Interlayer Polymerization in Chemically Expanded Graphite for Preparation of Highly Conductive, Mechanically Strong Polymer Composites

Peng Wang,†,‡ Jiajia Zhang,†,‡ Lei Dong,†,‡ Chang Sun,†,‡ Xiaoli Zhao,†,‡ Yingbo Ruan,†,‡ and Hongbin Lu*†,‡

†State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Collaborative Innovation Center of Polymers and Polymer Composites, Fudan University, 220 Handan Road, Shanghai 200433, China
‡Shanghai Xiyin New Materials Corporation, 135 Guowei Road, Shanghai 200438, China

Supporting Information

ABSTRACT: The large-scale application of graphene−polymer composites needs a simple, low-cost method that simplifies the preparation process of graphene and optimizes the structure and properties of composites. We propose the first interlayer polymerization in chemically expanded graphite (CEG) with large specific surface areas, which allows CEG to be spontaneously exfoliated into single- and few-layer graphene in poly(methyl methacrylate) (PMMA). Our results demonstrate that besides weakened interlayer interactions, the surface wettability of CEG to monomers is a critical prerequisite for the desired graphene exfoliation, dispersion, and performance optimization of composites. The slightly oxidized CEG (LCEG) improved to some extent the affinity for the monomer but is not sufficient to achieve complete exfoliation of LCEG, so that the resulting composites reveal the mechanical and electrical properties that are far poorer than those of the surface-modified LCEG-based composites. The latter not only exhibit a significantly enhanced elastic modulus, increased as much as 3-fold relative to that of the neat PMMA, but also show an extremely high electrical conductivity, of >1700 S/m. Such a novel interlayer polymerization approach is expected to accelerate the use of industrial applications of a wide range of graphene-based composites.

INTRODUCTION

Graphene is an ideal filler that endows polymers with a variety of functionalities such as electrical and thermal conductivity, electromagnetic interference shielding, flame retardancy, and mechanical reinforcement.1−4 However, it is still quite challenging to establish an eco-friendly, industrially viable route that can produce superior graphene-based polymer nanocomposites.5−7 Despite significant efforts over the past decade, some basic issues remain critical hurdles for their practical production and applications, including (1) low-cost, large-scale production techniques of high-quality graphene, (2) molecule-level dispersion in the polymer, and (3) optimized interface interaction between graphene and the polymer. To address these issues, a novel, cost-effective approach and corresponding fundamental understanding are strongly desired. In one previous report,8 we had proposed a scalable method for preparing high-quality graphene via chemically expanded graphite (CEG) under environmental conditions; the latter possesses open, porous microscopic structures with a huge specific surface area (>840 m²/g), nearly 1 order of magnitude larger than that of thermally expanded graphite (TEG). These features open new opportunities for developing industrially promising techniques for preparing graphene−polymer composites with significantly improved mechanical properties and functionalities.

The strong aggregation tendency and inherent inert surface of graphene sheets make them hard to disperse in matrices and incompatible with most polymers.5−7 Therefore, in many cases, graphene oxide or reduced graphene oxide was frequently used as the precursor,9 in which the residual oxygen-containing groups allow a variety of organic molecules, oligomers, and polymers to be covalently or noncovalently linked to the graphene surface to improve the dispersion of graphene and interface structures. Although significant performance improvements have been demonstrated, the production of graphene oxide involves the use of a large amount of oxidant, time-consuming washing/solid−liquid separation processes, and the introduction of various structural defects that impair the inherent properties of graphene.10−12 These constitute the critical factors that restrict large-scale applications of graphene−polymer nanocomposites.
Interlayer polymerization occurs in the interlayer galleries of graphite, which allows graphite to be exfoliated spontaneously into individual graphene sheets and dispersed homogeneously in polymer matrices. This may simplify largely the production process of graphene composites. Early studies have demonstrated that the K-intercalated graphite could initiate the interlayer ionic polymerization of some unsaturated hydrocarbons such as 1,3-butadiene, isoprene, and styrene in the presence or absence of organic solvents. However, this route involves the use of a large amount of highly active alkali metal and long-time high-temperature intercalation reaction (4 days at 250–410 °C) and is impractical for the industrial production of composites. Although these hydrocarbon monomers can diffuse spontaneously into the K-intercalated graphite, they cannot enter the interlayer galleries of unintercalated graphite because of the large surface energy difference and diffusion resistance within the interlayer galleries. Therefore, to achieve interlayer polymerization, a more realistic approach is to employ expanded graphite in which enlarged interlayer distances contribute to boost the rate of diffusion of monomers, especially when their surface can be wetted well by monomers. In this regard, there have been attempts to thermally expand graphite to optimize the performance of composites; unfortunately, however, the relatively small specific surface area (∼100 m²/g) does not allow it to be exfoliated effectively, mostly existing in aggregates of dozens of graphene layers (∼3 nm thick) in the resulting composites and limited performance improvements.

