Gas barrier performance of graphene/polymer nanocomposites

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A B S T R A C T
Because of its unique electrical, mechanical, and thermal properties, graphene is being explored for various applications and has attracted enormous academic and industrial interest. Graphene and its derivatives have also been considered as promising nanoscale fillers in gas barrier application of polymer nanocomposites (PNCs). In this study, recent research and development of the utilization of graphene and its derivatives in the fabrication of nanocomposites with different polymer matrices for barrier application are explored, and most synthesis methods of graphene-based PNCs such as solution and melt mixing, in situ polymerization, and layer-by-layer process are covered. Graphene layers in the polymer matrix are capable of producing a tortuous path, which acts as a barrier for gases. A high tortuosity leads to superior barrier properties and lower permeability of PNCs. The influence of the intrinsic properties of these fillers (graphene and its derivatives) and their state of dispersion in polymer matrix on the gas barrier properties of graphene/PNCs is discussed. Analytical modeling aspects of barrier performance of graphene/PNCs are also reviewed in detail. Key permeability modeling techniques for gas separation mixed matrix membranes are also discussed.

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Abbreviations: phr, weight parts per 100 weight parts polymer; RH, relative humidity; AFG, amine-functionalized graphene; BPEI, branched poly(ethyleneimine); CVD, chemical vapor deposition; DA-G, dodecyl amine-modified graphene; DA-GO, dodecyl amine-functionalized graphene oxide; DA-RGO, dodecyl amine-functionalized reduced graphene oxide; DMAc, dimethylacetamide; EFG, exfoliated graphite; EP, epoxy resin; EVOH, ethylene vinyl alcohol; FG, functionalized graphene; fGO, functionalized graphene oxide; FGS, functionalized graphite sheets; GNPs, graphite nanoplatelets; GONS, graphene oxide nanosheet; HDPE, high-density polyethylene; IGO, isocyanate-treated graphite oxide; IIR, poly(isobutylene—isoprene) rubber; LbL, layer-by-layer; LLDPE, linear low-density polyethylene; EMIMAc, 1-ethyl-3-methylimidazolium acetate; OTR, oxygen transmission rate; PET, poly(ethylene terephthalate); PLA, polylactic acid; PAN, polyacrylonitrile; PANI, polyaniline; PC, polycarbonate; PDDA, poly(diallyldimethylammonium) chloride; PE, polyethylene; PEI, poly(ethyleneimine); PEN, poly(ethylene-2,6-naphthalate); PI, polyimide; PMMA, poly(methyl methacrylate); PND, polynorbornene dicarboximide; PP, propylene; PPC, poly(propylene carbonate); PS, polystyrene; PU, polyurethane; PVA, poly(vinyl alcohol); PVC, poly(vinyl chloride); RGO, reduced graphene oxide; SEM, scanning electron microscopy; SBR, styrene butadiene rubber; SPVDF, sulfonated polyelectrolyte fluoroelastomer; TEM, transmission electron microscopy; TRG, thermally reduced graphene; TPU, thermoplastic polyurethane; WAXD, wide-angle X-ray diffraction; XRD, X-ray diffraction; XNBR,羧基化丁腈橡胶但adiene rubber.

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1. Introduction

Because of their functionality, lightweight, ease of processing, and low cost, polymers have replaced conventional materials in packaging applications over the past 20 years. Most frequently used polymers in food packaging are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET) [1,2]. However, despite their high versatility, a limiting property of polymeric materials in food packaging is their intrinsic barrier properties (resistance to oxygen, carbon dioxide, and water vapor) [2]. The penetration of gas in polymer films has a critical effect on their service performance. The barrier properties of polymers can be significantly enhanced by inclusion of impermeable lamellar fillers, such as clay and graphene, with sufficient aspect ratio to alter the diffusion path of gas-penetrant molecules [3]. These nanofillers make the diffusing molecules follow longer and more tortuous pathways to pass through the nanocomposite film (Fig. 1) [4].

As a result, a significant decrease in permeability is observed [6]. The gas barrier performance of polymer nanocomposites (PNCs) is determined by mainly three factors: filler properties (resistance to gas diffusion, aspect ratio, and volume fraction), the intrinsic barrier property of the polymer matrix, and the “quality” of dispersion (agglomeration/specific interface, free volume generated by mediocre interface management, and the texture/orientation of filler platelets) [7]. The crux of successful development of PNCs is coupled with the levels of exfoliation of the layered nanofillers in the polymer matrix [8].

Clays are the widely used nanofillers for the barrier applications of PNCs, because of their high aspect ratio and compatibility with various polymers [9–12]. Compared with clays, graphene-incorporated polymers show not only enhanced gas barrier properties but also enhanced mechanical strength, electrical conductivity, and thermal properties when properly dispersed in a polymer matrix [4]. For example, graphene has a high mechanical strength (Young’s modulus of ~1100 GPa and fracture strength of 125 GPa) [13], thermal conductivity (~5000 W m⁻¹ K⁻¹) [14], and electrical conductivity (6000 S/cm) [15] with a high transparency. In the reviewed literature, graphene has been highlighted as another strong gas barrier material, because perfect graphene layers do not allow diffusion of small gas molecules through its plane [4,16,17]. Numerous studies have been dedicated to investigate the potential of graphene for improving the mechanical, thermal, and gas barrier properties of polymers [18–34].

Over the last few years, graphene has attracted enormous attention because of its unique properties. Recently, Berry has presented a comprehensive review on permeability of graphene and its application in fluid-encasement for wet electron microscopy, selective gas permeation, nanopore-bio-diffusion, and barrier coating against rusting and environmental hazards [35]. Nevertheless, there is an emerging trend in using PNCs made up of graphene and its derivatives for gas barrier applications. Derivatives of graphene are graphite oxide and graphene oxide; the latter is produced by exfoliating and reducing the former [36]. Therefore, this study focuses on gas barrier performance of PNCs composed of graphene and its derivatives with a strong emphasis on their formulation methods. A comprehensive review on modeling aspects of gas barrier performance of these PNCs is also presented. First, the current progress in the production of graphene/PNCs is reviewed. Then, gas permeability of PNCs is discussed with respect to their structure and processing methods. Finally, theoretical modeling techniques to determine the barrier performance of PNCs are presented.

2. Graphene-based polymer nanocomposites

Graphene, a monolayer of sp²-hybridized carbon atoms bonded in the hexagonal lattice, has attracted enormous research interest in recent years [13,15,16,37–57]. It has been viewed as the basic structural unit of all other graphitic carbon allotropes, including graphite, carbon nanotubes, and fullerences (Fig. 2) [55]. Because of its superior material properties, graphene has attracted significant attention and has become one of the most widely investigated materials. Defect-free, single-crystalline, monolayer graphene not only has excellent mechanical properties [13] and high transparency [44], but is also gas-impermeable [4,45,49]. Many attempts have been made to use graphene and its derivatives as inorganic nanofillers to enhance the physical properties of PNCs and also to provide enhanced gas barrier properties, because of their intrinsic unique properties and good dispersion in common solvents [4,48,58,59]. The relatively high aspect ratio of graphene-based two-dimensional materials can certainly allow much longer pathways for gas-penetrant molecules than other nanofillers, provided they are fully exfoliated and well dispersed in PNCs [60]. For example, Compton et al. reported that the barrier properties of graphene nanosheets are approximately 25–130 times superior to...
those of clay nanofillers at low concentrations [61,62]. Fully exfoliated and well-dispersed graphene structures in polymer matrix may maximize the gas barrier properties of graphene/PNCs [4,60].

2.1. Production of graphene and its derivatives

In the past decade, many methods have been proposed to prepare graphene of various dimensions, shapes, and quality, including epitaxial growth on single-crystal SiC [42], direct growth on single-crystal metal film [43,63,64] or polycrystalline film [54,65,66] by chemical vapor deposition (CVD), and chemical reduction of exfoliated graphene oxide layers (Fig. 3) [67–70]. The quality and hence the application of graphene are strongly affected by the production method [56]. Although the aforementioned methods are suitable for producing high-quality graphene, they have some technical disadvantages, which limit their mass production [45]. For example, the CVD process is expensive because of its high energy consumption, and the underlying metal layer has to be removed too. The major drawbacks of synthesis of graphene on SiC are the high cost of the SiC wafers and higher temperatures (>1000 °C) [56]. Moreover, CVD and epitaxial growth often produce only few large-size, defect-free graphene sheets, which are not a suitable source for PNCs that require a large amount of graphene sheets preferably with modified surface structure [58]. By contrast, the liquid-phase exfoliation of graphite can result in large-scale production of graphene sheets required for polymer composite applications. This process is based on exposing the materials to a solvent with a surface tension that favors an increase in the total area of graphite lamellae [58]. By contrast, the liquid-phase exfoliation of graphite can result in large-scale production of graphene layers without the need for dispersion in a solvent [58].

