A Facile "Graft From" Method to Prepare Molecular-Level Dispersed Graphene–Polymer Composites

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ABSTRACT: Graphene–polymer composites of positive-charged poly(dimethyl aminoethyl acrylate), negative-charged poly(acrylic acid), and neutral polystyrene were prepared by "graft from" methodology using reversible addition fragmentation chain transfer (RAFT) polymerization via a pyrene functional RAFT agent (PFRA) modified graphene precursor. Fluorescence spectroscopy and attenuated total reflection infrared (ATR-IR) evidenced that the PFRA was attached on the graphene basal planes by π – π stacking interactions, which is strong enough to anti-dissociation in the polymerization mixture up to 80°C. Atomic force microscopy (AFM) revealed that the thickness of a graphene–polymer sheet was about 4.0 nm. Graphene com-

INTRODUCTION In the nanocarbon family, graphene is the most recent member but has already attracted enormous interests due to its unique electric, optical, mechanical, and thermal properties. Mechanical exfoliation,¹ thermal deposition,^{2,3} oxidation of graphite,⁴ and liquid-phase exfoliation of graphite⁵⁻⁸ are the mostly frequently used methods to synthesize graphene. Nowadays, Hummers oxidation-reduction method is the mostly adopted method to produce graphene in large scale. Li et al.^{9,10} have successfully synthesized stable aqueous dispersions of graphene nanosheets via electrostatic stabilization negating the requirement for polymeric and surfactant stabilizers. Graphene has been extensively explored for the applications in optoelectronic devices,^{11,12} electrode materials,13 supercapacitors,14 sensors,15 biomedical,¹⁶ and catalytical materials.¹⁷ A lot of research also focused on the preparation of graphene-polymer composite materials for various purposes. One of them is to use graphene as conductive fillers to afford nanocomposites with controlled electrical conductivity. Graphene can also be used to enhance the polymer's mechanical,¹⁸ thermal¹⁹ and photoelectrical²⁰ properties. For example, a small percentage of graphene filler may exhibit significant enhancement of the glass transition temperature of graphene composite with poly (acrylonitrile).²¹

posites of different polymers with the same polymerization degree exhibited similar conductivity; however, when the polymer chain was designed as random copolymer the conductivity was significantly decreased. It was also observed that the longer the grafted polymer chains the lower the conductivity. *ATR-IR* spectroscopy and thermogravimetric analysis were also performed to characterize the as-prepared composites. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: functionalization of polymers; nanocomposites; reversible addition fragmentation chain transfer

The methods for the preparation of graphene-polymer composites can be very versatile. From the point of the binding mode between graphene and polymer they can be generally classified as covalent and noncovalent methods. The covalent bonding method can be used to form stable composites; however, the covalent bonding will disrupt graphene's conjugated structure, thus will compromise graphene's natural properties, for example, conductivity.²² Therefore, an alternative to covalent bonding could have significant potential advantages. π - π stacking interactions usually occur between two relatively nonpolar aromatic rings having overlapping π orbitals. Pyrene-functional precursors have been successfully prepared²³⁻²⁵ and attached onto aromatic macromolecules such as carbon nanotubes,^{26–30} graphene oxide,^{31,32} fullerene, and so forth.³³ The modification of graphene using π - π stacking should have advantages over previous attachment strategies as the conjugated structure of graphene will be retained after modification. π - π stacking interactions are also strong which are comparable to covalent attachment.

To prepare graphene–polymer composites via π – π stacking, two methodologies can be adopted. One is called "graft to" method, through which polymer chains with π -orbital rich functional groups can bind onto the graphene basal planes. Liu et al. have used this method to prepare thermo- and

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pH-sensitive graphene-polymer nanocomposites.^{34,35} The other method is called "graft from," through which polymer chains can be directly grafted from the graphene surface. This method was rarely documented. One difficulty in using "graft from" method is what polymerization can be used and how to make it happen. Reversible addition-fragmentation transfer (RAFT) polymerization is one of the solutions. RAFT polymerization is a controlled living radical polymerization which was first proposed by CSIRO,36 and has received a lot of attention for a large range of applications, such as in bioand nanotechnology.³⁷⁻³⁹ In addition, the RAFT approach has been widely exploited for controlling the end-functionality of polymers, by either modification of the RAFT functionality in the polymer^{37,40-44} or by using pre-functionalized RAFT agents.^{45,46} One recent research by Etmimi et al.⁴⁷reported the preparation of graphite oxide (GO) composite of polymer via "graft from" method. By modification of GO with carboxylic acid functional RAFT agent, the in situ polymerization afforded the composite in one step.