We here report a novel interlayer polymerization method in chemically expanded graphite (CEG) for preparing high-performance composites in a cost-effective, scalable manner. Different from the in situ polymerization in TEG, during which 20–30 layers of graphite microsheets were usually formed in the resulting composites, interlayer polymerization in the surface-modified CEG (mLCEG) can spontaneously exfoliate mLCEG into single- and few-layer graphene nanosheets. This not only prevents the time- and energy-consuming preparation process of graphene but also provides a convenient approach to optimizing the interface adhesion between graphene and the matrix. It is found that in this process, besides impaired interlayer interactions, the good surface affinity for monomers is particularly critical for achieving spontaneous exfoliation of graphene. We also demonstrate a significant enhancement of the mechanical and electrical properties of the resulting composites and underlying mechanisms.

■ RESULTS AND DISCUSSION

Interlayer Polymerization of MMA in CEG. Two key points to accomplish the interlayer polymerization of monomers in graphite are how to weaken the interlayer interaction of graphite and to allow monomers to wet the graphene surface well so that the polymerization can occur in the interlayer galleries of graphite. To attain these two ends, we first prepare CEG under ambient conditions following a method similar to that previously reported. As shown in panels a–c of Figure 1, CEG shows a large change in volume compared with that of graphite, with open, highly surface accessible pore structures. Methylene blue analysis gives a specific surface area (SSA) of >800 m²/g, nearly 1 order of magnitude higher than that of TEG. Because of the limited oxidation capability of the H₂O₂/H₂SO₄ system, the graphene surface of CEG is nearly intact and only very few defects are formed in the process of expansion, with a Raman intensity ratio (I_D/I_G) of 0.05 (Figure S1a). To improve the wettability to monomers, we introduce oxygen functional groups on the graphene surface of CEG by relatively mild oxidation (1 weight equivalent of KMnO₄ was used, relative to graphite, at 35 °C for 1 h), which is called LCEG. Such oxidation is spatially uniform because of the significantly reduced diffusion resistance in LCEG, as shown in the two-dimensional Raman mapping image of panels b and c of Figure S1. Furthermore, the number of defects introduced is limited after oxidation and reveals an I_D/I_G ratio of 0.42. It differs from the traditional Hummers method, where the oxidation kinetics is typically diffusion-controlled and the oxidant prefers to attack the carbon atoms in the peripheral region. In addition, to establish covalent linkage between graphene and polymer matrices, we introduce polymerizable C=C bonds on the graphene surface by the coupling reaction of hydroxyl groups on the LCEG surface and 3-methacryloxypropyl trimethoxysilane (MPS) (see Figure S2). The subsequent interlayer polymerization makes polymer chains graft covalently onto the graphene surface and results in exfoliation into separate single- or few-layer graphene sheets. The whole process is illustrated in Figure 1d.