Salt sonication, graphite splits into individual graphene layers [52,56,71]. Currently, the most promising approach for large-scale production of graphene-based materials is based on exfoliation and reduction of graphite oxide [37,58]. In general, graphite oxide is produced using Hummers’ methods where graphite is oxidized using strong oxidants such as KMnO4, KClO3, and NaN3O2 in the presence of nitric acid or its mixture with sulfuric acid [68]. Then, graphite oxide is reduced to graphene oxide via chemical or thermal reduction. Exfoliated graphene oxide sheets are produced by chemical reduction, and stable colloids of graphene oxide can be obtained using solvents such as water, alcohol, and other aprotic solvents combined with sonication or stirring [58]. Using reducing agents such as hydrazine [41,72,73], dimethyldihydrazine [49], sodium borohydride followed by hydrazine [74], hydroquinone [75], and ultraviolet (UV)-irradiated TiO2 [76], colloidal graphene oxide can be further chemically reduced, resulting in chemically reduced graphene. Chemical reduction of graphene oxide provides an efficient route for production of graphene. However, the hazardous nature and cost of the chemicals used in reduction may limit its application [58]. On the contrary, thermally reduced graphene oxide (RGO) can be produced by rapid heating of dry graphite oxide under an atmosphere of inert gas and high temperature [77–79]. It is evident from the fact that, heating graphite oxide in an inert environment at 1000 °C for 30 s leads to reduction and exfoliation of graphite oxide, producing thermally reduced graphene layers. Compared with chemical reduction methods, thermal reduction can produce chemically modified graphene layers without the need for dispersion in a solvent [58].

2.2. Preparation of graphene/polymer nanocomposites

Dispersion of graphene and its derivatives in polymer is important for the fabrication of graphene/PNCs. If homogeneous dispersion of graphene can be achieved, the gas barrier performance of graphene/PNCs can be improved significantly. Numerous attempts have been made to improve graphene exfoliation in polymer matrices [80–94]. Most graphene/polymer nanocomposites have been developed using three strategies: solution mixing, melt mixing, and in situ polymerization.

A filler that has good compatibility with polymer matrix usually decreases permeability, mainly because of the reduction of the transport cross section and the increase of the tortuous paths for gas molecules [95]. It is well known that most polymers and graphene have poor compatibility, and hence the polymer chains could not tightly adhere to the graphene nanosheets. Thus, a narrow gap will be formed surrounding the graphene nanosheets. Moreover, graphene nanosheets tend to aggregate (layer-by-layer (LbL) stacking) because of the poor compatibility of the graphene and polymer matrix. The gas molecules would flow through the narrow gap or the relatively highly permeable polymer matrix rather than graphene. Therefore, the PNCs exhibit a low gas barrier

![Fig. 2. Graphene is the building block of all graphitic forms. It can be wrapped up into zero-dimensional buckyballs, rolled into one-dimensional nanotubes, or stacked into three-dimensional graphite [58]. (A color version of this figure can be viewed online.)](image1)

![Fig. 3. Methods of mass production of graphene [56]. (A color version of this figure can be viewed online.)](image2)
performance with decreased diffusional pathways. Surface modification of graphene with organic modifying agents is a suitable choice to solve this problem [96]. The functional groups present on the graphene nanosheet surface can improve the compatibility of graphene with the polymer matrix, which leads to good dispersion and well-exfoliated graphene in PNCs with same volume fraction of graphene. It has also been reported that functionalization to enhance compatibility of graphene with the polymer matrix may help to reduce the composite viscosity of the solution, which is beneficial for the preparation of PNCs by solution mixing method [97].

2.2.1. Solution mixing

Solution mixing has been widely used as an effective technique for fabrication of graphene/PNCs, because of the ease of processing graphene and its derivatives in water or organic solvents [98−103]. This method generally involves mixing of colloidal suspensions of graphene-based materials with the desired polymer, either itself already present in the solution or by dissolving the polymer in the same solvent used for filler dissolution by simple stirring or shear mixing [104,105]. Sonication is often performed for better dispersion of graphene nanofillers. Because unmodified graphene has low solubility in most organic solvents [52], functionalization of graphene is needed to increase it [106−108]. Modified graphene can be easily dispersed in a suitable solvent, such as water, acetone, chloroform, tetrahydrofuran, dimethylformamide, or toluene [19]. After complete mixing, the entire solvent must be removed by evaporation or distillation, and the filler-containing polymer material is then molded to give shape to the composite [38,109]. It has been reported that organic solvents may be strongly absorbed on the graphene oxide [110]. The crucial challenges in solution mixing are minimizing the residual solvents [38] and obtaining good dispersion properties of the fillers in viscous polymeric solutions [4]. Although solution mixing generally leads to better particle dispersion than melt mixing process, slow solvent evaporation often induces particle reaggregation. In addition, the use of large amounts of solvent and the associated environmental pollution have prevented this technique from large-scale production of graphene/PNCs [109,111].

2.2.2. Melt mixing

Melt mixing is a typical method for the preparation of thermoplastic PNCs [112]. No solvent is required in this method, and graphene or its derivatives are mixed with the polymer matrix in the molten state. A thermoplastic polymer is mixed mechanically with graphene or its derivatives at elevated temperatures using conventional methods, such as extrusion and injection molding [113−115]. Traditional mixing equipment such as extruder, internal mixer, and two-roll mill can be used, which are usually available in most compounding units [109]. The polymer chains are then intercalated or exfoliated to form nanocomposites [19]. In the melting process, no solvent is involved during the preparation of the composite [116], making it an economical and environmentally friendly method for mass production of PNCs for industrial applications [9,58,116]. In this process, strong shear forces are required to blend the highly viscous molten polymers and graphene or its derivatives. The high viscosity of the material often causes nonuniform dispersion of graphene platelets [17,98,99,117−119]. Although melt mixing is the most economically viable and environmentally friendly approach, it is not a suitable option for matrices or inclusions that are prone to thermal degradation [106]. Because of the thermal instability of most chemically modified graphene, melt mixing has typically been limited to thermally stable forms such as few-layer graphene or RGO [58]. Another challenge for melt mixing is the low bulk density of graphene in dry powder form, which complicates extruder feeding. In addition, graphene buckling may cause rolling or shortening of the graphene derivatives [4].

2.2.3. In situ polymerization

In situ polymerization is another efficient route for the preparation of homogeneously dispersed graphene or its derivatives in a polymer matrix without a prior exfoliation step [109,112]. In this process, uniformly dispersed graphene nanosheets in solvent can be mixed with a monomer (and/or oligomer) solution with an initiator (e.g., photoinitiators and thermal initiators). After the initiator is dissociated by radiation or thermal energy [19,120,121], exfoliated graphene nanosheets can be mixed or cross-linked with polymer chains and the in situ compounding technique confers strong interactions between the filler and the polymer via chemical bonding [109]. It was found that in situ polymerization is not suitable if the polymerization takes place at the surface of graphene or between graphene layers [122,123]. During polymerization, however, the viscosity usually increases, which may reduce the processability of nanocomposites [38,58]. Compared with melt and solvent mixing methods, in situ polymerization can provide enhanced dispersion properties and better compatibility between graphene and the polymer through the introduction of additional functional groups on the surface of graphene or its derivatives [4]. In situ polymerization should also be performed in the solution state to eliminate the residual solvents [4,112]. Moreover, this method requires monomer units and a large amount of reagent for polymerization, and thus less applicable in the case of naturally existing polymers [17].

In addition to these three common methods, many other methods are used to prepare graphene/PNCs. For example, LbL assembly process has been proposed as a feasible route to construct alternating layers of nanoplatelets and polymer and, subsequently, to impart the parent polymer with markedly enhanced gas barrier properties [124−128].

3. Barrier properties of graphene/polymer nanocomposites

It has been reported that defect-free graphene is impermeable even to helium [53,129]. Because of the high aspect ratio and high electronic density of the carbon rings, graphene is capable of repelling atoms and gas molecules and therefore has a very low solubility in gases. Moreover, graphene can encapsulate cells, and is also impermeable for water and proton diffusion. For instance, Mohanty et al. demonstrated that bacterial cells can be encased in a graphenic chamber by wrapping them with protein-functionalized graphene. The strongly repelling π clouds in the interstitial sites of graphene’s lattice reduce the Darcian permeability of bacteria from 7.6 to 20 to 0 nm/s [130]. Xu et al. used graphene as an atomically flat coating for atomic force microscopy to determine the structure of the water adlayers on mica. The graphene coating can tightly seal and stably “fix” the water adlayer structures on the surface of mica [131]. Algarra-Siller et al. also report that water can be locked between two graphene sheets to form “square ice”, a phase having symmetry qualitatively different from the conventional tetrahedral geometry of hydrogen bonding between water molecules [132]. Hu et al. reported that monolayers of graphene are highly permeable to thermal protons under ambient conditions, whereas no proton transport is detected for bilayer graphene [133]. Achatz et al. exposed single-layer graphene on top of a fused silica substrate to cycles of high and low pH. They found that protons transferred reversibly from the aqueous phase through the graphene to the other side where they underwent acid–base chemistry with the silica hydroxyl groups [134].

The properties of PNCs depend strongly on how well the fillers
are dispersed. The influence of graphene and its derivatives on the barrier properties of PNCs prepared by different processing methods is presented in Table 1. It should be noted that the last column in the table shows the reduction in percentage of permeability of PNCs obtained by different routes. From a theoretical point of view, the presence of impenetrable graphene nanosheets, which are homogeneously dispersed in the polymer matrix, leads to an increase of the diffusion path (tortuosity) and consequently a decrease of the gas permeability of the graphene/polymer composites [168]. The barrier properties of graphene/polymer composites are affected strongly by the aspect ratio, dispersion and orientation of the graphene nanosheets, the graphene nanosheets/polymer interface, and the crystallinity of the polymer matrix [150].

