymerization technique. The *in situ* polymerization is an experimental technique in which the reinforced nanomaterials are physically combined with the monomeric units with the assistance of ultrasonic frequencies or high shear in the presence of a suitable solvent. The *in situ* polymerization reaction starts with the addition of an appropriate initiator together with modifying the restraints predominantly with the experimental temperature. The polymerization procedure can proceed in presence as well as in absence of solvent, augmenting the properties of the polymer nanocomposites.^[155] This methodology exhibits the excellent and homogeneous dispersion of reinforced materials within the polymer matrix. In this technique, the carbonaceous reinforced nanomaterials, predominantly CNTs, nanographite, graphene etc. can actively participate. Jia *et al.* reported the *in situ* polymerization of CNT and PMMA using azo-bis-iso butyronitrile as the initiator which unlocks their π bonds forming covalent bonds within the polymer nanocomposite.^[156] The pictorial representation of traditional methods for fabricating polymer nanocomposites is shown in Fig. 12.

entation of traditional methods for fabricating polymer nanocomposites is shown in Fig. 12.

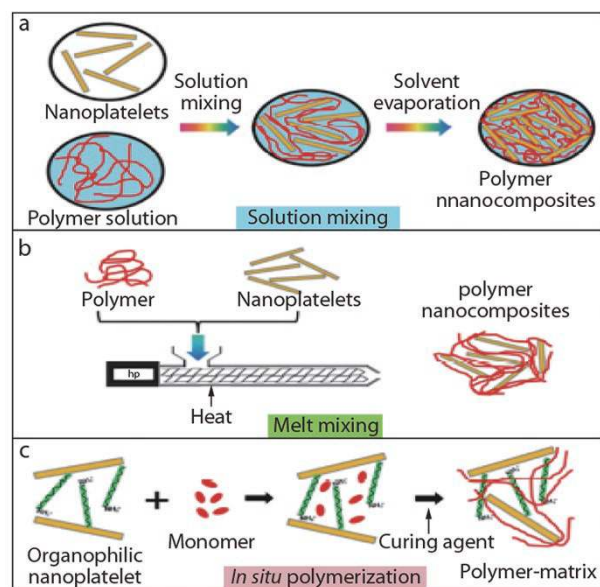


Fig. 12 Representative traditional methods for fabricating polymer nanocomposites. (a) The process of solution mixing includes two stages: solution mixing and solvent evaporation. (b) Melting mixing is a method of stirring the polymer and nanoplatelets above viscous flow temperature of polymer. (c) *In situ* polymerization is mixture of monomer and nanoplatelets, and then polymerization forming TPNs. (Reprinted with permission from Ref. [157], Copyright (2017) Elsevier).

Functionalization of reinforced nanomaterials/polymer matrices and emergence of click chemistry. Generally, polymers are hydrophobic in nature; consequently, all of the carbon-based reinforced nanomaterials will yield phase-separated composites with a polymer matrix. The surface functionalization or modification is a prerequisite while dispersing reinforced nanomaterials in the host polymer matrix. In this technique, the functionalization of either surface of the reinforced material or the polymer matrix *via* chemical route can effectively enhance the interfacial interaction between the reinforced nanomaterials and the polymer matrix of the nanocomposite. The physiochemical properties of the polymer nanocomposite significantly depend upon the interfacial interaction between the reinforced nanomaterials and the polymer matrix.^[158]

Over and done with various processing techniques, it has been noticed that these methodologies suffer from certain detriments such as weak interfacial interaction, chances of non-uniform dispersion, poor efficiency, ineffectual to regulate reaction conditions and inadequate regulation on molecular weight of the polymer.

Despite the abundant developments in the field of polymer nanocomposites, extensive research is still required to present a novel processing technique which can offer strong interfacial interaction along with the complete and homogeneous dispersion of NGPs within the polymer matrix.

This review also acknowledges the recently emerged click chemistry which plays a significant role in describing the interfacial interaction between the polymer and reinforced ma-

materials for synthesis of advanced and high-performance macromolecular structures. Click chemistry has attained an impressive scientific attention since it was introduced by Sharpless *et al.* for the synthesis of even more complex natural products.^[159] Click reactions can be initiated with ease in presence or absence of a solvent which is easily removable or even with water as the solvent. This reaction allows easy product isolation and also exhibit a proliferation in the thermodynamic driving force greater than 20 kcal·mol⁻¹ and finishes off rapidly to completion.

The benefits of using click type reactions include segmental in nature, stereo selective, fast reaction kinetics, impressive product yield, no or minimal bi-product, modest and mild experimental conditions, superficial purification, aqueous condition and broad spectrum.