The enlarged interlayer space was observed directly through X-ray diffraction (XRD). As shown in Figure 2a, the strong 002 diffraction peak at 26.5° in graphite was largely weakened after chemical expansion. The mild oxidation after expansion further decreased the 002 intensity of LCEG, along with an increased peak width (the inset of Figure 2). Interestingly, however, the MPS-decorated LCEG (mLCEG) reveals a larger 002 intensity as opposed to that of LCEG, although it is slightly weaker than that of CEG. Apparently, such changes in the interlayer distance are closely related to their preparation process. Although significant increases in volume occurred in the chemical expansion, the oxidation capability of H₂O₂ is limited so that inevitably a certain degree of interlayer order exists in the resulting CEG. The residual unexpanded, stacked graphene layers were intercalated by KMnO₄ during the oxidation, resulting in the appearance of a new diffraction peak at 10.96°.
(0.79 nm, comparable to the interlayer distance of graphene oxide) and the increased extent of disorder in the LCEG sample. Intuitively, the introduction of oxygen functional groups can improve the wetting of the graphene surface to polar solvents such as alcohol and water. However, when LCEG was functionalized (using MPS) in the mixture of ethanol and water, the obtained mLCEG reveals an increased 002 peak intensity accompanying the appearance of a new diffraction peak (13.92°, 0.62 nm). This implies that the grafted MPS molecules reduced the wetting capability of mLCEG to polar solvents, which resulted in an increased extent of order. The covalent grafting of MPS molecules on LCEG was verified by Fourier transform infrared spectroscopy (FTIR), and the results are shown in Figure 2b. For LCEG, the characteristic bands at 3432, 1580, 1107, and 1058 cm⁻¹ arise from O−H, aromatic ring, C−OH, and epoxy group stretching vibrations, respectively. After MPS grafting, some new characteristic bands at 1316 and 1113 cm⁻¹ are attributed to C−Si and Si−O stretching vibrations of MPS, respectively. Also, because of the presence of a -CH₂ group of grafted MPS molecules, the intensities of the peaks at 2918 and 2850 cm⁻¹ of mLCEG became stronger compared to the intensities of those of LCEG. Compared to the situation of MPS grafted on graphene oxide, the peak intensities of C−Si and Si−O bands are weaker, because of the limited number of MPS molecules on LCEG. This can also be reflected in their X-ray photoelectron spectra. For LCEG, no Si signals were observed in the range of 95−110 eV, but a weak Si 2p signal (101.13 eV) can be identified, as shown in Figure 2c. These observations are consistent with the thermogravimetric analysis (TGA) of LCEG and mLCEG; that is, ~6.8 wt % of MPS molecules were grafted onto mLCEG (Figure 2d).
The grafted MPS molecules facilitate the interlayer polymerization of the monomer in LCEG and allow polymer chains to be covalently linked to the graphene surface. We employed benzoyl peroxide (BPO) to initiate the interlayer polymerization of methyl methacrylate (MMA) in mLCEG at 80 °C (the resulting composite was called P-mLCEG), and for comparison, the polymerization of MMA in the presence (P-LCEG) or absence (f-PMMA) of LCEG was also conducted under the same condition. To elucidate the validity of covalent grafting, we removed the free PMMA molecules in P-mLCEG and P-LCEG after polymerization by thoroughly washing them with N-methyl pyrrolidone (NMP). Figure 3a shows their TGA results, from which the decomposition of the grafted PMMA was found to occur in the temperature range of 520–610 °C, significantly higher than that of free PMMA reported previously (280–420 °C) due to the restricted release of volatile components during the decomposition. The number of PMMA molecules grafted on P-LCEG is quite small, only 1.23 wt %, which primarily arises from the attack of radicals on the highly active sites on a slightly oxidized graphene surface. In contrast, P-mLCEG reveals more grafted PMMA molecules (8.78 wt %, as shown in the inset of Figure 3a) because of the introduction of C=C bonds. The presence of grafted PMMA is also reflected in their FTIR spectra. As shown in Figure 3b, two absorption bands of -CH2 groups of PMMA at 2850 and 2926 cm−1 can be observed, but the signal intensity of P-LCEG is significantly weaker than that of P-mLCEG, verifying the presence of grafted PMMA molecules.

To further observe the morphology of PMMA-grafted LCEG, the thoroughly washed P-mLCEG sample (solid content of 4 wt %) was treated for a few minutes in NMP with mild bath sonication. Figure 4a shows the representative transmission electron microscopy (TEM) image, in which some light and dark domains or spots, although their number is limited, can be observed on the whole graphene sheets. This is in sharp contrast to the situation with high polymer grafting densities in which a thin polymer layer was formed on the graphene surface. The representative AFM images of 4 wt % P-mLCEG and P-LCEG are presented in Figure S3. It was found that the graphene sheets in P-LCEG revealed a thickness of 11.5–25.7 nm, corresponding to 10–20 layers, considering the contribution of the grafting PMMA. For P-mLCEG, although a small amount of grafting PMMA molecules exist, the graphene sheets obtained have a thickness of ~1.62 nm, suggesting a single-layer or few-layer structure. A limited grafting density is beneficial for balancing dispersion of graphene sheets in solvents or polymer matrices and preserving their inherent properties. Panels b and c of Figure 4 compare the dispersion stability of P-mLCEG and LCEG in NMP, and the concentrations of both samples are 2 mg/mL. A short-time sonication (~5 min) is sufficient to disperse P-mLCEG in NMP very well, and no precipitate forms even after the samples have stood for 15 days. However, for LCEG, it is difficult to form a homogeneous suspension under the same condition, despite the presence of a small amount of oxygen functional groups that improve the compatibility with NMP to some extent. After 15 days, nearly all LCEG or partially exfoliated graphene sheets had settled down to the bottom of the bottle. In addition, the mLCEG/ and P-LCEG/NMP suspensions (2 mg/mL) were prepared following an identical procedure. It was found that both likewise formed a precipitate after standing for 15 days, as shown in Figure S4. This implies that only grafted MPS molecules or free polymer chains (formed by polymerization outside graphene sheets) are insufficient for improving the dispersion of LCEG in NMP. These results manifest the critical role of interlayer polymerization in improving the exfoliation efficiency of LCEG and the dispersion stability.

