

Enhanced Performance of Biodegradable Poly(butylene succinate)/Graphene Oxide Nanocomposites via in Situ Polymerization

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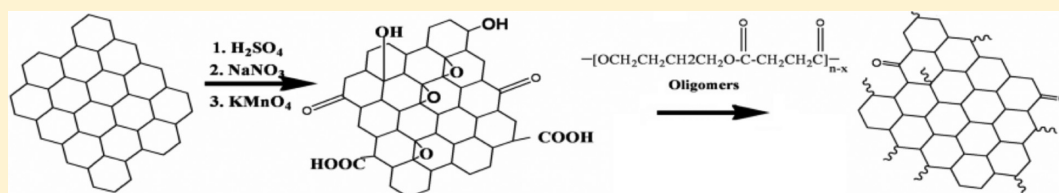
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Supporting Information



ABSTRACT: Poly(butylene succinate) (PBS)/graphene oxide (GO) nanocomposites were facily prepared via in situ polymerization. The properties of the nanocomposites were studied using FTIR, XRD, and ¹H NMR, and the state of dispersion of GO in the PBS matrix was examined by SEM. The crystallization and melting behavior of the PBS matrix in the presence of dispersed GO nanosheets have been studied by DSC and polarized optical microscopy. Through the mechanical testing machine and DMA, PBS/GO nanocomposites with 3% GO have shown a 43% increase in tensile strength and a 45% improvement in storage modulus. This high performance of the nanocomposites is mainly attributed to the high strength of graphene oxide combined with the strong interfacial interactions in the uniformly dispersed PBS/GO nanocomposites.

INTRODUCTION

In recent years, a great amount of attention has been paid to biodegradable polymers for their potential applications in solving environmental problems with the disposal of synthetic and nonbiodegradable polymers. It has become a great field of interest to academia, industry, disease institutes, and the government with respect to the updating of biodegradable polymers. As a potential commercial representative, poly(butylene succinate) (PBS), a linear aliphatic polyester¹ that can be chemically synthesized by the polycondensation of 1,4-butanediol and succinic acid, plays an important role in the biodegradable polymer field because of its many interesting properties, such as biodegradability, melt processability, and thermal and chemical resistance.² Unfortunately, it still lacks the mechanical and thermal properties needed for industrial application; incorporating another material into the PBS matrix may be an effective way. Among the manufacturing methods available to PBS-based polymers, copolymerization and blending have been shown to be effective in improving its mechanical properties and biodegradability.^{3–5}

Graphene oxide (GO), a graphene sheet bonding oxygen in the form of carboxyl, hydroxyl, and epoxy groups, is a layered

carbon nanomaterial prepared by the oxidation of natural graphite flakes, followed by ultrasonication treatment of its aqueous solution.^{6,7} Because GO nanosheets have similar chemical properties with nanotubes and an analogous structure with layered clay⁸ but with more strength, it has great potential to improve not only the mechanical and barrier properties but also the functional properties such as the electrical and thermal conductivities of the polymers.^{9–12} Despite the potential advantages, one of the key issues in successfully manufacturing the nanoplate-filled polymer nanocomposites is that graphene nanosheets should be uniformly dispersed in polymer matrices. Generally, methods for preparing polymer nanocomposites have mainly focused on solution mixing. For example, PMMA, PAN, PAA, and polyesters have been successfully applied in nanocomposite fabrication with GO.^{13–15} This method is simple, but it results in poor interaction between fillers and polymer matrices. Recent reports have disclosed some methods to resolve this problem, such as surface modification and in situ