Currently, a large number of scientists and engineers have amended both the polymer and reinforced materials by means of effective click chemistry for synthesis and progress of apparent multidimensional polymer nanocomposite. By adopting click reaction as a processing technique, the physiochemical properties of the polymer nanocomposites can be tailored easily. The click reaction exhibits no supplementary reaction, broad spectrum applicability, stereo selective reaction, desired side groups, strict control on reaction conditions and impressive product yield. The Huisgen 1,3 dipolar reaction procedure resulted in the formation of five-membered rings, *i.e.*, 1,4-triazole and 1,5-triazole regioisomers between alkyne and azide constituent. During click reaction, the variety of noble metals such as Ru, Pt, Ni and Pd can also be used as metallic catalyst, but until now only Cu(I) has achieved the scientific prominence. The addition of Cu(I) accelerates the click reaction and it is therefore named as a copper catalyzed azide-alkyne reaction (CuAAC). The preference given to Cu(I) over other metal catalysts is due to its capability and efficiency to include alkyne terminals in both π and σ interactions and it also provides an opportunity for instantaneous replacement of the ligands in its coordination sphere, primarily in an aqueous medium. Cu(I) is thermodynamically unstable and it gradually oxidizes into Cu(II) and Cu under aerobic conditions. The production of Cu(II) ceases the reaction as it is catalytically inactive. The introduction of thermodynamically unstable Cu(I) places its importance in the reaction as it is relatively stable in organic solvents.^[160] Salts of Cu(I) such as CuI, CuTf, C₆H₆ and CuBr are found to be very resourceful catalysts in organic solvents. Sometimes, these catalytic systems are equally engaged in atom transfer radical polymerization (ATRP), the combination of both click reaction and ATRP has been extensively explored.^[161,162]

Click chemistry is one of the comprehensively investigated reactions in recent years and applied in numerous fields of science and technology. Moreover, the carbon-based reinforced materials have the tendency to stack through π - π stacking during the reaction. Therefore, the chemical functionalization of reinforced materials allows them to be used for abundant applications such as miniature and wearable electronics, gas sensors, biomedical and intensive care field, and sustainable energy storage devices. Since the commencement of click chemistry in 2001, the assorted organization of click chemistry reaction mechanism has been em-

ployed in material science. Recently, Brown *et al.* elaborately discussed the evolution of click chemistry in material science.^[163] Salavagione *et al.* exploited the click reaction methods for coalescing the modified graphene and free short polymeric chains to cultivate an encouraging approach for engineering the graphene/polymer interface and to accomplish high performance lightweight graphene-based polymer nanocomposites.^[164] Very recently in 2016, Salavagione *et al.* boosted the interfacial interaction in order to prepare conductive polymer nanocomposites by using click chemistry.^[165]

2. FUTURE SCOPE

Carbonaceous reinforced materials are comparatively at a primary stage of development. Nanocomposites based on nanoclays have encountered victory. Conversely, there are numerous vital issues that need to be resolved before comprehensive understanding of the reinforced materials in polymer nanocomposites is accomplished.

It has been reported by numerous literature published that dispersal of reinforced nanomaterials is crucial in attaining desired physiochemical properties of nanocomposites. Conversely, many processing approaches used to synthesize these polymer composites are not feasible economically. Solvent processing technique, layer-by-layer assembly technique and electrospinning technique though resulting in perfect homogeneous dispersions of reinforced materials in the polymer are not so lucrative. Melt processing technique, the only economically feasible processing technique, mostly leads to poor and non-homogeneous dispersion and less than optimum properties. The complications accompanying with the reinforcement of melt processed composites mechanically necessitate imperative consideration. At higher volume fractions, SWCNTs persist agglomerated. MWCNTs are comparatively easier to disperse even at much higher volume fractions. There is a proliferation in the interfacial area with reduction in the diameter of CNTs. For example, at 0.5 wt% of nanotubes, MWCNTs has 70% of the interfacial area of SWCNTs.^[166] Hence, SWCNTs lose their inherent benefit of higher surface area to volume ratio. Similarly, composites do not perform well at much higher loading as well as at extremely lower loadings. This puts a capping on the extent of reinforcement. Synthesis, growth and quality of polymer composites with CNTs, graphene or clay depend upon many factors such as types of CNTs, number of layers of graphene or clay, material purity, dimensions of CNTs, surface area to volume ratio of CNTs, extent of loading of reinforced nanomaterials, its dispersal in the matrix, its orientation and configuration, and interaction between the polymer matrix and the reinforced nanomaterials. However, there are no methodical and comprehensive studies reported that equate the effects of surface area to volume ratio, pureness of reinforced nanomaterials, degree of functionalization and type of functional group on the characteristics of the composite thus prepared. For instance, for graphene flakes with an aspect ratio of 1000, minimal reinforcement is obtained, while for graphene with an aspect ratio of 2000, both modulus and mechanical strength got doubled.^[167]