Pyrene functionalized polymers have been prepared by varied methods, such as RAFT^{34,35,48} and click chemistry.^{23,49} Some of these polymers^{34,35} have been utilized to modify graphene via "graft to" method, but did not study their electrical and mechanical properties. However, to the best of our knowledge, via noncovalent π - π stacking interactions to attach RAFT agent onto graphene basal planes for directly grafting polymers from graphene surface was not reported yet. Herein, we adopted "graft from" method to prepare graphene-polymer composites. A pyrene terminal RAFT agent was synthesized and attached onto graphene surface via π - π stacking, followed by the *in situ* polymerization to achieve positive-charged, negative-charged and neutral graphenepolymer composites. These composites were also used to prepare composite papers, whose electrical conductivity and mechanical properties were investigated.

EXPERIMENTAL

Materials

N, *N*'-Dicyclohexyl carbodiimide (DCC, 99%) and 4-dimethylaminopyidine (DMAP) (99%) were purchased from Adamasbeta. 1-Pyrenebutyric acid was purchased from Sigma Aldrich. Dimethyl aminoethyl acrylate (DMAEA) was from Aladdin. Acrylic acid (AA) and styrene (St) were purchased from Tianjin Damao Dioxane and 2,2'-azobis(2-methylpropionitrile) (AIBN) and hydrazine (60%) were from Tianjin Regent H₂SO₄ (98%), HCl (37%), KMnO₄, P₂O₅, and K₂SO₄ were purchased from Qingdao Laiyang Technology Development Region. Ethylene glycol (EG), ethyl acetate, dichloromethane (DCM), tetrahydrofuran (THF), and *n*-hexane were purchased from Tianjin Fuyu.

Measurements

¹H NMR spectra of RAFT agents were obtained using a JNM-ECP600 spectrometer. AFM samples were prepared by dropcasting modified graphene on mica surface. AFM images were obtained by a Molecular Imaging Picoscan II in tapping mode and the analysis of the AFM images was performed using the WSxM software (version 3, Nanotec Electronica S.L., Spain). All the samples for SEM analysis were prepared by vacuum filtration. All the SEM images were taken using a LEO-SEM (Supra 55VP, Zeiss) using an In-Lens detector and the accelerating voltage was adjusted to obtain the best image.

Transmission electron microscope (TEM) analysis was performed at 100 kV using JEOL-TEM 2010. The 0.005% ethanol solution was dropped on carbon-coated copper grid and allowed the solution to evaporate under ambient conditions.

Attenuated total reflection infrared (ATR-IR) spectra of graphene samples were recorded in the frequency range of 500–3600 cm⁻¹ using a Bruker IFS 66 spectrometer with a FRA 106/S module. The laser source was a Nd:YAG laser.

Thermogravimetric analysis. Thermal decomposition properties of the graphene and garphene–polymer composites were recorded on a Perkin–Elmer thermogravimetric analyzer (Pyris 1 TGA). Analyses were conducted over the temperature range from 25 to 800° C with a programmed temperature increment of 10° C/min under a nitrogen atmosphere.

The resistance of the graphene composite films was measured by a four-probe resistance analyzer.

Preparation of Chemically Converted Graphene (CCG)

Graphene was prepared with the reduction of GO which was synthesized from natural graphite powder (KNGTM-150) following the methods of Hummers and Offeman. ^{50,51} A preoxidation was required to completely oxide the graphite. The graphite powder (2 g) was dispersed in the mixture of concentrated H_2SO_4 (10 mL) and P_2O_5 (1 g) at 80°C. The resultant dark blue mixture was thermally isolated and allowed to cool to room temperature in 6 h, then diluted, filtered, and washed with water till the filtrate became neutral. The product was then dried and mixed with cold concentrated H₂SO₄ (50 mL), followed by the addition of KMnO₄ (6 g) slowly under stirring and cooling condition to make sure the temperature below 20°C. The solution was then stirred at 35°C for 2 h, followed by the addition of distilled water (400 mL). 30 % H₂O₂ solution (5 mL) was added slowly, after which the mixture changed to bright yellow. The product was dispersed in water, filtered, washed with aqueous HCl solution (10% in volume) and then dried under vacuum to afford GO powder for preparation of graphene. The GO powder (15 mg) was dissolved into dioxane (45 mL) through sonication. The resulting suspension was subjected to reduction by hydrazine (60%, 20 μ L) at 95°C for 12 h. The graphene dispersion was sonicated, filtered, and dried in air and then in vacuum to afford graphene paper.