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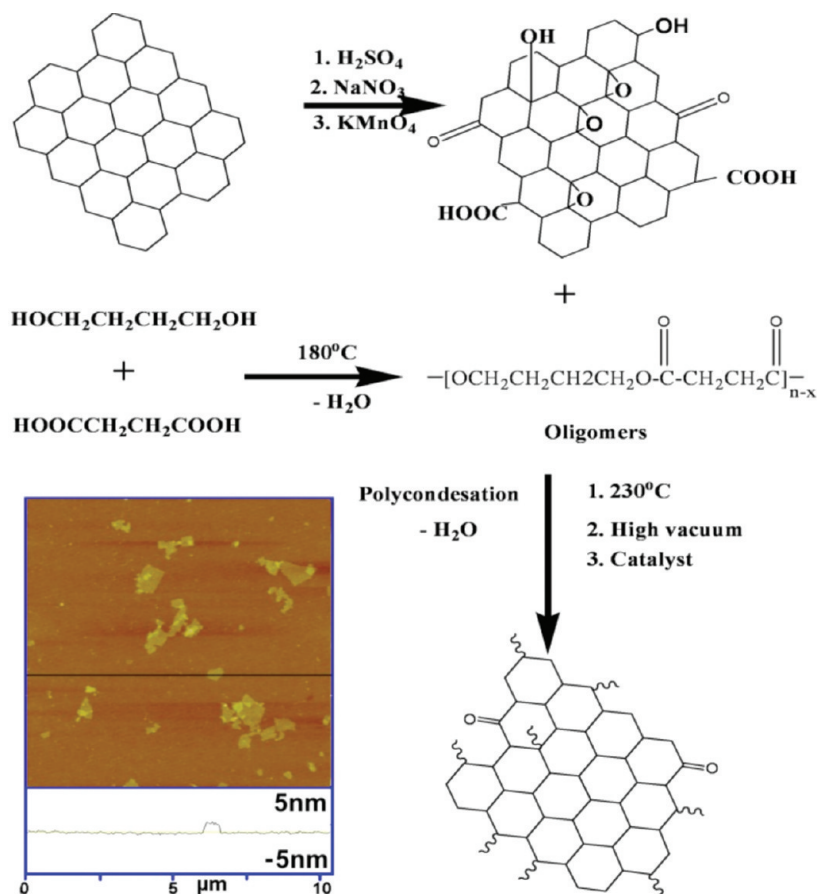


Figure 1. Synthesis of PG nanocomposites by the in situ polymerization of 1,4-butanediol and succinic acid in the presence of GO. The insert AFM image shows the morphology of GO.

polymerization approaches. Salavagione et al.¹⁶ successfully fabricated GO/poly(vinyl alcohol) (PVA) nanocomposites by direct esterification among the carboxylic group in GO and the hydroxyl group in PVA. Graphene-reinforced nylon-6 composites and esterified GO and PVA nanocomposites have been successfully synthesized by in situ polymerization.¹⁷ Using this method, GO can be dispersed in polyesters on the molecular level and noticeable reinforcement can be observed for those nanocomposites.

Herein, we reported an effective protocol for preparing PBS/GO nanocomposites on the basis of carboxyl and epoxy groups of GO by in situ polymerization. To our knowledge, this is the first time that the PBS/GO nanocomposites have been successfully fabricated. The existence of oxygen functional groups located on the edges and basal plane of GO makes it possible to interact with the PBS matrix. Because of covalent bonding, the GO nanosheets interact strongly with the PBS matrix and GO nanosheets were homogeneously dispersed in nanocomposites because of the high content of grafted PBS chains on graphene oxide nanosheets. The results showed that both the tensile strength and storage modulus dramatically increase via only a small amount of graphene oxide loading. The crystallization behavior and thermal properties of the PBS/GO nanocomposites were studied in detail with various techniques.

EXPERIMENTAL SECTION

Graphite powders with an average particle size of 1 mm and a purity of >99% were purchased from Alfa Aesar. Potassium permanganate

(KMnO_4) and tetrabutyl titanate were purchased from Sigma-Aldrich. Titanium(IV) isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, 98%) was purchased from Acros Organics. Other chemical reagents were purchased from Sinopharm Chemical Reagent Beijing Co. (Beijing, China). All materials were used without further purification.

A typical procedure for preparing PG nanocomposites with 0.5 wt % GO content was depicted as follows: GO (0.5 g) and 5 mL of distilled water were loaded into a 250 mL three-necked, round-bottomed flask, and the mixture was sonicated at 60°C for 2 h to obtain a homogeneous solution of GO, followed by introducing 63 g of 1,4-butanediol and 59 g of succinic acid. After the flask was equipped with a mechanical stirrer and a N_2 inlet, the mixture was held at 200°C for 2 h and at 230°C for 4 h under vacuum with continuous stirring. The color changed gradually from slightly brown to black. After cooling to room temperature, the hard bulk was chopped into small pieces and dipped in distilled water for 6 h to remove monomer and low-molecular-weight oligomers completely. The washed black pieces of composites were dried at 60°C in vacuum for 48 h. In the end, we obtained PBS-grafted GO(PG) nanocomposites noted as PG-0.5, PG-1, and PG-3 according to the feed weight percentage of GO. The preparation procedure of GO and the testing of PG are detailed in the Supporting Information.