Extensive research work has been reported using a single variety of reinforced nanomaterials in a polymer matrix. Con-

current assimilation of several varieties of reinforced nanomaterials may considerably enhance the properties of nanocomposites. The collaboration in physiognomies among multiple reinforced nanomaterials needs to be reconnoitered. For example, single dimensional reinforced materials might obstruct with the stacking of two-dimensional platelets. Integrating CNTs into glass fibre composites prevents the formation of cracks due to great nucleation site density as provided by CNTs.^[168] Transference of load between reinforced nanomaterials and polymer has been achieved by both noncovalent and covalent amendments with functional groups. Integration of covalently functional bonds disturbs the conjugation of CNTs and graphene, leading to an adverse effect on the electrical properties of the subsequent composites. It has been reported that an amalgamation of non-covalent and covalent modifications on CNTs can augment compatibilizer-polymer interaction, leading to enhanced electromechanical properties.^[169,170] Consequently, it is evocable to cultivate a deeper understanding of the interface between the non-covalently modified CNT/graphene and the polymeric matrix to permit concurrent enhancement of both electromechanical properties of the resulting composites. It has been experimentally investigated that reinforced nanomaterials can behave as nucleating agent and affect polymer crystallinity.^[171–173] Therefore, extensive scientific efforts should be made to associate the degree of change in crystallinity of the polymer matrix with the mechanical properties of the polymer nanocomposite. Similarly, the effect of surfactants and reinforced nanomaterials on the glass transition temperature of the polymer nanocomposites should be carefully investigated.^[174] Functionalization of organoclays that are steady at elevated temperatures is also greatly anticipated. Organically functionalized clay begins to degrade at approximately 180 °C,^[175,176] which would certainly influence the extensive usage of high temperature polymers like PEEK. A promising integration of high conductivity and flexibility in processing is generated by hydrogels made from conducting polymers. Wang *et al.* proposed a stretching/competitively-coordinating/releasing (SCR) strategy to prepare a self-buckled polyacrylamide/alginate hydrogel (SPAH) to demonstrate an extremely stretchable and healable ionic conductive hydrogels developed for human-motion detection by surface competitive coordination.^[177] In addition, Li *et al.* defined cryopolymerization that allowed superelasticity and highly deformation-tolerant electrochemical energy storage devices for anisotropic polyaniline hybrid hydrogels, which can withstand large and complex deformations, thus facilitating emerging printable and wearable electronics.^[178]

3. SUMMARY AND CONCLUSIONS

The recent advancements made in the field of material nanoparticle reinforced polymer nanocomposites and their impending applications has been reviewed. The synthesis and improvements in nanomaterial reinforced polymer matrix has been one of the most thought provoking areas of research and development over two decades. Among the numerous reinforced nanomaterials used, clays, carbon nanotubes and graphene have been the most comprehensively studied. The research initiated with polymer-clay based nanocomposites in

the late 1980s, succeeded by polymer-CNT based nanocomposites in the late 1990s. Research articles on polymer-graphene based nanocomposite started publishing around 2006 and have grabbed exponential progression since 2010.

The polymer matrices reinforced by nanometer-sized particles have unlocked the opportunity of amending modulus and toughness of composites using insignificant filler quantity. The degree of reinforcement relies on a few fundamental characteristics of filler like its type, kind of functional group on it, its surface area to volume ratio, its quantity, polymer type and processing methodology. Perfectly uniform and homogeneous dispersion of the reinforced nanoparticles in the polymeric matrix and their strong interaction with the polymer matrix is unconditionally important for an ideal reinforcement. Composite properties disrupt at higher reinforced nanoparticle content, demonstrating complications in smooth dispersal of the reinforced nanoparticles.

The orientation of reinforced nanoparticles in the polymer matrix increases its mechanical properties but results in anisotropy. The configuration is much easier in the case of SW-CNTs because of their single dimensional structure. Composites prepared with alternative layers of reinforced nanoparticles and polyelectrolyte have exhibited impressive potential in terms of their mechanical properties. These reinforced materials can have high loading. The layer-by-layer assembly approach minimizes destruction to the reinforced material during assembly. Solution based strategies provide better mechanical reinforcements than melt based strategies.

Commercial scale production and usage of polymer nanocomposites can only be imaginable if the reinforced nanoparticles are easily and perfectly dispersed in the polymer melt by means of commonly used polymer processing techniques like extrusion and injection molding techniques or fibre spinning both in melt and solution phases. A pie chart detailing the basic statistics of publications related to all different types of nanocomposites is shown in Fig. 13(a) (topics covering "nanocomposites and applications," $N=2725$, Source: July 26, 2017 PubMed data). With a publication share of 48% among all other nanocomposites, polymer nanocomposites and their applications are of great research interest. In Fig. 13(b), the findings are limited to the publications already cited in the review article referred ($N=523$).^[179]

CNTs functionalized covalently deliver better polymer reinforcement, allowing for better load transference between the polymer matrix and the reinforced nanotubes. Though, covalent functionalization can abolish inherent electrical properties of CNTs,^[180] necessitating higher percolation threshold. CNTs can amend the electro-thermal conductivity, flame retardancy, and the thermal steadiness of the composites.