Spontaneous Exfoliation and Dispersion in Composites. Intuitively, interlayer polymerization would facilitate the exfoliation of CEG; however, our results reveal that such exfoliation is highly dependent on the chemical environments of interlayer galleries. Even though the interlayer interaction is largely impaired in CEG, the wetting capability of the graphene surface to monomers actually dominates where or how the interlayer polymerization takes place in CEG. LCEGs have ~20 wt % oxygen functional groups, as revealed via TGA (Figure 2d), which afford a certain affinity for polar monomers. Nevertheless, when MMA was polymerized in the presence of LCEG, the reaction mostly took place on the outside surface of the well-expanded graphene so that the inherent multilayer stacked structure was still reserved to a large extent, especially for high-concentration systems. We prepared two kinds of PMMA composites containing different contents of LCEG and mLCEG, for which 0, 1, 4, and 10 wt % represent the nominal weight percents of LCEG and mLCEG, that is, the weight fraction of LCEG and mLCEG in the composites. TGA results indicate that these values are nearly equal to the residual weight percent after heating to 800 °C (Figure S5 and Table S1). As shown in Figure S5, the composite containing 10 wt % LCEG partially preserved the initial stacking structure, where two characteristic diffraction peaks are essentially the same as those of CEG or ECEG. For low LCEG contents of samples (1 and 4 wt %), their XRD patterns indicate the presence of irregular
order structures, which reflects inhomogeneous particle dispersion in composites and the presence of intercalation structures. This implies that the interlayer polymerization in LCEG is practically unable to facilitate the exfoliation of LCEG because of the limited wetting capability to MMA. By comparison, because of the presence of grafting MPS molecules on the mLCEG surface, improved surface wetting allowed the majority of graphene sheets to be well exfoliated. Even for the composite with 10 wt % mLCEG, only quite a weak 002 diffraction can be detected, which nearly disappeared in the two low-content composites. This clearly demonstrates the importance of surface wettability for the interlayer polymerization in CEG. Although it weakened interlayer interactions, the monomer wettability of the graphene surface determines virtually whether an expected dispersion and interface optimization can be achieved in the resulting composites.

Such differences in exfoliation and dispersion can be further observed by rheological characterization. Figure 6 shows the change in storage modulus (G') with frequency in the linear region of P-mLCEG and P-LCEG with different solid contents. It is seen that the G' of the 1 wt % P-mLCEG composite at low frequencies is 147.9 kPa, nearly 2 orders of magnitude higher than that of neat PMMA (4.73 kPa) and far higher than that of the 1 wt % P-LCEG composite (28.48 kPa). For 10 wt % mLCEG, its G' is as high as 3126.4 kPa, which is also 1 order of magnitude higher than that of 10 wt % LCEG (356.3 kPa). At the same graphene content, a higher elastic modulus implies more effective interface interaction and better load transfer between graphene and PMMA. On the other hand, remarkable reinforcements are also closely related to the exfoliation state of graphene sheets in PMMA. Better exfoliation implies larger interface volume fractions in composites and lower thresholds to form a percolated particle network. This can be verified likewise from the rheological characterization. The G' of 1 wt % P-mLCEG is nearly independent of frequency in the low-frequency region (Figure 6a), which suggests the formation of a percolated graphene network and the transition from a liquidlike to a solidlike behavior. This transition is obviously different from that of 1 wt % LCEG. As shown in panels of c and d of Figure 6, 1 wt % mLCEG reveals dominantly an elastic response; that is, G' > G'' over the whole frequency range. For 1 wt % LCEG, a transition from viscous to elastic behavior (G' > G'') appears at 0.18 Hz, indicating that the percolation network was not formed because of the limited exfoliation and dispersion of graphene in this system. This indicates again that it is important for interlayer polymerization to fulfill two critical prerequisites simultaneously, that is, surface wettability of monomer and reduced interlayer diffusion resistance. Next, we analyze the structural difference caused by the improved surface wettability in mLCEG.

To clearly observe the structural details of two kinds of composites (P-LCEG and P-mLCEG), we prepared ultrathin samples for TEM imaging using a microtome equipped with a diamond knife. As shown in Figure 7 and Figure S6, for P-LCEG, exfoliation of graphene sheets is insufficient and some thick edges can be discerned. On the whole, the exfoliation is more complete at low graphene contents (1 and 4 wt % P-LCEG). For 10 wt % P-LCEG, thick graphene edges become clearer, and furthermore, continuous, LCEG-free polymer domains are present, indicating a limited LCEG dispersion in such systems. Nevertheless, it is obviously superior to the situation of composites containing lightly oxidized thermally expanded graphite (P-mLTEG) (see Figure S7). Even at low solid contents (1 and 4 wt % P-mLTEG), the exfoliation of mLTEG remains insufficient and very few PMMA molecules entered the interlayer space of mLTEG. For 10 wt % P-mLTEG, large aggregates appear (Figure S7c), which resulted in significant structural inhomogeneity. In contrast, P-mLCEG
exhibits much better exfoliation and dispersion structures. In 1 wt % P-mLCEG, exfoliated sheets are uniformly dispersed in the matrix, in which the number of continuous, graphene-free domains appears to be far smaller than in P-LCEG composites. Especially for 10 wt % P-mLCEG, although the incompletely exfoliated sheets inevitably exist, the overall dispersion of graphene sheets is much more uniform than that in the LCEG composites. These structural differences provide evidence of the conclusion obtained from XRD and rheological analysis, suggesting more effective load transfer and mechanical reinforcement in P-mLCEG systems.