Synthesis of 3-(Benzylsulfanylthiocarbonylsulfanyl)propionic Acid (BSPA)

The RAFT agent, BSPA was synthesized using published procedures. 40,52

Synthesis of 1-(3-(Benzylsulfanylthiocarbonylsulfanyl)propionic) Glycol Ester

To the solution of EG (0.570 g, 9.190 mmol), DCC (0.454 g, 2.206 mmol) and DMAP (0.027 g, 0.220 mmol) in THF (5 ml) was dropwise added BSPA (0.5 g, 1.838 mmol) solution in THF (5 mL). The mixture was kept stirring at room temperature for



12 h, followed by filtration to remove the solid byproduct. The filtrate was concentrated under vacuum and purified via silica gel column chromatography using *n*-hexane/ethyl acetate (3/1) as eluent to yield an orange oily product, which was characterized by ¹H NMR [Fig. 1(a)] in CDCl₃ (0.279 g, 57%).

¹H NMR (CDCl₃ 298 K, 600 MHz), δ (ppm from TMS): 2.80– 2.84 (t, 2H, C--C H_2 --CO), 3.62–3.65 (t, 2H, C--C H_2 --OH), 3.81–3.84 (t, 2H, S--C H_2 --C), 4.21–4.25 (t, 2H, O--C H_2 --C), 4.60–4.61 (s, 2H, C--C H_2 --S), 7.25–7.34 (m, 5H, aromatic protons of benzene).

Synthesis of Pyrene-Functionalized RAFT Agent

1-Pyrenebutyric acid (0.123 g, 0.428 mmol) was added to a solution of 1-(3-(benzylsulfanylthiocarbonylsulfanyl)-propionic) glycol ester (BSPGE) (0.136 g, 0.428 mmol), DCC (0.106 g, 0.514 mmol), and DMAP (0.006 g, 0.051 mmol) in THF (5 mL) and DCM (2 mL). The resulting mixture was kept stirring at room temperature overnight. The orangebrown mixture was filtered to remove the solid byproduct. The filtrate was then concentrated under vacuum and purified via silica gel column chromatography using DCM/hexane (50/20) to afford the light-orange oily product, which was analyzed by ¹H NMR [Fig. 1(b)] in CDCl₃ (0.121 g, 48%).

¹H NMR (CDCl₃ 298 K, 600 MHz), δ (ppm from TMS): 2.192-2.275 (m, 2H, C—C H_2 —C), 2.478-2.511 (t, 2H, CO—C H_2 —C), 2.788-2.817 (t, 2H, C—C H_2 —CO), 3.814-3.464 (t, 2H, C—C H_2 —C), 3.588-3.644 (t, 2H, S—C H_2 —C), 4.287-4.386 (m, 4H, O—C—C H_2 —O), 4.557-4.594 (s, 2H, C—C H_2 —S), 7.25-7.35 (m,5 H, aromatic of benzene), 7.883-8.358 (m, 9H, aromatic of pyrene).

"Graft from" Method to Prepare Graphene–Polymer Composite Papers Polymerization in the Presence of Free Pyrene-Functionalized RAFT Agent

The freshly prepared graphene (9.7 mg) was redispersed in 5 mL dioxane with the assistance of Ultrasonic Cell Crusher.

The resulting suspension was mixed with the pyrene-functionalized RAFT agent (PFRA; 58 mg), followed by mild sonicating for 10 min and stirring overnight at room temperature to afford a graphene/PFRA mixture. The monomer (St, AA, or DMAEA) was added in the above mixture in a molar ratio of monomer: PFRA:AIBN at 400:1:0.33. The solution was deoxygenated with nitrogen for 30 min, and then stirred in oil bath for 12 h at 80°C for St, 70°C for AA, and 70°C for DMAEA. Another system for random copolymerization of AA and DMAEA monomers (AA:DMAEA:PFRA:AIBN = 200:200:1:0.33) was incubated at 70°C for 12 h.

The polymer generated by the free PFRA and residual monomer was removed by centrifugation of the above mixture at 12,000 rpm for 30 min. The precipitate was collected and redispersed in dioxane (40 mL) by mild sonication, and this process was repeated for another two times to completely remove the free polymer. The obtained homogeneous dispersion was filtered with Teflon membrane ($\Phi = 0.22 \ \mu$ m) and dried overnight at 60°C and in vacuum for 48 h to afford the composite films which were peeled off from the Teflon membrane for analysis.