RESULTS AND DISCUSSION

The general strategy for grafting PBS chains to graphene oxide nanosheets is described in Figure 1. PBS/GO nanocomposites were synthesized by the in situ polymerization of 1,4-butanediol and succinic acid in the presence of GO (around $1\ \mu\text{m}$ as shown in the inset of Figure 1), initiated by tetrabutyl titanate. The functional groups on GO nanosheets offer a strong interaction with polar monomers, thus resulting in a

homogeneous dispersion of GO nanosheets in the resultant PBS/GO nanocomposites. At elevated temperature, the esterification of 1,4-butanediol and succinic acid along with the consumption of monomers occurs. Synchronously, part of the 1,4-butanediol was immobilized onto the nanosheets by an esterification reaction between the carboxyl acid groups of GO and the active hydroxyl group of 1,4-butanediol. After undergoing esterification for 2 h, 1 mL of tetrabutyl titanate was added and then held under vacuum, with the temperature rising to 230 at 10 °C/min. Along with the condensation of the polymer chains, the viscosity of the mixture increased gradually. Also, the melting PG composites with a lower feed ratio of GO obviously exhibited the Weissenberg effect under constant stirring at the end of the reaction, indicating that high-molecular-weight PBS had been synthesized. To speculate on the length of grafted PBS chains on GO nanosheets, we investigated the molecular weight of free PBS collected from the supernatant of a PG composites solution after centrifugation.

The molecular weight of PG decreased while the feed fraction of GO increased, from 96 500 g/mol for neat PBS to 35 400 g/mol for PG-3.0 nanocomposite. (The calculation and result are detailed in the Supporting Information and Table S1.) In the process of condensation polymerization, the excess carboxylic acid groups on GO nanosheets inevitably disrupt the stoichiometric balance of carboxylic acids and hydroxy groups in the reaction system by grafting polymer chains onto graphene oxide nanosheets and simultaneously terminating the potential propagation of active chain ends. Thus, the higher feed ratio of GO to monomer and the higher content of carboxylic acids of GO indicate a smaller molecular weight of grafted polymer chains corresponding to the lower weight fraction of grafted polymers. Similar conclusions were obtained during the in situ polymerization approach to graphene-reinforced Nylon-6 composites¹⁷ and CNT-grafted polyurea from amino-functionalized CNTs.¹⁸

To verify the nanocompositions of PG, we measured the infrared spectra of the products. As shown in Figure 2 for the

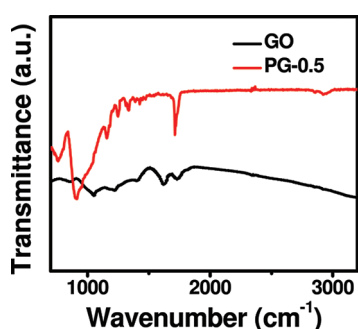


Figure 2. FTIR spectra of GO and PG-0.5 nanocomposites.

GO sample, the characteristic vibrations include the weak C=O peak in carboxylic acid and carbonyl moieties at 1730 cm^{-1} , the C-OH peak at 1380 cm^{-1} , the C-O-C peak at 1240 cm^{-1} , and the C-O stretching peak at 1065 cm^{-1} . For the PG nanocomposites, the infrared spectra retained most of the band of PBS, although some of them changed in intensity or even disappeared because of the modification. The weak C=O peak in carboxylic acid and carbonyl moieties at 1730 cm^{-1} and a new C-O-C peak at 1240 cm^{-1} for PG-0.5 suggest the solicitation of the polymerization and the covalent bonding

between PBS and GO.¹⁹ This phenomenon is also observed in the ^1H NMR spectrum (Supporting Information and Figure S1).