**Dynamic Mechanical Properties and Improved Load Transfer Efficiency.** Improved dispersion and interface interaction facilitate the performance optimization of graphene-based composites. Dynamic mechanical analysis (DMA) allows us to observe directly the correlation between mechanical properties and microscopic structures. Panels a and b of Figure 8 show the change in storage modulus with increasing graphene contents; their values at 45 °C are listed in Table 1. As a reference, the results for the composites containing MPS-modified lightly oxidized thermally expanded graphite (P-mLTEG), which were prepared following the same procedure that was used for P-mLCEG, are also included. For the P-mLCEG composites, the storage moduli increase 26.3, 100.4, and 299.6% for 1, 4, and 10 wt % composites, respectively. By comparison, the P-LCEG composites reveal limited improvements, only increasing 108.5% even for 10 wt % P-LCEG, although better than that of 10 wt % P-mLTEG (83.2% increase) (see Figure S8 and Table 1). It is worth noting that the storage moduli of P-mLCEG composites increase more significantly than those of P-mLTEG composites, indicating better load transfer and mechanical reinforcement in P-mLCEG systems.
noting that such a 3-fold increase in the storage modulus for 10 wt % P-mLCEG has never been reported in the literature of graphene-based PMMA composites, indicating a significant advantage of interlayer polymerization in preparing high-content graphene composites. Interlayer polymerization not only prevents the preparation process of graphene that is time- and energy-consuming but also contributes to the optimization of the interface adhesion between graphene and the matrix. Such improved interface interactions are embodied in their segmental relaxation behavior. As shown in Table 1, the P-LCEG composites reveal only ~5 °C increases in the glass transition temperature (T_g) caused by poor exfoliation and dispersion, which is similar to the irregular T_g change of the P-LTEG composites. By comparison, the P-mLCEG composites exhibit significantly increased T_g values with increasing mLCEG contents, such as a 18 °C increase for the 1 wt % mLCEG composite. For graphene-based composites, an increased T_g is indicative of some restricted segmental relaxation behavior, which is closely related to the improved interface adhesion. 24,25 For this point, damping spectra provide further evidence.

For polymer chains around the interface, because of the restriction of graphene, their relaxation or segmental motion begins at higher temperatures upon mechanical loading. With increasing graphene contents, the volume fraction of restricted segments increases, which results in an increased T_g reduced damping loss, and a widened loss factor peak. In this sense, the tan δ peak height can be used to characterize such restricted relaxation behavior and the load transfer efficiency between graphene and the matrix. 26,27 Panels c and d of Figure 8 compare the damping spectra of the P-LCEG- and P-mLCEG composites. It is clear that for both types of composites the width of tan δ peaks increases but the height (Δh) decreases with increasing graphene contents, suggesting a typical restricted relaxation behavior and effective interface load transfer. On the other hand, however, the difference between two types of composites is also obvious. For the P-mLCEG composites (the inset in Figure 8c), Δh decreases gradually from 1.25 of the neat PMMA to 0.24 of the 10 wt % P-mLCEG, while for the 10 wt % P-LCEG composite (Figure 8d, inset), the Δh decreases to 0.42. A smaller Δh value in the P-mLCEG composite indicates stronger interface adhesion, which reflects the contribution of polymer chains covalently grafted to the graphene surface. Because of the presence of grafted polymer chains, the graphene sheets were well exfoliated in the matrix and the dispersion becomes uniform, thus yielding increased T_g values with increased mLCEG content. However, for the LCEG composites, the situation is different; the T_g did not continuously increase with an increase in LCEG content, despite a small amount of covalently grafted PMMA chains [1.23 wt % (Figure 3a)]. The reduced and unchanged T_g values for the 1 and 10 wt % P-LCEG composites indicate the presence of inhomogeneous structures. This is similar to the situation of intercalated clay–polymer nanocomposites. 28 For the latter, our studies and those of others 24,29 have suggested several possible segmental relaxation modes, that is, bulk polymer chains (segmental relaxation without restriction of particle surfaces, unchanged T_g), restricted polymer chains at the interface (increased T_g), and polymer chains in a shielding environment in which no other neighboring polymer chains interfere with the relaxation of individual chains (decreased T_g). As a result, the T_g of composites is actually an overall reflection of the segmental relaxation behavior of polymer chains in different local environments. For well-exfoliated graphene sheets, increased graphene contents imply an increased volume fraction of restricted chains, thus an increased T_g as observed in the mLCEG composites. However, if the graphene sheets are not well exfoliated or incompletely exfoliated and/or intercalated structures exist, polymer chains in such composites experience the restriction of different local environments and thus reveal irregular relaxation features or T_g variations, depending on their practical situation or relative proportion in these local environments. When the majority of polymer chains are located in a shielding environment, the composite will reveal a decreased T_g. For the P-LCEG composites, because of the poor surface wetting capability, the exfoliation of graphene sheets is insufficient, which results in the formation of similar shielding environments, and thus, a decreased or unchanged T_g appears with an increase in LCEG content.

