

Instant Modification of Graphite Nanosheets by the Grafting of a Styrene Oligomer Under Microwave Radiation

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ABSTRACT: Instant grafting polymerization of styrene initiated by microwave radiation on the surface of graphite nanosheets (GNs) was carried out. The stability of the modified GN dispersions in different solvents indicated significant changes in the surface properties of GNs. In comparison with GNs without modification, the modified GNs showed more stable suspensions in a nonpolar organic solvent such as toluene and were more likely to

form a precipitate when dispersed in distilled water, a polar solvent. Fourier transform infrared and thermogravimetric analysis were used to confirm the functionalized GNs. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1377–1380, 2008

Key words: composites; conducting polymers; fillers; graft copolymers; nanocomposites

INTRODUCTION

Graphite nanosheets (GNs) have a large aspect ratio (diameter to thickness), which confers an advantage in forming a conducting network in a polymer matrix, leading to a much lower percolation threshold.^{1–4} Conventional methods for making polymer/GN composites include blending polymers with graphite particles and intercalating polymers into interlayers of graphite.^{5–8} Because of the incompatibility and weak interaction between GNs and polymers, polymer/GN composites with excellent physical properties cannot be achieved by those methods, although GN particles can be dispersed in a polymer matrix quite homogeneously under intensive blending.

To improve the compatibility between polymer matrices and GNs, various approaches have been developed. Among them, modifying GNs through the grafting of an organic oligomer onto the graphite surface is one of the most effective methods. Wang and Pan⁹ spent nearly 6 days to graft polystyrene (PSt) onto expanded graphite (EG), forming EG-*g*-PSt with cationic initiation. They also reported the grafting polymerization of ethylene oxide onto EG

particles.¹⁰ Tsubokawa et al.¹¹ reported that poly(methyl methacrylate) and PSt were grafted onto the surface of graphite particles by the anionic polymerization of methyl methacrylate and styrene (St), respectively, in the presence of graphite treated with *n*-butyllithium.

These grafting processes are time-consuming, and some are time-inefficient; however, chemistry under microwave radiation is known to be different. Microwave processing can modify the chemical activation parameters and chemical sites of polymer composites because of further polarization of the dipoles under microwave radiation.^{12–15} This has been applied to a variety of organic syntheses in which high yields and rapid reactions can be achieved under controlled temperatures and pressures.^{16,17} Moreover, a carrier such as graphite, which generates a high-temperature gradient because of strong coupling with microwaves, can considerably increase the reaction rate.^{18,19}

In this work, we report that a St oligomer was successfully and instantly grafted onto the surface of GNs with the help of microwave radiation. The GNs acted both as reagents and as microwave-absorbing support. The surface property of GNs could be modified instantly by the treatment.

EXPERIMENTAL

Materials

The GNs used here were prepared by ultrasonic techniques from natural graphite, as detailed in ref. 20. St (Shanghai First Chemical Reagent Plant, Shanghai,

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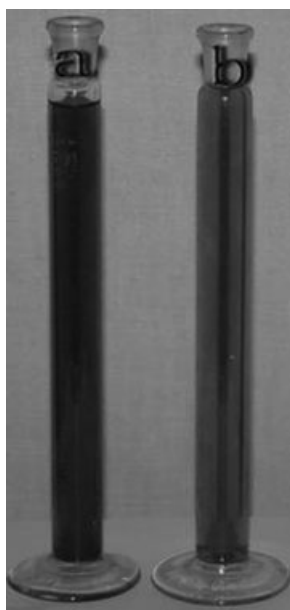


Figure 1 Photograph of GNs and modified GN dispersions in toluene after standing for 1 h: (a) GN-g-PSt and (b) pristine GNs.

China) was washed with an aqueous solution of sodium hydroxide, dried over anhydrous sodium sulfate, and then distilled under reduced pressure.

Grafting polymerization

St was added to the dried GNs drop by drop. The sample was put in an airtight ceramic beaker in a domestic microwave oven and subjected to a series of irradiations. Microwave power was supplied by a domestic microwave oven (NN-S3240WF, Panasonic, Shanghai, China), which was operated at 2.45 GHz with the power up to 700 W. Each 1-min exposure was followed by a 1-min pause in the irradiation for an overall exposure time of 6 min. Finally, the product was extracted with chloroform in a Soxhlet extractor for 8 h (the extraction was confirmed to be complete) before it was dried *in vacuo* at 50°C for 24 h.

Stability of the modified GN dispersion

The treated sample (GN-g-PSt; 0.0020 g) was added to toluene and distilled water (50 mL), and then these two mixtures were ultrasonicated in a water bath at 30°C for 5 min to obtain homogeneous dispersions; the dispersions were allowed to stand at room temperature. Profiles of the dispersions were captured by a digital camera.

Characterization and measurements

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Nexus FTIR spectrometer in

increments of 2 cm⁻¹. Thermal degradation of GN-g-PSt was investigated with a thermogravimetric analyzer (TA-5200, TA) from room temperature to 700°C with a heating rate of 10°C/min under flowing nitrogen.