Polymerization Without Free PFRA Agent

PFRA (58 mg) was added to the graphene (9.7 mg) suspension in dioxane (5 ml), followed by mild sonicating for 10 min and stirring overnight at room temperature to afford a graphene/PFRA mixture. The mixture was centrifugated at 10,000 rpm, the precipitate was collected and redispersed in dioxane. This procedure was repeated for three times to completely remove the free PFRA to afford pure graphenepolymer composite. The final product was dried in vacuum at room temperature and weighed to obtain the grafted density of PFRA (10 wt%) and the polymerization was designed based on the actual amount of PFRA attached on graphene. The feed ratio of monomer (St, AA, or DMAEA):PFRA:AIBN was designed at 400:1:0.33 and other conditions for polymerization was the same as that for the polymerization in the presence of free PFRA as described above. The obtained homogeneous dispersion was filtered with Teflon membrane ($\Phi = 0.22 \ \mu m$) and dried overnight at 60°C in vacuum for 48 h to afford the composite films which were peeled off from the Teflon membrane for further analysis. The same procedure was performed to prepare graphene-polystyrene (PS) composites with different PS chain length by controlling the monomer/PFRA molar ratio at 100, 200, 300, 500, and 600, respectively. The graphene-PS composite papers were obtained and their tensile strength (TS) and conductivity characterized.

RESULTS AND DISCUSSION

Modification of Graphene with PFRA and the *In Situ* Polymerization

The synthesis of PFRA was started from the synthesis of the hydroxyl-functionalized RAFT agent via the condensation reaction between a RAFT acid, BSPA with excess EG in the presence of DCC and DMAP to afford the hydroxyl terminal RAFT agent, BSPGE. The same condensation method was subsequently used to synthesize the PFRA via the reaction





SCHEME 1 The modification of graphene with PFRA via π - π stacking interactions and the subsequent in situ polymerization to directly grafting polymer on graphene. Inset a: freshly prepared graphene in dioxane after 24 h; Inset b: graphene modified with PFRA in dioxane after 1 week; Inset c: graphene–polymer composite generated by *in situ* polymerization in dioxane after one week.

between pyrene butyric acid and BSPGE. As shown in Scheme 1, the PFRA was then utilized to modify the graphene basal plane via π - π stacking to afford the graphene–RAFT composite. The *in situ* polymerizations can be used to directly generate polymer brushes on both sides of graphene to yield sandwich-like graphene–polymer composites, where polymer layers are on both sides of graphene sheets (Scheme 1).

The successful synthesis of hydroxyl and PFRA were confirmed by ¹H NMR, respectively (Fig. 1). It is noteworthy that pure graphene sheets are relatively hydrophobic and easy to proceed irreversible aggregation (inset a of Scheme 1). However, when the graphene sheets were modified with PFRA a stable graphene suspension in dioxane was formed (inset b of Scheme 1). It is believed that the attachment of PFRA onto graphene basal planes is via the π - π stacking interactions. It is well known that pyrene is a fluorophore and its fluorescence will be quenched when it is attached onto graphene due to photoinduced electron transfer.^{53,54} Therefore, the successful attachment of PFRA onto graphene via π - π stacking can be demonstrated by monitoring the fluorescence of pyrene groups. As shown in Figure 2(a), the fluorescence spectrum reveals that the fluorescence of pyrene group was significantly quenched after being attached onto graphene.

The RAFT controlled polymerization using PFRA as chain transfer agent was performed. As shown in Figure 3(a), the monomer conversion increased concomitantly with polymerization time and the radical concentration remained constant with conversion as indicated by the pseudo-first order plot. The experimental (measured from GPC) and theoretical molecular weights (MWs) were found to be proportional to the monomer conversion. The theoretical MW values were slightly higher than the experimental ones and the polydispersity index (PDI) of the purified PS was less than 1.17, indicating a well-controlled polymerization consistent with the known traits of living radical polymerization [Fig. 3(b)].