On the other hand, graphene composites with different microstructures will also reveal special fracturing behavior. Figure 9 shows field-emission scanning electron microscopy (FESEM) images of freeze-fractured cross sections of P-mLCEG and P-LCEG composites. For the 1 wt % P-mLCEG composite, the profile of some graphene sheets can be identified, as denoted by the arrows in Figure 9a, exhibiting a good dispersion of graphene sheets. However, for 1 wt % P-LCEG, no graphene sheets can be found apart from some microcracks (Figure 9b), and furthermore, the fracture surface is quite smooth, as well. When the filler content increased to 4 wt %, the morphology of both composites changed remarkably. For the P-mLCEG composite (Figure 9c), some separated graphene sheets are found to be uniformly dispersed in the matrix, as denoted by the arrows, which act as barriers to resist the growth of microcracks and result in a dense and crumpled morphology. 30–32 However, for the P-LCEG composite (Figure 9d), obvious graphene aggregations can be seen.
because of the poor dispersion, some of which were pulled out from the matrix and left some microvoids on the cross section, due to poor interface adhesion. When the filler content further increased to 10 wt %, some aggregations of graphene sheets appeared even in the P-mLCEG composite, as indicated by the two ovals (Figure 9e). Apparently, at high graphene contents, even for the polymer-decorated mLCEG, interlayer polymerization has difficulty guaranteeing its complete exfoliation into separate graphene sheets. Nevertheless, many well-separated graphene sheets are found to uniformly disperse in the matrix (denoted by the arrows), and furthermore, in the densely distributed cross section, no graphene sheets were pulled out from the matrix, indicating strong interface interactions. By comparison, 10 wt % P-LCEG shows the presence of aggregated graphene sheets in the cross section (Figure 9f), where some aggregated sheets were pulled from the matrix, reflecting the relatively weak interfacial adhesion in this system.32 Once loading has been performed, these weak interfaces turn into stress concentration points that induce the formation and extension of cracks, resulting in the appearance of some large holes. Clearly, these specific morphological features reveal the reason why the P-LCEG composites have elastic moduli much smaller than those of the P-mLCEG composites, especially for the high graphene contents of composites.

**Exceptional Electrical Properties.** The electrical property of the graphene-based polymer composites was closely related to the dispersion state of graphene in the matrix. LCEG preserves the crystal structure of graphene and thus is expected to significantly improve the electrical performance of polymer composites. Table 2 presents the values of electrical conductivity of P-mLCEG with different solid contents. The electrical conductivity of pure PMMA is \( \sim 10^{-14} \) S/m.33 With the addition of 1.5 wt % mLCEG, the electrical conductivity of P-mLCEG increased about 12 orders of magnitude, to \( 1.63 \times 10^{-2} \) S/m, which is far beyond the electrical percolation threshold.34 For the well-dispersed graphene–polymer composites, the filler–filler distance required by the electron tunneling mechanism is typically <5 nm.35,36 This implies that the good graphene dispersion in the P-mLCEG composite shortens the intersheet distance and results in the formation of conductive networks through the whole composite. When the mLCEG content reached 10 wt %, the electrical conductivity of P-mLCEG increased to 1719 S/m. To the best of our knowledge, this is one of the highest values reported for graphene-based systems in the literature,37 which nearly becomes a conductor that can be incorporated into an electrical circuit, as shown in Figure 10.

![Figure 10](image-url)

**Figure 10.** (a) Electrical circuit containing a 10 wt % P-mLCEG composite sheet. (b) Log \( \sigma \) vs \( p^{-1/3} \) for the P-mLCEG composites.

The ability to transform an insulating polymer into a conductor is strongly desired. The electrical conductivity of 10 wt % mLCEG even approaches those of some of doped conductive polymers such as polythiophene, exhibiting good application potential. For filler-type conductive composites, a segregated structure facilitates the formation of conductive networks in composites and lowers their electrical percolation thresholds.38–40 However, once such conductive networks are established, the percolation theory cannot explain further increases in electrical conductivity with an increase in filler content. For the P-mLCEG composites, the dispersion of graphene is uniform, even for 10 wt % P-mLCEG, as shown in Figure 7. The conduction mechanism should be tunneling conduction in the P-mLCEG composite.41–43 The charge transform barrier was mainly coming from the insulating disordered PMMA matrix between the graphene sheets. Thus, the average width of the insulating PMMA phase between the graphene sheets or intersheet junction resistance will determine the final electrical conductivity of the P-mLCEG composite.45 For such systems, their electrical conduction is dominated by the electron tunneling effect, and the relationship between \( \sigma \) and the tunnel distance (\( d \)) is expressed as41–45

\[
\sigma \propto \exp(-Ad)
\]

where \( A \) represents the tunnel parameter and the relationship between \( d \) and the weight percent (\( p \)) of conducting fillers is written as

\[
d \propto p^{-1/3}
\]