RESULTS AND DISCUSSION

Stability of the modified GN dispersion

To clarify the properties of the modified GNs, the stabilities of the functionalized GN dispersions in various solvents were compared with the stability of untreated GNs. As expected, the treated GNs formed better and more stable dispersions in a nonpolar organic solvent such as toluene (Fig. 1). However, in a polar solvent, the original GNs in the distilled water evolved into a more stable colloidal dispersion (Fig. 2). The results indicated that the surface properties of the GNs had been changed during the modification processes. The St oligomer (nonpolar group) on the surface of the GNs lowered the surface tension of the treated GNs and improved the affinity of the GNs to the nonpolar organic solvents; this prevented the modified GNs from forming aggregates, leading to better and more stable dispersions of GNs in the organic solvents.^{11,21} The original GNs produced from EG, however, which were quite abundant in polar groups, such as carboxyl groups and hydroxyl groups,²⁰ appeared to disperse well in water, a polar medium.



Figure 2 Photograph of GNs and modified GN dispersions in distilled water after standing for 1 h: (a) GN-g-PSt and (b) pristine GNs.

It is obvious that modified GNs with improved properties hold promise not only in the field of coatings but also in the field of polymer composites.

Amount of PSt grafted onto the GNs

Thermogravimetric analysis (TGA) measurements were carried out for the purified treated samples to determine the amount of PSt grafted onto GNs. The weight loss for each sample was different. The somewhat typical result is shown in Figure 3. As demonstrated in Figure 3, the pristine GNs showed little weight loss before 432°C. However, a sharp weight loss occurred from ~ 380 to 432°C. In comparison with the pristine GNs, the weight loss of the functionalized GNs before 432°C was considered to be the thermal degradation of the organic part, which was due to the grafted PSt. Although the amount of PSt grafted onto GNs by microwave induction was 8 wt %, which was lower than that by conventional chemical processing (13.4 wt %),⁹ microwave-induced rapid graft functionalization is a simple and effective technique.

FTIR analysis of GN-g-PSt

FTIR is a powerful technique for the characterization of chemical components. Before FTIR measurements of GN-g-PSt powder were taken, the irradiated sample was extracted with chloroform until no PSt homopolymer remnant in the filtrate could be detected by FTIR. Figure 4(a) presents a typical FTIR spectrum of GN-g-PSt. For comparison, the FTIR spectrum of the original GNs is also shown in Figure 4(b). Although the absorption peak of GN-g-PSt seems weak, the characteristic absorption bands of PSt at 695 and 3021 cm⁻¹ can be clearly observed in Figure 4(a). It is certain, however, that the band at

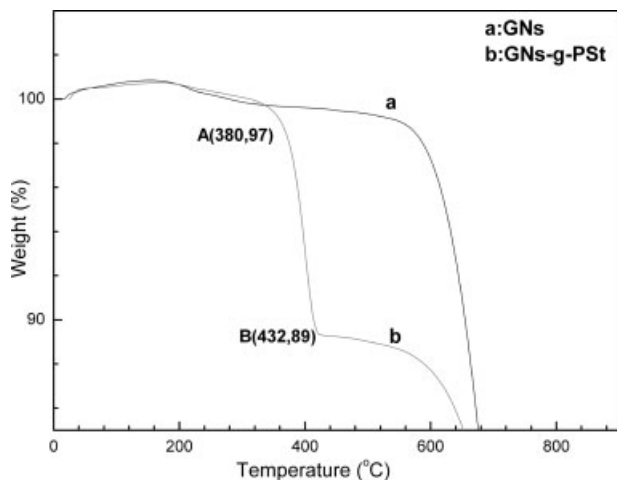


Figure 3 TGA curves of (a) pristine GNs and (b) GN-g-PSt.

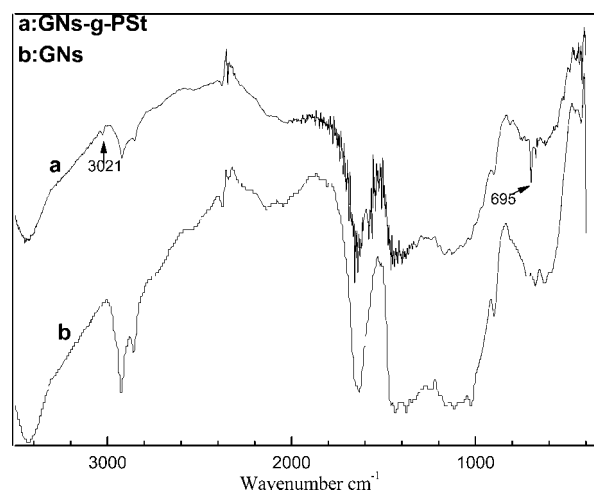


Figure 4 FTIR spectra of GNs and GN-g-PSt.

695 cm⁻¹ is subjected to the out-of-plane bending of C—H in the benzene ring, and the absorption at 3021 cm⁻¹ corresponds to aromatic C—H stretching. The PSt grafted onto GNs shows weak peaks possibly due to the high IR absorption of GNs and a lower grafting degree induced by microwave irradiation. For comparison, a blend sample of GNs with 8 wt % PSt was subjected to FTIR measurement, and no distinct PSt peaks were observed either. Thus, we still want to declare the effectiveness of the modification.

CONCLUSIONS

GNs could be modified instantly via the grafting of an St oligomer onto their surface induced by microwave radiation. The modified GNs showed much better dispersibility in a nonpolar solvent than unmodified ones, which had better dispersibility in a polar solvent such as water. The grafted PSt played an important role in the improvement of the GN surface properties. The grafting degree of the instant reaction can be up to 8 wt %. Further study should be focused on the mechanism of the grafting polymerization initiated by microwave radiation and the properties of modified GNs.

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