Among the enormous research on preparation of graphenepolymer composites most of them using physical mixing methods, where the molecular level homogeneous composites are difficult to be achieved.⁵⁵ In recent studies by Liu et al. functional polymers with pyrene terminal groups have been synthesized and used to modify graphene via π - π stacking interactions and the polymeric properties were successfully imparted to graphene–polymer composites.^{34–56} The in situ polymerization method present in this paper will simplify the composite preparation. Using the same RAFT agent modified graphene precursor different polymer composites can be directly generated via RAFT-controlled polymerization. The length of the polymer chain can also be freely tailored just by controlling the monomer feed. Furthermore, because the RAFT agent is much smaller than the polymer



FIGURE 2 (a) Fluorescence emission spectrum of PFRA before and after being attached onto graphene at excitation wavelength of 350 nm. (b) Graphene–polymer composite paper.



FIGURE 3 Polymerization of styrene using PFRA in dioxane at $80^{\circ}C$ ([M]/[RAFT]/[AIBN] = 400:1:0.3). (a) Monomer conversion at varying polymerization times. (b) MW and PDI of the PS against monomer conversion [filled and empty diamonds represent the experimental (obtained from GPC) and theoretical MW values, respectively, while filled triangles represent PDI].

chains the density of the RAFT molecules attached on graphene will be much higher. Therefore, the density of the polymer chains via *in situ* polymerization will be much higher comparing to the postpolymerization grafting methods.

Analysis of Graphene and Graphene–Polymer Composites Using TEM, SEM, and AFM

The morphology of graphene prepared using Hummers method was analyzed by atomic force microscope (AFM). As shown in Figure 4(a), the thickness of graphene sheets was measured to be 1.1 nm, which is consistent with the values previously reported.^{34,57-59} When poly(dimethyl aminoethyl acrylate (PDMAEA) polymer chains were grafted onto the basal planes of graphene via π - π stacking interactions the thickness of the graphene-PDMAEA composite nanosheets was found to be 4.0 nm [Fig. 4(b)], evidencing the successful surface polymer grafting. Graphene sheets after modification with PDMAEA were also analyzed using TEM. As shown in Figure 4(c) separate graphene-PDMAEA composites were clearly recognized, evidencing that the as-prepared graphene composites were well dispersed. These graphene-PDMAEA composites can be easily prepared into composite papers by simple filtration, which exhibited layered structure through the side view imaging by scanning electron microscopy (SEM) [Fig. 4(d)].

Characterization of the Unmodified Graphene and its Polymer Composites Using ATR-IR Spectroscopy

Total reflection infrared (ATR-IR) spectroscopy was used to qualitatively characterize the graphene and its composites. After reduction trace residual C=O at 1675 cm⁻¹ still existed and the =C-H peak is hardly observed [Fig. 5(a)]. When the graphene was modified with PFRA the C=O characteristic peak at 1738 cm⁻¹ evidenced the successful RAFT attachment [Fig. 5(b)]. The spectrum of graphene-PDMAEA is shown in Figure 5(c). The peak at 2800 cm⁻¹ should be attributed to C-H stretch absorption in CH₃N- of PDMAEA. Peaks at 1720, 1230, and 900 cm⁻¹ can be assigned to C=O, C-O stretch, and =C-H bend respectively. The 1594 and

1354 cm⁻¹ peaks can be attributed to the C—H band and C—C stretch. In Figure 5(d), graphene–poly(acrylic acid) (PAA) exhibited the strong peaks of OH stretch at 3305 cm⁻¹, C—H, O—H, and C—O stretch at 2971, 2930, and 1180 cm⁻¹, respectively. Peaks at 1641, 1537, 1457, and 1370 cm⁻¹ can be attributed to the C=O, C—H band, and C—C stretch.

Conductivity of Composite Papers

The conductivity of the graphene composite papers with different polymers but the same degree of polymerization was analyzed using a four-probe resistance analyzer. As shown in Figure 6(a), the pure graphene paper has the highest conductivity while the conductivity values of the graphene composites with different polymers were similar but more than 10 times lower. By designing the polymers with positivecharged PDMAEA, negative-charged PAA, and neutral PS we like to explore whether the polymer charge will influence the electron transfer behavior. The similar conductivity values for the composites prepared from different charged polymers indicated that the polymer charges may not significantly affect the electron transfer through the composite matrix. It is surprising to observe that conductivity of graphene composite paper prepared from PAA/PDMAEA random copolymer is much lower than those of other composite papers of the homopolymers, which can be attributed to the phase separation due to the irregular random polymer chains. However, we found that the graphene content had significant effect on the composite conductivity. As shown in Figure 6(b), the increasing polymer percentage resulted from the longer chain length can significantly decrease the conductivity of composite papers. It can be envisioned that the longer polymer chains will insulate the graphene sheet better, thus greatly reduce the electrical communication between the graphene sheets. Similar conclusion was also obtained by He and Gao.²² They studied the effect of polymer composition on the conductivity of the graphene-polymer composites. The composites designed with the same polymer percentage but different polymer chain length exhibited different conductivity. The longer the polymer chain the higher the conductivity of the composites was