By combining eqs 1 and 2, we find the value of log \( \sigma \) is proportional to \( p^{-1/3} \), that is

\[
\log(\sigma) \propto p^{-1/3}
\]

Figure 10b shows the variation of log \( \sigma \) with \( p^{-1/3} \), which exhibits a good linear relationship and indicates the validity of the tunneling mechanism in the P-mLCEG composites. The prerequisite of the tunneling mechanism is the ideal dispersion of filler in the polymer matrix. Obviously, even for 10 wt % mLCEG, the dispersion of graphene was still able to meet such a requirement. The schematic tunneling transport mechanism in the P-mLCEG composites is shown in Figure 11; it clearly signifies that with an increase in filler content, the insulating PMMA gap between graphene sheets became smaller and smaller and more and more direct intersheet contacts were formed. As a result, the electronical conductive network became denser and denser as the filler content gradually increased. Especially for P-mLCEG with 10 wt % mLCEG, at this content, the quite small insulating PMMA phase gap between graphene sheets and many direct intersheet contacts promote the fast transport of an electron throughout the whole composite, and thus, an extremely high electrical conductivity (1719 S/m) was achieved. This was significantly different from other graphene–polymer composites in which the aggregation of graphene sheets always inevitably occurs in high-content cases. Once

**Table 2. Electrical Conductivities of P-mLCEG Composites with Various Filler Contents**

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<tr>
<th>mLCEG (wt %)</th>
<th>electrical conductivity (S/m)</th>
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<tr>
<td>1.5</td>
<td>( 1.63 \times 10^{-2} )</td>
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<tr>
<td>4</td>
<td>17.55</td>
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<td>10</td>
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aggregation occurs, some large insulating polymer gaps largely resist the transport of charge carriers, so that in this case, \( \sigma_{\text{max}} \) (maximal electrical conductivity) is usually far below 100 S/m.\(^{36,44}\) Here, our P-LCEG composites are an example; the electrical conductivity of P-LCEG was only 78 S/m when the filler content increased to 10 wt %. We demonstrated a much poorer graphene sheet dispersion state in P-LCEG composites compared with that in P-mLCEG composites. In addition, our composites are also different from the traditional conductive polymer composites with segregated structures in which electron transport could occur only in the peripheral region of polymer granules instead of throughout the whole polymer matrix. Thus, the transport efficiency is restricted, and their \( \sigma_{\text{max}} \) is also relatively low (usually below 1000 S/m).\(^{3,40}\) As a result, interlayer polymerization not only largely simplifies the preparation process of graphene composites but also affords an intriguing pathway for significantly improving the mechanical properties and functionalities like electrical conductivity.

## CONCLUSIONS

We have demonstrated the first interlayer polymerization in chemically expanded graphite (CEG) in which the CEG was spontaneously exfoliated into single- and few-layer graphene in graphene-poly(methyl methacrylate) (PMMA) composites. The large specific surface areas (SSAs of >800 m\(^2\)/g) and low levels of oxidation of CEG improve the surface wettability of CEG to monomers. In particular, the grafted MPS molecules on mLCEG not only facilitate interlayer polymerization but also allow polymer chains to be covalently linked to the graphene surface, resulting in superb graphene dispersion, and good interface adhesion in the resulting composites. This significantly differs from the in situ polymerization within the thermally expanded graphite (TEG), whose limited SSAs (~100 m\(^2\)/g) prevent the majority of graphene sheets from being well exfoliated in the composites, primarily existing in a form of aggregated, thick graphite microsheets (consisting of 20–30 graphene layers). The PMMA composites prepared by such CEG-based interlayer polymerization exhibit exceptional improvements, including an 18 °C increase in the glass transition temperature, a 3-fold increase in the storage modulus, and an electrical conductivity of 1719 S/m. Such a technical route has several advantages, including a low rate of energy consumption, simplified production procedures, controlled interface interactions, and outstanding composite performance. It is believed that such a CEG-based interlayer polymerization route provides the possibility of large-scale production of industrial-grade graphene–polymer composites.

## EXPERIMENTAL SECTION

**Materials.** Natural graphite flake (~500 μm) was purchased from Sigma. Concentrated sulfuric acid (H\(_2\)SO\(_4\), ~98%), hydrogen peroxide (H\(_2\)O\(_2\), 30%), and potassium permanganate (KMnO\(_4\)) were purchased from Jiangsu Tongsheng Chemical Co. N-Methyl-2-pyrrolidone (NMP), benzoyl peroxide (BPO), 3-methacryloxypropyltrimethoxysilane (MPS), methanol, ethanol, glacial acetic acid, and methyl methacrylate (MMA) were purchased from Sinopharm Chemical Reagent Co. All chemicals except for MMA were used as received without further purification. MMA was filtered to remove the polymerization inhibitor prior to use.