Differential scanning calorimetry (DSC) experiments on pure PBS and nanocomposite samples were carried out to understand the effect of GO incorporation on the crystallization behavior of the PBS matrix. The result shows that the crystallinity of PBS in PG-0.5 decreases from 64.9 to 61.2% (shown in Table S2; XRD analysis of PG with different concentrations are detailed in the Supporting Information and Figure S2). There is no obvious change in the crystallinity, which could be attributed to the rapid crystallization rate. During nonisothermal crystallization, the true link in the obtained exotherms from DSC measurements and the nucleation behavior of the GO nanosheets can further be examined by POM. To do POM experiments, a cooling rate of 10 °C/h from the melt was chosen as a model cooling rate, and we are interested to see the effect of the incorporation of GO nanosheets on the crystal growth behavior. The POM images of pure PBS and nanocomposite samples were taken at four different temperature: 110, 105, 100, and 95 °C. It is clear that PBS spherulites are grown faster in the presence of highly dispersed GO nanosheets as shown in Figure 3. This observation supports the fact that GO nanosheets acting as nucleating agents accelerate the crystallization.

Figure 4a–c shows the storage modulus (G'), loss modulus (G''), and $\tan \delta$ plots with temperature for pure PBS and PG nanocomposites. G' is related to the ability of material to store energy when an oscillatory force is applied, and G'' is related to the ability to lose energy. As shown in Figure 4a, the storage modulus of PG nanocomposites increases with increasing GO loading, while further increases in GO loading above 0.5 wt % lead to a slight increase in the modulus over the whole range of temperature. Because the GO loading is 3 wt %, the storage modulus reaches the maximum value (ca. 0.54 GPa), which is 38% higher than that of neat PBS (ca. 0.39 GPa). This implies that GO could enhance the rigidity of the nanocomposites because of its high surface area and good miscibility in the PBS matrix. The glass-transition temperature (T_g) is widely determined by the $\tan \delta$ peak temperature in DMA. As shown in Figure 4c, there is a slight increase in T_g (ca. 12 °C) at 1 wt % GO compared to that of neat PBS, indicating that the movements of the PBS polymer chains are restricted to a certain degree because of the PBS polymer chains grafted to the GO nanosheets.

The mechanical properties of PG nanocomposites are presented in Figure 5. It is evident from the figure that there is an increase in tensile stress with the addition of GO content. This indicates an increase in the stiffness of the film due to the addition of GO. It is to be noted that the elongation at the break gradually decreases with the increase in GO content. The stress at the break also increases very dramatically from 37 to 53 MPa for a 3% (w/w) GO sample with a percent increase of 43%. Both the increase in tensile stress at the break and the decrease in tensile strain are exponential with respect to the GO concentration. This figure also suggests that with the content of GO increasing, the tensile stress increases slowly. Furthermore, the mechanical properties of the samples in different directions were tested, and no obvious difference was observed. This shows that the PG nanocomposites have isotropic mechanical properties, which is also confirmed by the scanning electron microscopy (SEM) images. (See Figure