Bulk graphite can be exfoliated into expanded graphite when exposed to strong oxidizers such as sulfuric acid, nitric acid, or potassium permanganate [169]. The scalability and low cost of this process make expanded graphite attractive for industrial applications, and their enhanced processability allows it to be incorporated into polymer matrices [157]. Kalaitzidou et al. investigated the effect of exfoliated graphite nanoplatelets (GNPs) on the permeability of PP composites, fabricated by melt mixing using a twin-screw extruder followed by injection molding, as a function of exfoliated GNP concentration and aspect ratio. The increase in permeability of exfoliated GNPs, even at low loadings of 3 vol%, enhances the oxygen barrier properties of PP by at least 20% [150]. Kim et al. prepared PNCs reinforced with graphite platelets and functionalized graphite sheets prepared by partial pyrolysis of graphite oxide. Dispersion of unexfoliated graphite and functionalized graphite sheets in poly(ethylene-2,6-naphthalate) (PEN) was explored with melt mixing process. Hydrogen permeability of PEN with 4-wt% functionalized graphite sheets was decreased by 60%, while the same amount of graphite reduced permeability by only 25% [149].

Prusty et al. The permeability of PAN/EG nanocomposites reduced by 65% than the EP with 1.0-wt% m-GNPs, the gas barrier properties increased an order of magnitude than EP and PAN nanocomposites. The in situ emulsion sonication technique by Prusty et al. The permeability of PAN/EG nanocomposites reduced by approximately 13 times with increasing EG content up to 4 wt% [157]. As mentioned earlier, the gas barrier properties of nanocomposites depend on not only the loadings of nanofiller, but also their alignments. Jiao et al. prepared highly ordered magnetic graphite nanoplatelet (m-GNP)/epoxy resin (EP) composites via coating the GNP with magnetic nanoparticles (Fe₃O₄), and then aligning the modified GNP in EP using low magnetic field (40 mT). Fe₃O₄ nanoparticles were tethered onto the surface of GNP by wet chemical coprecipitation method. From the scanning electron microscopy (SEM) images of composites, it was confirmed that the m-GNPs in the EP matrix have aligned parallel to the direction of the magnetic field (Fig. 4). For the ordered m-GNP/EP composites prepared with 1.0-wt% m-GNPs, the gas barrier properties enhanced an order of magnitude than EP and >65% than the randomly dispersed GNP/EP composites [139]. Al-Jaabreen et al. prepared PET/GNP nanocomposites by melt mixing process. The maximum reduction of oxygen permeation of the nanocomposites was >99% with 1.5-wt% GNP. The authors suggested that the GNP have a twofold effect on oxygen permeability of nanocomposites, generated simultaneously by their inherent barrier properties and by inducing higher degrees of crystallinity [147].

On the contrary, large-scale production of graphene oxide has been compounded with various polymers [170–173]. For example, Kang et al. fabricated carboxylated acrylonitrile butadiene rubber (XNBR)/graphene nanocomposites, which have superior mechanical and gas barrier properties, using a simple and environment-friendly latex co-coagulation method. The addition of 1.9 vol% of graphene oxide decreased the gas permeability coefficient of XNBR by 55% [111]. Zhu et al. prepared graphene oxide from graphite using a modified Hummers’ method, and then used graphene oxide as a nanofiller to synthesize polyimide (PI)/graphene oxide by in situ polymerization (Fig. 5). As expected, the oxygen transmission rate (OTR) resulted in a 93% decrease from 377.78 for pure PI to 26.07 cm³ m⁻² 24 h⁻¹ atm⁻¹ for 30-wt% graphene oxide-loaded composite [155].

Huang et al. prepared high-barrier poly(vinyl alcohol) (PVA)/graphene oxide nanosheet nanocomposite films by solution mixing. Addition of 0.72 vol% of graphene oxide nanosheets resulted in a >98% decrease in the O₂ permeability coefficients of PVA film from 21.17 × 10⁻¹² to 0.24 × 10⁻¹⁵ cm³ cm⁻² s⁻¹ Pa⁻¹, attributed to the excellent impermeable properties of graphene oxide nanosheets, their complete exfoliation, uniform dispersion and high alignment in the PVA matrix, and the strong interfacial adhesion between graphene oxide nanosheets and PVA matrix [138]. Dodecyl amine-functionalized graphene oxide (DA-GO) and dodecyl amine-functionalized reduced graphene oxide (DA-RGO) were produced using amidation reaction and chemical reduction by Ren et al. Then, high-density polyethylene (HDPE)/DA-GO and HDPE/DA-RGO nanocomposites were prepared by solution mixing method and hot pressing process. Crystalline, dynamic mechanical, gas barrier, and thermal stability properties of HDPE were significantly improved by the addition of DA-GO or DA-RGO. However, the performance of HDPE nanocomposites reinforced with DA-GO was almost similar to that of DA-RGO, which indicated that the reduction of DA-GO was not necessary and the interfacial adhesion and aspect ratio of graphene layers had hardly changed after reduction [96]. Morimoto et al. developed an environmentally friendly technique for fabricating poly (methyl methacrylate) (PMMA)/graphene oxide nanocomposites in which PMMA was polymerized by soap-free emulsion polymerization and incorporated with graphene oxide using water as a processing medium. The addition of 1% w/w of graphene oxide to the PMMA matrix decreased the permeability by 50%, and the nanocomposite with 10% w/w of graphene oxide was found to be almost completely impermeable (Fig. 6) [67].

As mentioned earlier, graphene oxide prepared by oxidation of graphite with strong oxidants contains many hydrophilic groups. Shim et al. reported a method to efficiently convert these hydrophilic groups into alkyl and alkyl ether groups by a one-step reaction of bimolecular nucleophilic substitution with alkyl bromide (Fig. 7). The functionalized graphene oxide (GO) can be homogeneously dispersed as exfoliated monolayers in various organic solvents, while it is precipitated in water. The oxygen permeability coefficients of PET/graphene oxide (1 wt%) and PET/GO (1 wt%) were found to decrease by 38% and 85%, respectively, compared with that of neat PET [137].

Chen et al. synthesized a transparent gas barrier film composed of PVA and graphene oxide through combined methods of solution mixing and isothermal recrystallization (Fig. 8). When O₂ was passed through the PVA/graphene oxide nanocomposite, it followed a tortuous diffusion path because graphene oxide sheet was impermeable to gases. This reduced the permeability of PVA. However, the O₂ molecules could still pass through the spaces between the graphene oxide sheets. Furthermore, isothermal recrystallization was used to further enhance the barrier property. The graphene oxide acted as a nucleating agent, and some PVA crystals were formed around the graphene oxide sheets. In the
unique PVA crystal/graphene oxide hybrid structure, the newly formed PVA crystals fill in the spaces between the graphene oxide sheets, thereby linking them together with PVA crystals forming a bridge. When O_2 was passed through PVA crystal/graphene oxide hybrid structure, it was forced to follow a longer diffusional pathway, leading to an ultralow permeability of the composite. The recrystallized PVA/graphene oxide film with only 0.07 vol% graphene oxide showed an O_2 permeability of