Graphene-based composite is impressive due to enhanced mechanical properties, electrical conductivity, thermal conductivity, and thermal constancy over pristine polymers, which are similar to CNTs. Graphene reinforced polymers exhibit as high as 50 °C or larger escalation in thermal steadiness. The percolation threshold of graphene was comparable to that of CNTs.^[181] The conductivity is influenced by synthesis methodology on the surface functionalization, particularly on the number of defective sites evolved during the redox process on the surface.^[182] Homogeneously dispersed

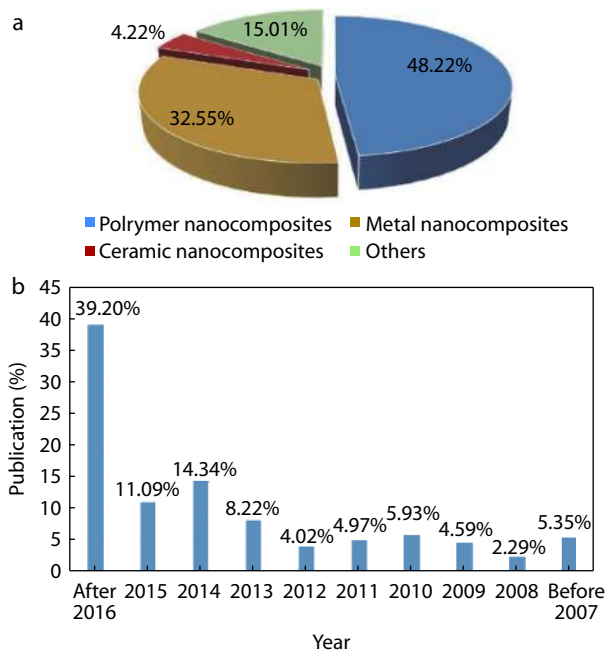


Fig. 13 The basic statistics of publications relating to nanocomposites: (a) pie chart describing the share of all different types of nanocomposites with total number of publications ($N=2725$) for a topic title of “nanocomposites and applications” based on PubMed data (26/07/2017) and (b) the equivalent data confined to this review article ($N=523$). (Reprinted with permission from Ref. [179], Copyright (2018) Elsevier Ltd).

graphene also abridged the barrier properties. One of the biggest underlying issues with the increased usage of graphene sheets is their low bulk density, which makes difficult handling.

Similar to other reinforced nanomaterials, the mechanical and barrier properties of nanoclay-polymer nanocomposites are significantly influenced by the extent of dispersion of the silicate layers in the polymer matrix. Nanoclay can be modified with a wide variety of organo-modifiers to enhance its compatibility with several polymers and to assist in attaining the intercalation and exfoliation morphologies which is crucial for accomplishing the desired mechanical properties. Processing can be executed using three primary approaches: solution blending, *in situ* polymerization, and melt blending or extrusion. Recently, melt intercalation is considered as the most promising technique for the fabrication owing to its adaptability and compatibility with recent and advanced polymer processing instruments and environmental friendliness due to non-participation of solvents. Accumulation of pristine and organically reformed clay increases the thermal stability of polymers. One of the serious concerns about clay is its stability at elevated temperatures.

Layer-by-layer assembly ensures morphology control at the nanoscale and allows a much higher loading of reinforced nanomaterials as compared to other processing techniques. Such morphological control has enabled composites to achieve record properties. Additionally, layer-by-layer technique can also be successfully exploited to integrate inorganic nanoparticles, and nanotubes into organic polymers. Processing approaches such as electrospinning or layer-by-layer

assembly technique are not appropriate candidates to discover their widespread usage in industrial or manufacturing units owing to their low production rates and yields.

Whereas, clay-based nanocomposites have found copious applications in the automotive industry, there has been an exaggerated anticipation for CNT-polymer based nanocomposites, principally due to high material costs and processing complexities. Cost remains a debatable issue with both CNTs and graphene. Pricing for research grade nanomaterials is very high for SWCNTs, MWCNTs and Graphene.^[183,184] Nanoclay is relatively economical and melt-compounded composites comprising nanoclay have found extensive usage in industrial applications such as in automobiles.^[185] CNTs and graphene might bring some applications in advanced multifunctional composites, replacing carbon fibre, or even in the area of flexible and printable electronics.

BIOGRAPHY

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