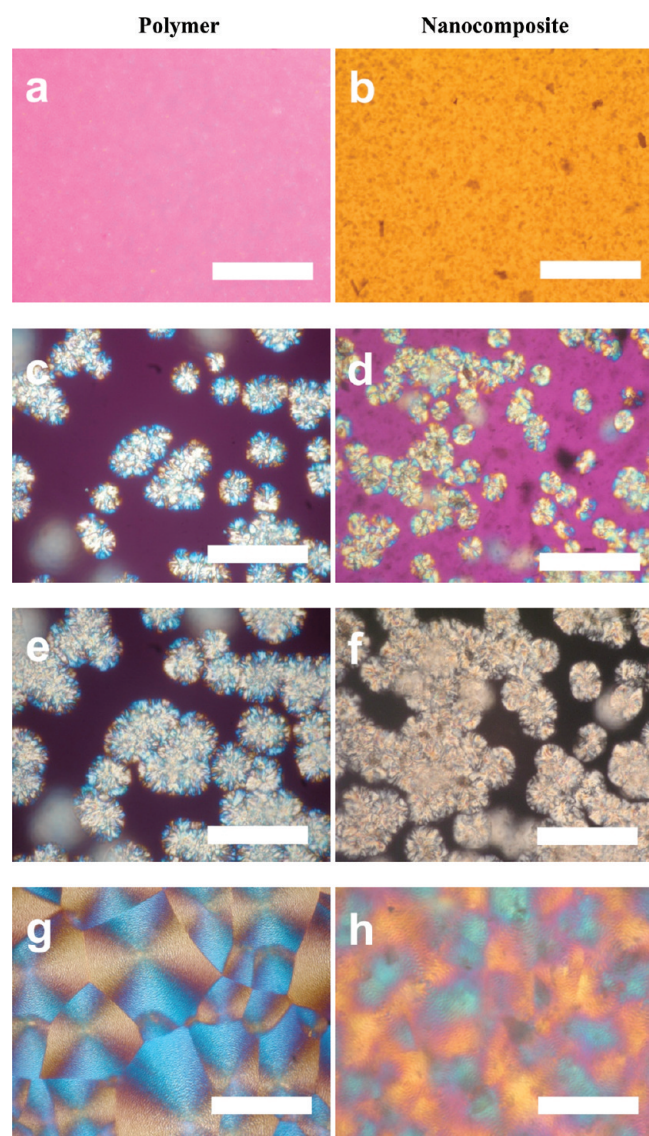


Figure 3. Polarized optical microscopy (POM) image of pure PBS (left column) and PG-1 (right column) at (a, b) 110, (c, d) 105, (e, f) 100, and (g, h) 95 °C during nonisothermal crystallization from the melts at a cooling rate of 10 °C/h. All scale bars are 100 μm .

S3, where the sample has nearly the same morphology in two vertical directions.)

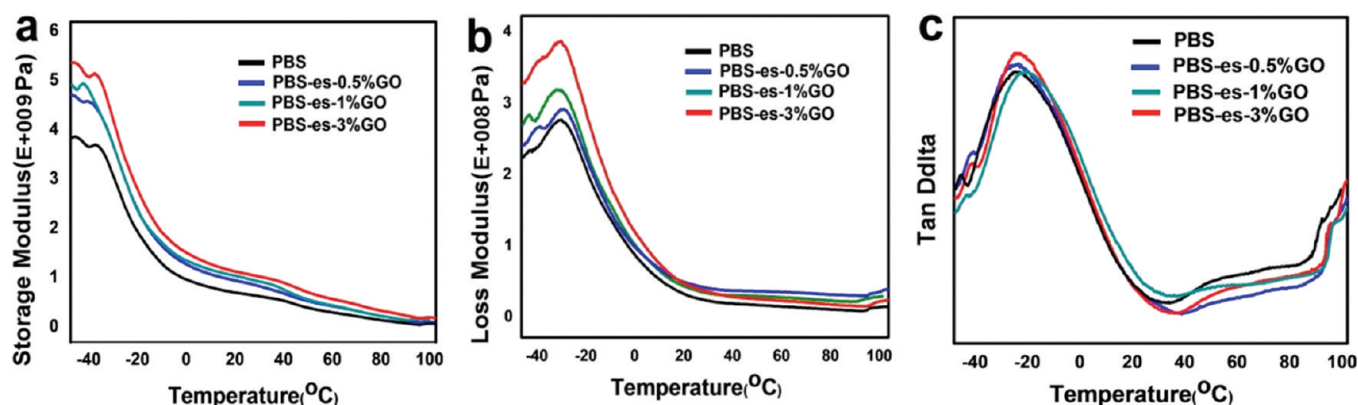


Figure 4. Mechanical property–temperature plots of different PG nanocomposites: (a) storage modulus, (b) loss modulus, and (c) $\tan \delta$.

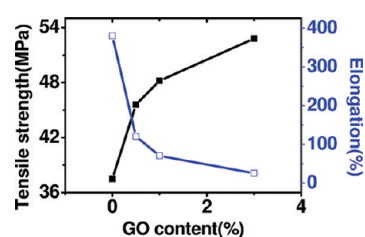


Figure 5. Mechanical properties of PG.

CONCLUSIONS

This letter demonstrates a simple, low-cost procedure for generating PG nanocomposites by in situ polymerization. Through the addition of GO nanosheets, the storage modulus and tensile stress of PG-3.0 are 45% and 43% higher than those of pure PBS. The glass-transition temperature is also improved to a certain extent. These results can be ascribed mainly to the homogeneous dispersion and alignment of GO nanosheets in the PBS matrix and the strong interactions between both composites. This demonstrates that GO nanosheets can be utilized effectively within the polymer matrix. Preliminary results show that PG nanocomposites have excellent performance and have the potential for large-scale application in many fields.

ASSOCIATED CONTENT

Supporting Information

Preparation of GO and testing of PG. Measurement of the molecular weight. ^1H NMR of PG-0.5, XRD patterns of PG, and scanning electron microscopy of PG-1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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