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Filler</th>
<th>Filler loading</th>
<th>Processing</th>
<th>Gas</th>
<th>Permeability</th>
<th>Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA [6]</td>
<td>GONS</td>
<td>1.37 vol%</td>
<td>Solution</td>
<td>O_2</td>
<td>1.145 x 10^-14 cm^3 cm^-2 s^-1 Pa^-1</td>
<td>45</td>
</tr>
<tr>
<td>Cellulose [18]</td>
<td>GNP</td>
<td>5 wt%</td>
<td>Solution</td>
<td>O_2</td>
<td>-0.8 x 10^-16 m^3 m^-2 s Pa</td>
<td>-27</td>
</tr>
<tr>
<td>PS [61]</td>
<td>Graphene</td>
<td>2.27 vol%</td>
<td>Solution</td>
<td>O_2</td>
<td>1.84 barrer</td>
<td>61</td>
</tr>
<tr>
<td>IIR [62]</td>
<td>TRG</td>
<td>5 phr</td>
<td>Solution</td>
<td>O_2</td>
<td>28.4 ml/m^2/24 h</td>
<td>26</td>
</tr>
<tr>
<td>PMMA [67]</td>
<td>Graphene oxide</td>
<td>1 wt%</td>
<td>Solution</td>
<td>O_2</td>
<td>-1.25 ml/[m^2/day/atm] (RH = 50%)</td>
<td>50</td>
</tr>
<tr>
<td>HDPE [96]</td>
<td>DA-GO, DA-RGO</td>
<td>1 wt%</td>
<td>Solution</td>
<td>O_2</td>
<td>1.75 x 10^-18 cm^3/cm^2 s Pa</td>
<td>67</td>
</tr>
<tr>
<td>LLDPE [135]</td>
<td>DA-G</td>
<td>1 wt%</td>
<td>Solution</td>
<td>O_2</td>
<td>19.5 fm/Pa.S</td>
<td>47</td>
</tr>
<tr>
<td>PLA [136]</td>
<td>Graphene oxide, GNP</td>
<td>0.4 wt%</td>
<td>Solution</td>
<td>O_2</td>
<td>1.2 x 10^-18 m^2 s^-1 Pa^-1</td>
<td>68</td>
</tr>
<tr>
<td>PET [137]</td>
<td>IGO</td>
<td>3 wt%</td>
<td>Solution</td>
<td>O_2</td>
<td>1.14 x 10^-3 barrer</td>
<td>97.4</td>
</tr>
<tr>
<td>PVA [138]</td>
<td>GONS</td>
<td>0.72 vol%</td>
<td>Solution</td>
<td>O_2</td>
<td>0.24 x 10^-16 cm^3 cm^-2 s^-1 Pa^-1</td>
<td>98.9</td>
</tr>
<tr>
<td>EP [139]</td>
<td>FeOx/GNP</td>
<td>1 wt%</td>
<td>Solution</td>
<td>He</td>
<td>2.2 x 10^-6 Pa m/s</td>
<td>94</td>
</tr>
<tr>
<td>PU [140]</td>
<td>Graphene oxide</td>
<td>1 wt%</td>
<td>Solution</td>
<td>He</td>
<td>0.970 ± 0.027 barrer</td>
<td>79</td>
</tr>
<tr>
<td>PANI [141]</td>
<td>Graphene</td>
<td>0.5 wt%</td>
<td>Solution</td>
<td>O_2</td>
<td>0.1056 barrer</td>
<td>86</td>
</tr>
<tr>
<td>PND [142]</td>
<td>AFG</td>
<td>5 wt%</td>
<td>Solution</td>
<td>O_2</td>
<td>-25 cc/m^3 day</td>
<td>79.3</td>
</tr>
<tr>
<td>PPC [143]</td>
<td>EFG</td>
<td>5 wt%</td>
<td>Solution</td>
<td>O_2</td>
<td>51.8 cm^2 m^-2 day^-1</td>
<td>45</td>
</tr>
<tr>
<td>EVOH [144]</td>
<td>TRG</td>
<td>0.5 wt%</td>
<td>Solution</td>
<td>O_2</td>
<td>8.517 x 10^-15 cm^3 cm^-2 s^-1 Pa^-1</td>
<td>99.98</td>
</tr>
<tr>
<td>PVA [145]</td>
<td>Graphene oxide, RGO</td>
<td>0.3 wt%</td>
<td>Solution</td>
<td>O_2</td>
<td>5.14 x 10^-15 mol s^-1 m^-3 Pa^-1 (60% RH)</td>
<td>99</td>
</tr>
<tr>
<td>TPU [106]</td>
<td>iGO, TRG</td>
<td>3 wt%</td>
<td>Solution, In situ, Melt</td>
<td>N_2</td>
<td>N/A</td>
<td>98.7</td>
</tr>
<tr>
<td>PVA [146]</td>
<td>Graphene oxide</td>
<td>0.07 vol%</td>
<td>Solution, Recrystallization</td>
<td>O_2</td>
<td>&lt;5.0 x 10^-30 cm^2 cm^-2 s^-1 Pa^-1</td>
<td>&gt;99.94</td>
</tr>
<tr>
<td>PET [147]</td>
<td>GNPs</td>
<td>1.5 wt%</td>
<td>Melt</td>
<td>O_2</td>
<td>0.1 cc/m^3/day/atm</td>
<td>99</td>
</tr>
<tr>
<td>PU [148]</td>
<td>RGO</td>
<td>2 wt%</td>
<td>Melt</td>
<td>O_2</td>
<td>4.13 x 10^-16 cm^3(STP)/cm-s-cmHg</td>
<td>90.5</td>
</tr>
<tr>
<td>PEN [149]</td>
<td>Graphite &amp; FGS</td>
<td>10 wt%</td>
<td>Melt</td>
<td>H_2</td>
<td>0.76 barrer</td>
<td>47</td>
</tr>
<tr>
<td>PP [150]</td>
<td>Exfoliated GNP</td>
<td>3 vol%</td>
<td>Melt</td>
<td>O_2</td>
<td>-175 cc/ml/cm^2 atm</td>
<td>-20</td>
</tr>
<tr>
<td>Nylon [151]</td>
<td>FG</td>
<td>0.3 wt%</td>
<td>Melt</td>
<td>O_2</td>
<td>10.1 cc/(m^3 day) (100% RH)</td>
<td>47</td>
</tr>
<tr>
<td>PC [152]</td>
<td>FGS</td>
<td>3 wt%</td>
<td>Melt</td>
<td>He</td>
<td>8.8 barrer</td>
<td>30</td>
</tr>
<tr>
<td>PS [153]</td>
<td>Graphene oxide</td>
<td>2 wt%</td>
<td>In situ</td>
<td>O_2</td>
<td>2.24 barrer</td>
<td>25</td>
</tr>
<tr>
<td>PEI [154]</td>
<td>RGO</td>
<td>12.5 wt%</td>
<td>In situ</td>
<td>H_2</td>
<td>~46 cc/m^3 day</td>
<td>86</td>
</tr>
<tr>
<td>PI [155]</td>
<td>RGO</td>
<td>30 wt%</td>
<td>In situ</td>
<td>O_2</td>
<td>26.07 cm^3 cm^-2 24 h^-1 atm^-1</td>
<td>93</td>
</tr>
<tr>
<td>PMMA [156]</td>
<td>Graphene</td>
<td>0.5 wt%</td>
<td>In situ</td>
<td>O_2</td>
<td>0.81 barrer</td>
<td>70</td>
</tr>
<tr>
<td>PAN [157]</td>
<td>Expanded graphite</td>
<td>4 wt%</td>
<td>In situ</td>
<td>O_2</td>
<td>-0.27 l/cm^3 min</td>
<td>92</td>
</tr>
<tr>
<td>BPEI [36]</td>
<td>Graphene oxide N/A</td>
<td>LbL</td>
<td>In situ</td>
<td>O_2</td>
<td>&lt;0.05 cm^2 m^-2 day^-1</td>
<td>99.6</td>
</tr>
<tr>
<td>PEI [158]</td>
<td>Graphene oxide N/A</td>
<td>LbL</td>
<td></td>
<td>O_2</td>
<td>0.05 cc/m^3 day</td>
<td>99.9</td>
</tr>
<tr>
<td>PDDA, SPVDF [159]</td>
<td>Graphene oxide</td>
<td>N/A</td>
<td>LbL</td>
<td>H_2</td>
<td>3.1 cm mm/m^3 day atm</td>
<td>92</td>
</tr>
<tr>
<td>PEI [160]</td>
<td>Graphene oxide</td>
<td>91 wt%</td>
<td>LbL</td>
<td>O_2</td>
<td>0.12 cc/m^3, atm. day</td>
<td>99</td>
</tr>
<tr>
<td>XNBR [111]</td>
<td>Graphene oxide</td>
<td>1.9 vol%</td>
<td>LbL, Co-coagulation</td>
<td>O_2</td>
<td>158.1 cc/m^3 atm</td>
<td>41</td>
</tr>
<tr>
<td>SBR [161]</td>
<td>Graphene</td>
<td>7 phr</td>
<td>Latex compounding</td>
<td>O_2</td>
<td>N/A</td>
<td>-</td>
</tr>
</tbody>
</table>

* melt, solution, and In situ in this column refer to melt mixing, solution mixing, and in situ polymerization, respectively.

b 1 barrer = 10^-10 cm^3(STP) cm/cm^2 s Pa [137,162–165] = 7.5005 x 10^-18 m^2 s Pa [160,167].

Fig. 4. SEM images of GNP/EP and m-GNP/EP composites. (a) GNP/EP composite with random alignment; (b) m-GNP/EP composite with highly-ordered alignment [139].
<5.0 \times 10^{-20} \text{ cm}^2 \text{ cm}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}. \text{ The superior O}_2 \text{ barrier properties were attributed to the unique hybrid of PVA crystals and graphene oxide sheets [146].}

Liu et al. presented a facile approach for the simultaneous in situ reduction of graphene oxide, its surface modification and preparation of polyethylenimine (PEI)/RGO nanocomposites with enhanced gas barrier properties (Fig. 9). PEI was used as both reducing agent and surface modifier for the preparation of water-dispersible graphene as well as a polymer matrix to obtain PEI/RGO composite for the gas barrier application. The gas barrier properties of PEI/RGO improved with increasing PEI content in the composite film. For example, the hydrogen permeation rate for PEI/RGO/PET was approximately seven times lower than that of the bare PET substrate when the PEI:graphene oxide feeding ratio was 7:1 [154]. Huang et al. fabricated a set of nanocomposites of poly(lactic acid) (PLA)/graphene oxide nanosheets (GONS). GONS were fully exfoliated and randomly dispersed in the PLA matrix. The O\textsubscript{2} and CO\textsubscript{2} permeability coefficients of PLA films were decreased by about 45% and 68%, respectively, at a low GONS loading of 1.37 vol%.

The enhanced gas barrier performance was ascribed to the impermeable property of GONS as well as the strong interfacial adhesion between GONS and PLA matrix [6].