FIGURE 4 Imaging characterizations of graphene before and after surface grafting of PDMAEA via π - π stacking. (a) AFM image of unmodified graphene, (b) AFM image of graphene–PDMAEA composite, (c) TEM image, and (d) side view of high resolution SEM image of graphene–PDMAEA composite.

obtained. It is obvious that when the polymer percentage is fixed the longer the polymer chain the less chains will exist on the graphene surface, therefore, the graphene will be less insulated.

Thermal and Mechanical Analysis

The graphene–polymer composites were also analyzed using thermogravimetric analysis (TGA) under nitrogen atmosphere to 800° C at a rate of 10° C/min. As shown in Figure 7(a), the TGA curve of graphene revealed 20% mass loss before the furnace temperature reached 500°C, which is due to the evaporation of absorbed water and decomposition of some residual oxygen-containing groups.⁵ The TGA curves of the graphene–polymer composites are similar in trend. It can be seen that they all contain about 10% volatiles like water, which can be removed below 200°C. The graphene–polymer composites are not thermally stable, and mostly lost below 400° C, which is similar to the results of Fang et al.⁶⁰ The TGA analysis also revealed that the gra-

phene composites of PDMAEA, PS, PAA, and PDMAEA/PAA have different polymer weight percentages of 48, 44, 30, and 41%, respectively. This result is consistent with their monomer MW. It can be seen from the TGA analysis the polymer percentage was low which is probably due to the free PFRA existed in the polymerization mixture which consumed the most monomers in a very short time. To increase the polymer ratio in the composites the in situ polymerization was performed in the absence of free PFRA in the polymerization mixture. The polymerization was performed following the procedure as described in the experimental. The as-prepared graphene-polymer composites were analyzed by TGA. As shown in Figure 7(b), the polymer percentage was significantly increased up to 99%. This protocol supplied a convenient tool to easily manipulate the polymer composition.

The TS of graphene and its polymer composites were also investigated. As shown in Figure 8(a), TS of the graphene



FIGURE 5 ATR-IR spectra of (a) graphene, (b) graphene–PFRA, (c) graphene–PDMAEA, and (d) Graphene–PAA.

composites were significantly enhanced for all the composites, among which TS of graphene-PDMAEA reached 24.8 Mpa. The TS enhancement might be attributed to Van der Waals

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force and the entanglement effect among polymer chains.⁶¹ The longer side groups of the PDMAEA polymer chains should accounts for the highest TS of graphene-PDMAEA composite



FIGURE 6 (a) Conductivity of papers of graphene and graphene composites with different polymers and (b) Conductivity of graphene-PS composite papers with different graphene contents.



FIGURE 7 TGA thermograms of graphene and graphene–polymer composite prepared by *in situ* polymerization in the presence (a) and in the absence (b) of free PFRA.

as the longer side groups will certainly enhance the chain entanglement and interfacial adhesion.^{62,63} We also observed TS is more sensitive to the percentage of polymer. As shown in Figure 8(b), TS of graphene–PS composite papers increased with the increasing content of PS, which is due to the increased interactions between the polymer chains.

CONCLUSIONS

In summary, we have successfully demonstrated a facile "graft from" method to prepare graphene composites of different polymers using RAFT polymerization via just one RAFT agent functonalized graphene precursor. This is a facile method that can maximally avoid the graphene aggregation, therefore can be used to prepare graphene–polymer composites at molecular level. Fluorescence spectroscopy evidenced that the PFRA agent was attached on the graphene basal planes by π - π stacking interactions. The π - π stacking interactions were found strong enough to stand 80°C polymerization condition without obvious de-association. It was also observed that the longer the polymer chain grafted the lower the conductivity. Our study revealed that the polymer charges might not play an important role in manipulating the electron transfer through the composite paper. Graphene composites of different polymers with the same polymerization degree exhibited similar conductivity; however, when the polymer chain was designed as random copolymer the conductivity was significantly decreased. This grahene-polymer composite preparation method is facile, efficient and can be used to tailor the graphene-polymer composites with versatile properties.



FIGURE 8 TS of graphene composites with different polymers (a) and with different graphene contents.

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