**Preparation of Chemically Expanded Graphite (CEG).** H\(_2\)O\(_2\) (20 mL) was added to a 1 L beaker, and H\(_2\)SO\(_4\) (180 mL) was subsequently added. After the solution was cooled to room temperature with an ice–water bath, graphite flake (2 g) was added to the beaker while its contents were being magnetically stirred (300 rpm) for 10 min, standing overnight to yield CEG.

**Oxidation of CEG.** To prevent significant heat release, the prepared CEG was poured into a 2 L beaker containing ice and water. After filtration, the filter cake was washed three times with deionized water. A 1 L beaker containing the filtered CEG was placed in an ice–water bath, to which 400 mL H\(_2\)SO\(_4\) was added, followed by the slow addition of 2 g of KMnO\(_4\) (i.e., 1 weight equivalent relative to graphite). Subsequently, the beaker was transferred to a 35 °C water bath, and its contents were magnetically stirred (600 rpm) for 1 h. The obtained dark green solution was poured into a 2 L beaker containing ice and water to prevent a significant increase in temperature. Ten milliliters of H\(_2\)O\(_2\) was then added to remove excess manganese salts. After filtration with a stainless steel sieve and washing three times with deionized water, the obtained wet CEG with a low extent of oxidation (LCEG) was used for further functionalization or directly for in situ polymerization.

**Silanization of LCEG.** Ethanol (100 mL) and ion water (50 mL) were added to a three-neck flask; 1 g of LCEG (calculated as the initial mass of graphite) was subsequently added. The mixture was stirred at 62 °C for 1 h. MPS (2.5 mL) was added to 37 mL of water, and the mixture stirred for 2 h at 62 °C to achieve silylation. After filtration and washing three times with methanol and water sequentially, the obtained silanized LCEG (mLCEG) was used directly for in situ polymerization.

**Preparation of PMMA-Graphene (P-mLCEG) Composites.** Methyl methacrylate (MMA, 30 mL), benzoyl peroxide initiator (BPO, 0.015 g), and 100 mL of NMP combined with different amounts of mLCEG were added to a 500 mL three-neck, round-bottom flask. The mixture was stirred at room temperature in an atmosphere of nitrogen for 4 h to let the MMA monomer fully wet mLCEG followed by polymerization at 80 °C for 7 h. After polymerization, the solution was slowly added to vigorously stirred methanol. The precipitate was filtered and washed three times with alcohol. The solid was dried in an oven at 80 °C for 24 h. Finally, the P-mLCEG composites with different graphene contents were obtained. For comparison, neat PMMA and PMMA-LCEG (P-LCEG) composites (upon addition of LCEG instead of mLCEG) were prepared by the same approach.

**Characterization.** X-ray diffraction (XRD) tests were conducted using an XPert PRO (PANalytical) diffractometer operating at 40 kV and 40 mA with monochromatic Cu K\(_\alpha\) radiation (\( \lambda = 1.54 \) Å). Thermogravimetric analysis (TGA) of all samples was performed (Mettler Toledo TGA 1) from 50 to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. FTIR was conducted on a Nicolet 6700 spectrometer at room temperature over a frequency range of...
X-ray photoelectron spectra were recorded on a RBD upgraded PHI-5000C ESCA system (PerkinElmer) spectrometer with Mg Kα radiation ($\lambda = 1253.6$ eV). Raman spectra of CEG were recorded using a 638 nm laser source (HORIBA JobinYvon XploRA). A transmission electron microscope (Tecnai G2 TF20 Twin, operating at 200 kV) was used to observe the microstructure of the composites and exfoliated graphene sheets. The samples of final composites were prepared by cutting with a diamond knife to ultrathin sheets using a microtome and collected on copper grids. Rheological behavior tests of P-mLCEG and P-LCEG composites were performed using a Rotary rheometer (ThermoFisher, HAAKE MARS III). An oscillation frequency sweep was performed at 180 °C from 8 to 0.1 Hz. The dynamic mechanical properties of the composites were measured using a dynamic mechanical analyzer (Mettler Toledo, DMA/SDTA861e) in stretch mode at a frequency of 1 Hz. The sample size was 10.5 mm ($14JC1400600$).

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Supporting Information

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Raman spectra of CEG, a representation of the chemical reaction of MPS with LCEG through -OH groups, and TEM images of P-mLCEG and P-LCEG composites with different filler contents (PDF).

Author Information

Corresponding Author

*E-mail: hongbinlu@fudan.edu.cn.

ORCID

Lei Dong: 0000-0002-4768-7896

Hongbin Lu: 0000-0001-7325-3795

Notes

The authors declare no competing financial interest.

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