Kim et al. used different graphene layers exfoliated from graphite oxide via two processes: chemical modification and thermal exfoliation to prepare thermoplastic polyurethane (TPU)/graphene nanocomposites by three different methods of dispersion: solution mixing, melt mixing, and in situ polymerization (Fig. 10). Transmission electron microscopy (TEM) and wide-angle X-ray diffraction (WAXD) results indicated that solution mixing techniques more effectively distribute thin exfoliated graphene layers in the polymer matrix than melt processing method. They found that in situ polymerized thermally reduced GO is not as effective as solution-mixed thermally reduced GO in reducing gas permeability. Up to 80-fold decrease in nitrogen permeation of TPU was observed with only 3-wt% phenyl isocyanate-treated graphite.
oxide [106]. Jin et al. fabricated a series of nylon 11 and 12-functionalized graphene (FG) nanocomposites by melt mixing with premixing. The nylon 11 films with FG loading as low as 0.3 wt% showed a significant decrease of oxygen permeability by approximately 47%. In addition to the dispersion of graphene and interface between the polymer and graphene, flexibility of graphene in the polymer matrix is an important factor to achieve the superior gas barrier properties due to the graphene-wrinkled structure in the polymer matrix [151]. The presence of low-wrinkled structure of graphene could provide a larger area of the effective tortuous paths, which could in turn enhance the barrier properties.

Compton et al. prepared a PS/graphene film with low O2 permeability and reduced transparency. At only 0.02 vol%, crumpled graphene nanosheets significantly densified PS films and thus decreased the free volume within the polymer matrix, which resulted in an unprecedented reduction in oxygen permeability. At such a low concentration of crumpled graphene nanosheets, the PS/graphene films were superior in reducing the O2 permeability of PS to those of some of the best reported polymer/clay nanocomposites with approximately 40 times more nanofiller loading [61,174]. Using solution mixing method, Mahmoudian et al. presented an approach for the preparation of regenerated cellulose (RC)/GNP nanocomposites via an ionic liquid, 1-ethyl-3-methylimidazolium acetate (EMIMAc). The nanocomposites exhibited enhanced gas barrier properties compared with RC, and the permeability of CO2 through the nanocomposites was higher than that of O2. It was suggested that the variation of permeability between different gases depended on the size of the gas molecules and their solubility in the polymer matrix [18,175].

Recently, LbL assembly process has been used as a simple and versatile thin-film fabrication technique [127,128,159,176–188]. The thickness, transparency, and gas permeability of LbL film can be precisely controlled by adjusting aqueous deposition mixture concentration [189], temperature [190], pH [191], and exposure time [160,192]. Yang et al. alternately deposited single layers of graphene oxide with branched polyethylenimine (BPEI) to investigate the oxygen barrier properties of these thin-film assemblies. A 10-bilayer film deposited on PET, produced by mixing 0.1-wt% BPEI and 0.2-wt% graphene oxide, decreased the OTR by a factor of 71 relative to an uncoated PET substrate, and the OTR of the BPEI/graphene oxide bilayer films was only 0.12 cc m⁻² day⁻¹, which was comparable to a 100-nm SiOx nanocoating [193], and two orders of magnitude higher than a 25-μm ethylene vinyl alcohol (EVOH) copolymer film [160,194]. Chen et al. also prepared transparent multilayered gas barrier films consisting of BPEI/graphene oxide on a PET substrate by Lbl assembly technique (Fig. 11). They investigated the effect of graphene oxide suspension pH on the oxygen barrier properties of the BPEI/graphene oxide film and found a relationship between them. The BPEI/graphene oxide film prepared using a graphene oxide suspension with a pH of 3.5 exhibited very dense and ordered structures and resulted in a minimum OTR (<0.05 cm⁻³ m⁻² day⁻¹). When the pH value of graphene oxide was < or >3.5, the BPEI/graphene oxide film showed a higher OTR [36]. Rajasekar et al. fabricated multilayered films containing poly( diallyldimethylammonium) chloride (PDDA) and sulfonated polyvinylidene fluoride (SPVDF) graphene oxide composites through LBL assembly process to enhance the hydrogen gas barrier properties. The hydrogen gas transmission rate of a 16-bilayer LBL assembly with 2-wt% graphene oxide was 11.7 cc/m² day atm, which was much lower than that of PET substrate (329.1 cc/m² day atm).

Fig. 8. Formation of gas barrier film of PVA/graphene oxide with hybrid structure [146]. (A color version of this figure can be viewed online.)

Fig. 9. Schematic of polyethylenimine (PEI)/RGO synthesis and the assembly process [154]. (A color version of this figure can be viewed online.)
and a one-bilayer LBL assembly without graphene oxide (277.9 cc/m² day atm) [159]. Yu et al. prepared a transparent and electrically conductive oxygen barrier film composed of graphene oxide and PEI. Graphene oxide was produced by oxidizing graphite via chemical methods. Alternating graphene oxide layers and PEI layers were deposited on a PET film surface by LbL process. As the number of deposition layers increased, the OTR decreased from 8.229 to <0.05 cc/m² day, the minimum sensitivity of the measurement [158].

4. Modeling of the barrier properties of graphene nanocomposites

The review on barrier properties of graphene nanocomposites is hitherto presented based on experimental findings. Nonetheless, there are analytical and numerical models that extract barrier properties of graphene nanocomposites. Therefore, in this section, models to determine the barrier properties of graphene nanocomposites are reviewed. These properties can be described by three common coefficients: permeability coefficient (P), diffusion coefficient (D), and solubility coefficient (S). The gas permeation in a nanocomposite is governed by a diffusion solubility mechanism [195] and it occurs due to a pressure gradient across the nanocomposite film. For steady-state diffusion across the film, gas permeability measurements can be performed using the constant-volume variable-pressure approach [196], where vacuum is applied on both sides of a film of effective thickness (tm) situated in the permeation cell, and the permeability coefficient is determined. The permeability of gas as a single molecule through a nanocomposite film is generally supposed to be a function of two processes: diffusion and solubility. The diffusion coefficient describes the kinetic aspect of the transport, and the solubility coefficient relates the penetrant affinity and the thermodynamic aspect of the transport. On the basis of Fick's and Henry's law, gas permeability can be expressed as follows:

\[ Q = DSAt \left( \frac{\Delta P}{tm} \right), \]

where D and S represent the diffusion and solubility coefficients of a gas in the graphene nanocomposite film, respectively; A is the effective area of the film (nm²); Q is the gas leakage quantity through the film (nm³); t is the time of gas permeation (s); and \( \Delta P \) is the pressure difference across the film (nmHg). According to the

Fig. 10. Schematic of thermoplastic polyurethane (TPU)/graphene composite preparation routes: (a) after oxidizing graphite in concentrated acids, functionalized graphene layers can be obtained via (b) rapid thermal expansion (thermally reduced graphite oxide) or (c) organic modification with isocyanate (R-NCO) in N,N-dimethylformamide (DMF) (isocyanate-treated graphite oxide); TPU/graphene composite prepared via (d) melt mixing, (e) solution mixing, and (f) in situ polymerization. (Black lines represent graphitic reinforcements. Hard and soft segments of TPU are denoted by short blue blocks and thin red curves, respectively) [106]. (A color version of this figure can be viewed online.)
diffusion solution model, the permeability in graphene nanocomposite film can be expressed as a product of the diffusivity and solubility as follows:

\[
P = DS. \tag{2}
\]

Equation (2) holds true when the value of \( D \) is independent of the concentration and the value of \( S \) follows Henry’s law, and it is often considered to describe the gas transport properties of composites reinforced with impermeable nanofillers in a polymer matrix [195,197]. In the diffusion solubility model presented earlier, penetrant molecules initially dissolve into the high-pressure side of a film, then diffuse across its thickness, and finally desorb at the low-pressure side. Thus, the permeability of a penetrant depends on both its diffusivity and solubility, and these properties can be systematically altered through judicious choice of molecular design and environmental factors. Nanocomposite films possess better barrier properties than homogeneous films [198], and the simplest model by Picard et al. [199] (Eq. (3)) can predict the penetrant solubility in the nanocomposite film as

\[
S = S_0(1 - \phi), \tag{3}
\]

where \( S_0 \) and \( \phi \) denote the penetrant solubility coefficient of the pure polymer matrix and the volume fraction of graphene-based nanofillers in the polymer matrix, respectively.

In the nanocomposite film, the dispersed graphene nanofillers act as impenetrable barriers, and therefore the penetrant follows a tortuous pathway to diffuse through the film thickness. This increases the effective pathway for diffusion of the gas, thus degrading the diffusion coefficient. This effective diffusion coefficient \( (D) \) of nanocomposites can be expressed as follows by introducing tortuosity factor \( (\tau) \):

\[
D = \frac{D_0}{\tau}, \tag{4}
\]

where \( D_0 \) is the diffusion coefficient of the pure polymer matrix [9], and tortuosity factor is defined as

\[
\tau = \frac{t_m}{t_m'}, \tag{5}
\]

where \( t_m' \) is the distance between tortuous pathways through the nanocomposite film thickness, that is, the shortest pathway for gas molecules [4,8], Fig. 12 shows a simple gas permeability model for a rectangular array of graphene layers for the case where gas molecules pass through the film in the perpendicular direction.

These layered graphene/PNC structures maximize the path length of gas diffusion and, as a result, significantly decrease the gas diffusion through layered film. The diffusion thickness \( (t_m) \), for the average number of \( N \) graphene layers dispersed in the film, can be determined as follows [4]:

\[
t_m = t_m + \left \langle N \right \rangle \frac{L}{2}; \quad \left \langle N \right \rangle = \frac{t_m}{D' + W}, \tag{6}
\]

where \( L \) and \( W \) denote the width and thickness of the graphene layer, respectively, and \( D \) is the effective distance between two adjacent graphene layers. Effective permeability coefficient \( (P) \) is obtained using Eqs. (2)–(4) as follows:

\[
P = \frac{1 - \phi}{\tau},
\]

where \( P_0 \) is the gas permeability of pure polymer matrix. The value of \( \tau \) depends on the shape and volume fraction of nanofillers, and several researchers calculated its value for different types of fillers. Although these studies are concerned only with a rather limited range of composites, they can be used to determine the different values of tortuosity factor for graphene/PNCs systems as it is a function of shape and size of the dispersed particles.

Several earlier studies focused on the use of composite theory [Eq. (3)] to determine the effective permeability in nanocomposites. Some of the pioneering research by Barrer et al. on permeation in composites included measurements on rubbery polymers containing inorganic fillers such as zinc oxide and silica [200,201]. Their experimental results were found to be in good agreement with the predictions of the composite theory [201]. Some other researchers developed various simple models to determine the gas transport behavior of PNCs filled with inorganic nanoplatelets [11,168,202–205]. For instance, Takahashi et al. [204] investigated the gas permeation properties of nanocomposites based on butyl rubber with high loadings of vermiculite. In their

\[\text{Fig. 11. Schematic of the preparation of BPEI/graphene oxide films through LbL assembly [36]. (A color version of this figure can be viewed online.)}\]

\[\text{Fig. 12. Regular arrangement of horizontally staked graphene layers in a parallel array perpendicular to the diffusion direction [4].}\]
study, permeability of the nanocomposite coatings to various gases was measured and validated to ensure the accuracy of permeation models for nanocomposites with flake-like fillers proposed by Cussler, Nielsen, Fredrickson and Bicerano, and Gusev and Lusti (Section 4.1). Chlorobutyl rubber nanocomposites were prepared by Saritha et al. [205] using organically modified Cloisite 15 A and characterized using X-ray diffraction (XRD) and TEM. The gas barrier properties of the nanocomposites were modeled using the composite theories of permeation and the tortuosity factors were predicted. In their study, the reciprocal tortuosity factors predicted by Gusev and Lusti, and Nielsen permeation models for given values of \( \alpha \phi \) of nanoparticles were found to be in good agreement with those of the experimental results. However, Cussler models show satisfactory agreement with the experimental tortuosity factor at lower values of \( \alpha \phi \), but vary at higher values, where \( \alpha \) is the aspect ratio of nanoparticle. Recently, Yoo et al. [4] have presented the state-of-the-art research on the use of graphene, GO, and RGO for barrier applications, including few-layered graphene or its derivatives in coated polymeric films. Their analytical results were in good agreement with those of experimental data.

4.1. Analytical modeling of barrier properties

Several empirical models have been proposed in various studies to predict the barrier properties of composite materials. These studies considered different contributions to transport, usually related to the “tortuous path” resistance in the nanocomposite system, described in a simplified way. Expressions for widely used empirical models are reported in this study without attempting an analysis of assumptions and derivations; more details are provided in the original studies. Different models, in particular, microscale-based analytical models, are presented in this study to determine the barrier properties of graphene/polymer composites. Different aspects, such as graphene geometry and orientation, graphene–matrix interphase, and agglomeration of graphene layers to model these composites systems were considered. Diffusion of a small solute through a nanocomposite film containing a suspension of impermeable particles is a classic problem in transport phenomena. One of the first examples was Maxwell’s theory [206], which predicts the effective permeability for a nanocomposite film containing a periodic array of spherical impermeable fillers as follows:

\[
\tau = 1 + \frac{1}{1 - \phi} - \frac{\phi}{2} \tag{8}
\]

The Maxwell model assumes that the contact between the filler and the surrounding matrix is perfect. It may also be noted that the Maxwell model assumes a dilute suspension of spherical fillers and may not provide good estimates for the nanocomposite containing graphene layers. Therefore, the Maxwell model is not used in this study to predict the barrier performance of nanocomposites containing graphene layers.

The situation is completely different for a nanocomposite film containing graphene layers oriented perpendicular to the diffusion path. For such case, the value of tortuosity factor is obtained from the following relation [168]:

\[
\tau = 1 + \alpha \phi \tag{9}
\]

The Nielsen approximation (Eq. (9)) describes the increase of the tortuosity of the gas diffusion path with volume fraction and aspect ratio of the graphene layer. Nielsen assumed that the nanoplatelets are completely exfoliated and dispersed along the perpendicular direction of diffusion. It may be noted that Eq. (9) is different from Maxwell’s relation, because the shape of the particle appears in the tortuosity factor; this indicates that the aspect ratio of particles has a significant influence on the diffusion direction. It may also be noted that Eq. (9) can predict the results accurately when the volume fraction (\( \phi \)) of graphene layers is \( \phi < 0.01 \). If \( \phi > 0.01 \), the graphene layers tend to aggregate in the polymer matrix, and Eq. (9) ceases to be valid. Therefore, the maximum value of \( \phi \) is considered as 0.01 to study the effect of aspect ratio of graphene layers. Fig. 13 demonstrate the effect of different values of aspect ratio (\( \alpha \)) of graphene layers on the relative permeability (\( P/P_a \)) of graphene/PNCs. It may be observed from the figure that the barrier performance of nanocomposite significantly improves with the increase of \( \alpha \). Significant improvement is observed in the barrier performance of nanocomposite even at low volume fraction of graphene layers of the order of 0.0015 and higher values of \( \alpha \) (\( \geq 1000 \)). For lower values of \( \alpha \) (\( \geq 50 \)), Nielsen’s model predicts a linear barrier improvement with \( \phi \). It may also be observed that the percentage of reduction in the relative permeability is found to be less for the higher values \( \alpha \) (\( \alpha \geq 500 \)) than the lower ones. These results indicate that graphene and its derivatives can be used effectively to improve the barrier performance of nanocomposites.

The experimental data are also found to be in good agreement with those predicted by Eq. (9). For example, as shown in Fig. 14(a), the experimentally measured permeability values of graphene/PS films by Compton et al. [61] are found to be in agreement with those obtained by Nielsen. Kim et al. [145] synthesized PVA/RGO composites using modified Hummers’ method and a solution mixing method. In their study, diffusivity of the PVA/RGO-coated film followed the qualitative feature of the Nielsen approximation.

Nielsen’s model is accurate in the dilute regime, but it is considered inadequate by Cussler et al. [207] when the volume fraction of fillers is semidilute (the volume fraction of fillers is low, but they overlap each other, \( \phi \ll 1 \) but \( \alpha \phi \gg 1 \)). In such case, another relation provided by Cussler et al. can be used for a nanocomposite film containing graphene layers (Fig. 12) oriented perpendicular to the direction of diffusion [207]:

\[
\tau = 1 + \frac{\alpha^2 \phi^2}{1 - \phi} \tag{10}
\]

It is not always possible to fabricate nanocomposite with graphene layers distributed at regular intervals, and these sheets may appear randomly in the film. Therefore, in case of (1) two courses of

Fig. 13. Effect of aspect ratio of graphene layers on the barrier performance of nanocomposite. (A color version of this figure can be viewed online.)
Fig. 14. Comparison between the experimental data and the results predicted by (a) Neilsen Model [Eq. (9)] and (b) Cussler Model [Eq. (10)] of the nanocomposite films containing GONSs. (A color version of this figure can be viewed online.)
these three effects. Both calculations and Eq. (17) show the separate conditions when each of these effects is important.

For the same geometry, as shown in Fig. 12, a slightly different model proposed by Wakeham and Mason [213] is given by

$$\tau = 1 + \frac{\alpha^2 \phi^2}{1 - \phi} + \frac{\alpha \phi}{\sigma} + 2(1 - \phi)\ln\left[\frac{1 - \phi}{2\sigma \phi}\right]$$

(18)

The difference between Eqs. (17) and (18) lies in the fourth term on the right-hand side. In Eq. (17), the fourth term is dependent on $\alpha$, whereas in Eq. (18) it is not. These two relations have been widely used for comparing the predicted barrier enhancement with either experimental or simulation results.

Minelli et al. [214] reported numerical and analytical modeling results for barrier properties in ordered nanocomposite systems. They proposed a new formulation capable of predicting the gas transport properties in simplified nanocomposite geometries and argued that their model correctly describes the enhancement in barrier effect for the systems for a wide range of filler loading and platelet dimensions, and can be reliably used to obtain relevant information on gas permeability in real nanocomposite systems. They proposed the following expression for the tortuosity factor:

$$\tau = \frac{\alpha \phi}{\sigma} \left(1 + \frac{1}{\sigma} \right)^2 + \frac{\alpha^2 \phi^2}{1 - \phi} \left(1 + \frac{1}{\sigma} \right)^4 + \frac{4\alpha \phi}{\pi} \left(1 + \frac{1}{\sigma} \right)^2 \ln\left[\frac{1 - \phi(1 + \sigma/\alpha)}{\sigma \phi(1 + \sigma/\alpha)(\sigma/2)}\right]$$

(19)

The first term on the right-hand side of Eq. (19) results from the tortuous path contribution to the mass transport resistance and the remaining terms refer to the tortuous path for the diffusing molecule.

As we can see, several models have been developed to determine the barrier properties of nanocomposites. At this point, it is desirable to compare the prediction of different models presented in this study. For this purpose, three different models are considered: Aris model [Eq. (17)], Wakeham and Mason model [Eq. (18)], and Minelli model [Eq. (19)]. Fig. 15 demonstrates the outcome of this comparison, which are made considering the two pore aspect ratios ($\sigma = 5$ and 10); the value of $\alpha$ is assumed 800 as the aspect ratio of the graphene layer was roughly estimated to be about 800 by TEM [6]. It can be observed that Wakeham and Mason model overestimates the barrier improvement in the dilute regime ($\phi < 0.002$) and all models predict almost the same results when $\phi > 0.002$. Fig. 15 also demonstrates that the values of $\sigma$ marginally influence the barrier performance.

In case of multilayered graphene layers embedded in the polymer matrix, the following extended form of Aris’ result can be used [212]:

$$\tau = 1 + \frac{\alpha^2 \phi^2}{1 - \phi} + \frac{\alpha \phi}{\sigma}$$

(20)

Considering the effect of orientation of graphene layers, the modified Nielsen model can be used to determine the tortuosity factor [11]:

$$\tau = 1 + \frac{2\alpha \phi}{3\sigma} \left(S + \frac{1}{2}\right)$$

(21)

where

$$S = \frac{1}{2} \left(3\cos^2 \theta - 1\right), \quad -0.5 \leq S \leq 1$$

(22)

where $S$ is the order parameter representing the orientations of graphene layers, as demonstrated in Fig. 16.

In case of high loading of graphene layers, Eq. (9) can be modified considering the degree of staking with the parameter ($N$) as follows:

$$\tau = 1 + \frac{\alpha \phi}{N}$$

(23)

Using Eqs. (22) and (23),

$$\tau = 1 + \frac{2\alpha \phi}{3(N)} \left(S + \frac{1}{2}\right)$$

(24)

From Fig. 16, the following three cases can be considered: perfect alignment of graphene layers, $S = 1$ ($\theta = 0^\circ$); random distribution of graphene layers, $S = 0$ ($\theta = 54.74^\circ$); and graphene layers do not provide barrier to the diffusion of gas molecules, $S = -1/2$ ($\theta = 90^\circ$). The effects of length, concentration, and orientation of graphene layers and degree of delamination on the relative permeability can be explored using Eq. (24). Dispersing longer graphene layers in a polymer matrix is particularly beneficial in several respects by (1) increasing the tortuosity, (2) reducing the dependence of the relative permeability on the orientation order of the graphene layers, and (3) slowing the degradation of barrier property with decreasing state of delamination, that is, increasing aggregation via intercalation. The last factor ultimately controls the barrier properties of graphene/PNCs, whereas the first two cases investigate their influence on the barrier performance of nanocomposites containing either a single or many layers of graphene.

Fig. 17 illustrates the variations of the relative permeability of nanocomposite with the volume fraction of graphene layers. It may be observed that the relative permeability of nanocomposite decreases when the graphene layers are horizontally dispersed ($S = 1$) in the matrix. For instance, when graphene ($N = 1$) is stacked horizontally in a polymer matrix with 1 vol%, it can reduce the gas permeation by approximately 89% in comparison to the pure polymer matrix. On the contrary, pronounced effect of random orientations ($S = 0$) of graphene layers on the barrier performance of the nanocomposite is observed. It may also be observed that the barrier performance of the nanocomposite decreases when the degree of graphene layer stacking increases. This is because the graphene layers tend to agglomerate with the increase in the value of $N$ and this aggregation increases the gas permeation rate.

Fig. 15. Comparison of theoretical model predictions ($a = 800$). (A color version of this figure can be viewed online.)
through the relatively highly permeable polymer matrix rather than graphene. Fig. 17 clearly demonstrates that the barrier performance of multilayer graphene/PNCs can be easily altered through effective utilization and orientation of graphene and its derivatives.

Recently, Huang et al. [6] have synthesized GONS/PLA films and reported their O₂ and CO₂ permeability coefficients. In their study, the enhanced gas barrier performance was attributed to the remarkable impermeable property of GONSs as well as to the strong interfacial adhesion between GONSs and PLA matrix. Fig. 18 illustrates the comparison of experimental results and analytical results predicted by Eq. (21). It may be observed that the experimental data are in good agreement with the analytical values, when \( S = 0 \), except the O₂ permeability coefficient at a GONS loading of 1.37 vol\%. Such a good agreement suggests that GONSs are prone to random dispersion throughout the PLA matrix, and is in accordance with the GONSs morphology observed in their work [6].

Sometimes nanocomposite may contain different sizes of graphene layers, and in such situation, it is preferred to know the graphene size that is dominating in the transport through a film. In this case, the tortuosity factor is given as follows [203]:

\[
\tau = \left[ 1 + \left( \frac{\phi_{\text{tot}}}{3W \sum_{i} N_i l_i^3} \right) \sum_{i} N_i l_i^2 \right]^2.
\]  
(25)

where \( \phi_{\text{tot}} \) is the total volume fraction of graphene layers, \( l_i \) is the average length of graphene layer in the size category \( i \), and \( N_i \) is the number of graphene layers in the size category \( i \). It may be noted that Eq. (25) is derived assuming that graphene layers in adjacent layers do not influence each other. Therefore, this model is not suitable for high volume fractions of graphene layers. Picard et al. [199] modified this model accounting for the distribution of the filler thickness and contribution of the surfactant layer to the impermeable phase volume fraction for larger agglomerates. In case of graphene/PNCs, the modified tortuosity factor is given as follows:

\[
\tau = \left[ 1 + \left( \frac{\phi_{\text{tot}}}{3W \sum_{i} N_i w_i} \right) \sum_{i} N_i w_i^2 \right]^2.
\]  
(26)

For the nanocomposite film containing random array of circular graphene layers, the tortuosity factor is given by Ref. [202]:

\[
\tau = 4 \left[ 1 + x + 0.1245x^2 \right]^2; \quad x = \frac{\pi D}{2W \ln \left( \frac{D}{2w} \right)} \phi.
\]  
(27)
Similarly, for the nanocomposite film containing random dispersion of nonoverlapping circular graphene layers, the tortuosity factor is [215].

\[
\tau = \exp \left[ \frac{D}{3.47W} \phi \right]^{0.71}, \tag{28}
\]

where D denotes the diameter of the graphene layer.

Accounting for the decrease in solubility, the modified form of the original polynomial equation [Eq. (27)] can be used to determine the tortuosity factor for the graphene/PNC film [204] as follows:

\[
\tau = 1 - \phi + 4 \left[ 1 + \frac{x + 0.1245x^{2}}{2 + x} \right]^{2} = \frac{\pi D}{2Wn} \phi \tag{29}
\]

Equation (28) was proposed by Gusev and Lusti [215]. An exponential function of \((D/W)\phi\), was obtained by finite element calculations. Furthermore, this relation was modified by Picard et al. [199] with respect to the solubility effects such that

\[
\tau = 1 + \frac{0.71D}{3.47W} \phi. \tag{30}
\]

5. Mixed matrix membranes for gas separation

Gas barrier performance of graphene/PNCs has been studied so far in this study. However, mixed matrix membrane (MMM) comprising permeable/impermeable particles, such as zeolites, carbon molecular sieves (CMS), activated carbon, silica, metal organic framework and carbon nanotubes, and polymeric material, presents an interesting approach for improving the overall performance of the resulting membranes [216–218]. Therefore, in this study, we discuss on the MMMs and present some of their permeability modeling techniques. In the recent years, gas separation membranes find many applications, such as carbon dioxide–nitrogen separation in flue gas, hydrogen–carbon dioxide separation for hydrogen production in fuel cells, oxygen–nitrogen separation for production of oxygen-enriched air or pure nitrogen, carbon dioxide–methane separation for natural gas, vapor–vapor separation, and dehydration of air [219,220].

The inorganic materials used for MMMs can be classified into porous and nonporous types [221]. The effect of porous fillers on the MMM is different from nonporous inorganic fillers and can be related to their structure and pore size. In general, porous fillers act as molecular sieving agents in the polymer matrix, and separate gas molecules by their shape or size [220,222]; these highly selective porous fillers allow the desired component to pass through the pores and thus the resulting MMM shows higher permeability compared to the neat polymeric membrane. Usually, highly selective polymers improve the separation performance of MMMs; therefore, glassy polymers with superior gas selectivity are preferred to highly permeable but poorly selective rubbery polymers [220,223–227]. However, the adhesion between the filler and surrounding glassy polymers is not perfect and weak organic–inorganic interaction between them causes voids at their interface [228]. In general, the permeability of gas in the filler–polymer interfacial region is significantly different from the permeability of the bulk polymer and depends on the structure of this region on a nanoscale. As a consequence of the nonperfect filler–matrix interfacial contact: (1) the polymer chains in contact with the filler surface become rigidified in comparison to the bulk polymer and (2) de-wetting of polymer chains from the filler surface may occur resulting in the formation of voids in the interfacial region [165]. When the filler–matrix interfacial region becomes rigid, its permeability \((P_{int})\) is reduced by chain immobilization factor, \(\beta\), relative to that of the polymer, such that

\[
P_{int} = \frac{P_{o}}{\beta}. \tag{31}
\]

On the contrary, when the filler–polymer interfacial region contains interfacial voids, its permeability is larger than that of the polymer. Considering the pore size \((d_{pore})\) is larger than the size of the diffusive molecule \((d_{mol})\), the interfacial permeability \((P_{int})\) is given by the product of the Knudsen diffusivity \((D_{Knudsen})\) of a gas molecule as

\[
D_{Knudsen} = \frac{d_{pore}}{3} \left( 1 - \frac{d_{mol}}{2W_{int}} \right) \frac{8RT}{\pi M} \tag{32}
\]

and the sorption coefficient \((S_{void})\) of the gas molecules in the void is given as

\[
S_{void} = \frac{1}{RT} \left( 1 - \frac{d_{mol}}{2W_{int}} \right)^{2}. \tag{33}
\]

where \(R\) is the universal gas constant, \(T\) is the absolute temperature, and \(W_{int}\) is the thickness of the rigid filler–matrix interfacial region. In Eq. (32), the term \((1 - d_{mol}/2W_{int})\) is added to account for the finite size of the migrating molecule when the void dimension is of the same order as the size of the gas molecule.

MMM permeation models can be classified into two models: one, which is used to predict permeation of an MMM comprising permeable particles and polymer matrix and the other that is applicable for an MMM comprising impermeable particles and polymer matrix. Accordingly, we introduce some important permeation models in this section to predict the barrier properties of MMMs.

5.1. MMMs containing permeable particles

Permeation models for MMMs containing permeable particles predict the effective permeability of a gaseous penetrant through the MMM as functions of its constituents and their volume fractions. On the basis of the shape factor of particles, Bouma et al. [229] modified Maxwell–Wagner–Siller model to predict the effective permeability of an MMM with a dilute dispersion of ellipsoids as follows:

\[
P = P_{o} \frac{n \phi_{p} + (1 - n) \phi_{f}(P_{o} - P_{p})}{n \phi_{p} + (1 - n) \phi_{f} + n \phi(P_{o} - P_{p})}. \tag{34}
\]

where \(n\) is the shape factor of particles and \(P_{p}\) is the permeability of the dispersed particles.

In Eq. (34), the limits of \(n = 0\) and \(1\) lead to a two-layer model and provide the following relations based on rule-of-mixture and inverse rule-of-mixture, respectively [220,222,230]:

\[
P = \phi P_{p} + (1 - \phi) P_{o}. \tag{35}
\]

\[
1 - \frac{\phi}{P_{p}} \frac{P_{o}}{P_{p}} = (1 - \phi). \tag{36}
\]

Note that Eqs. (35) and (36) can be treated as series and parallel two-layer models, respectively. In case of random orientation of particles, the geometric mean model can be used as follows [231]:
\[ P = P_0^{1-\phi}. \] (37)

Equation (34) reduces to the famous Maxwell’s relation when the value of \( n = 1/3 \) corresponds to dilute suspension of spherical particles as follows [222]:
\[ P = \frac{P_0}{1-\phi} \left( \frac{P}{P_0} \right)^{-0.333} = 1 - \phi. \] (39)

It is worth noting that Eq. (38) holds true when the loading of spherical particles is <20\% and interaction among adjacent particles is neglected [222,230,231]. It may also be noted that Eq. (38) does not account for particle size distribution, particle shape, and aggregation of particles [220,232]:

For higher loadings of particles, Bruggeman model can be used as follows [233]:
\[ \left( \frac{P/P_0 - P_0/P_0}{1 - P/P_0} \right) \left( \frac{P}{P_0} \right)^{-0.333} = 1 - \phi. \] (39)

Similar to Maxwell’s model, Eq. (39) also does not account for particle size distribution, particle shape, and aggregation of particles; in order to account for such effects, the following Lewis–Nielsen model [232,234,235] can be used:
\[ 1 + 2\phi \left( \frac{P/P_0 - 1}{P/P_0 + 2} \right) / (1 - \phi \left( \frac{1}{\phi_{max}} + 4\phi/\phi_{max} \right)), \] (40)

where
\[ \phi = 1 + \phi \left( \frac{1}{\phi_{max}} \right), \] (41)

where \( \phi_{max} \) is the maximum packing volume fraction of particles.

A Cussler model can be used to a dilute suspension of staggered flake spheres as follows:
\[ P = P_0 \left[ 1 + \frac{(1 + G)\phi \left( \frac{P/P_0 - 1}{P/P_0 + 2} \right)}{(1 + G)\phi \left( \frac{P/P_0 - 1}{P/P_0 + 2} \right) - \phi} \right]. \] (43)

where \( G \) is a geometric factor accounting for the effect of dispersed particle’s shape: \( G = 1 \), for long and cylindrical particles that are dispersed transverse to the gas flow direction; \( G = 2 \), for spherical particles or isometric aggregates; \( G = \infty \), for planar particles that are oriented parallel to the gas flow direction; \( G = 0 \), for dispersed particles that are oriented perpendicular to the gas flow direction.

5.2. MMMs containing impermeable particles

Impermeable particles improve the gas separation properties of the resulting MMM membranes by increasing the matrix tortuous pattern and decreasing the diffusion of the larger molecules [220,238]. Nanoscale inorganic particles may also disrupt the polymer chain packing and increase the free volume between polymer chains, which eventually increases the gas diffusion across an MMM membrane. Furthermore, the hydroxyl and other functional groups on the surface of these nanomaterials may also interact with polar gases (CO\(_2\) and SO\(_2\)) and thus improve the penetrant solubility in the resultant MMM membranes [220,239].

The developed permeation models (Section 4.1) for graphene nanocomposites can be used straightforward in the case of MMMs containing impermeable particles.

5.3. Permeation models for three-phase MMMs

In this study, the permeation models for two-phase MMMs are discussed so far considering perfect contact between a particle and the surrounding polymer matrix. In practice, particles are not perfectly bonded to the polymer matrix and poor adhesion occurs between them; such nonperfect bonding situation leads to (1) formation of a rigidified polymer layer around particles, (2) pore blockage in porous particles, and (3) creation of voids at the particle–polymer matrix interface. The existence of an interfacial layer between a particle and the surrounding polymer matrix can be considered as a third phase of resulting MMM, and three-phase permeation models can be used as follows:

(i) Maxwell’s modified model [222,232]:
\[ P = P_0 \left( \frac{2(1 - \phi) + (1 + 2\phi)\left( \frac{P_{eff}}{P_0} \right)}{(2 + \phi) + (1 - \phi)\left( \frac{P_{eff}}{P_0} \right)} \right), \] (44)

where
\[ P_{eff} = P_{i}\left( \frac{2(1 - \phi_k) + (1 + 2\phi_k)\left( \frac{P_0}{P_i} \right)}{(2 + \phi_k) + (1 - \phi_k)\left( \frac{P_0}{P_i} \right)} \right). \]

(ii) Felske’s model [232,240]:
\[ P = P_0 \left( \frac{2(1 - \phi) + (1 + 2\phi)\left( \frac{P_{eff}}{P_0} \right)}{(2 + \phi) + (1 - \phi)\left( \frac{P_{eff}}{P_0} \right)} \right), \] (45)

(iii) Felske’s modified model [241–243]:
\[ P = P_0 \left( \frac{1 + 2\phi(\beta - \gamma)/\left( \beta + 2\gamma \right)}{1 - \phi \beta(\beta - \gamma)/\left( \beta + 2\gamma \right)} \right), \] (46)

where \( P_{eff} \) is the permeability of two-phase particle–interphase medium, \( P_0 \) is the permeability of the interphase, \( \phi_k \) is the volume fraction of an inorganic phase in the combined inorganic phase and interphase, \( \gamma \) is the ratio of an interphase to the particle radius, and \( \beta \) is a function of loading of particles.

6. Conclusion

Graphene and its derivatives have been identified as powerful gas barrier materials, because perfect graphene does not allow
diffusion of small gases through its plane. Graphene-incorporated polymers can not only enhance gas barrier properties, but also enhance mechanical strength and improve electrical conductivity and thermal properties when properly dispersed in a polymer matrix. In this study, a thorough review of the production methods and gas barrier properties of PNCs composed of various polymer matrices and graphene has been presented. Many approaches have been attempted to prepare graphene/PNCs, including melt and solution mixing, in situ polymerization, and LBL and latex coagulation. For graphene/PNCs, the size, stacking orientation, and in situ polymerization are the most important factors affecting the gas barrier properties of nanocomposites. Compared to pure polymer matrix, the gas barrier performance of graphene/PNCs is often improved by one to three orders of magnitude. In order to achieve superior gas barrier performance of graphene/PNCs, the structure–property relationships of graphene/polymer also need to be fully understood. Further improvements in the gas barrier properties of graphene/polymer nanocomposites could be expected from the development of more compatible graphene/polymer systems, complete exfoliation and homogeneous dispersion of graphene layers in polymer matrix, and methods to prevent aggregation of graphene nanosheets in a polymer matrix, which enhance their structural stability at high temperatures. Finally, the mathematical modeling aspects of gas barrier properties of graphene/PNCs are also thoroughly investigated. These diffusion models are useful to evaluate the gas barrier performance the PNCs before actually making them and identify ideal set of geometric and material parameters of the nanofillers, and their optimal loading in a given matrix that lead to optimum gas barrier performance of PNCs.

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References

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