



# Electrical percolation and crystallization kinetics of semi-crystalline polystyrene composites filled with graphene nanosheets



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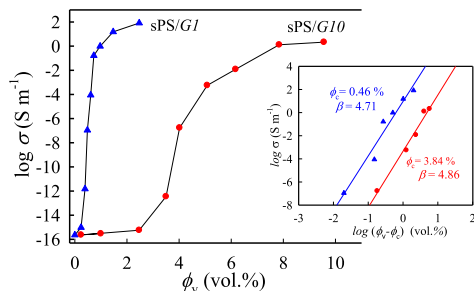
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## HIGHLIGHTS

- Composites of sPS/GNS and aPS/GNS have been compared.
- sPS/GNS composites have a higher percolation threshold for electrical conductivity.
- Composites containing GNS with a larger aspect ratio have a lower percolation threshold.
- To enhance sPS crystallization, 1D CNT is more effective than 2D GNS.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Syndiotactic polystyrene (sPS) is a semi-crystalline polymer with high melting temperature and good mechanical strength. Composites of sPS filled with different contents of graphene nanosheets (GNS) are prepared by coagulation method. Two types of GNS with different thicknesses (denoted as *G1* and *G10*) are studied to unveil the effect of aspect ratio on electrical conductivity and crystallization kinetics of the composite. Atomic force microscopy and transmission electron microscopy (TEM) show that *G1* is a wrinkled sheet with an average thickness of ~2 nm and that *G10* is a smooth flake with a thickness of ~50 nm; both possess a similar basal dimension of ~5 μm. The percolation thresholds for electrical conductivity ( $\phi_c$ ) of the *G1*-filled and *G10*-filled composites are 0.46 and 3.84 vol%, respectively. At a given GNS content, the electrical conductivity of the *G1*-filled composites is higher than that of the *G10*-filled composites. Both findings are attributed to the larger GNS aspect ratio of *G1* compared with *G10*. The deduced  $\phi_c$  of the *G1*-filled composites is significantly larger than that of GNS-filled amorphous atactic PS composites, indicating that the *crystallizability of the matrix* has an important influence on formation of GNS networks. Both *G1* and *G10* nanofillers are found to be good nucleating agents for the heterogeneous nucleation of sPS. Because of its wrinkled surface, *G1* is less effective than *G10* in inducing sPS crystallization. Compared with 2D sheet-like GNS, 1D CNTs are more effective in enhancing sPS crystallization through surface-induced nucleation as well as the chain-tube wrapping behavior in the sPS/CNT composites.

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## 1. Introduction

Syndiotactic polystyrene (sPS) is an engineering thermoplastic with an apparent melting temperature of ~270 °C and a

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rapid crystallization rate. By contrast, atactic polystyrene (aPS) is an amorphous thermoplastic with a service temperature lower than its glass transition of  $\sim 100$  °C. In composite applications, the thermal stability of sPS composites is much better than that of aPS composites. Depending on the crystallization conditions, sPS chains can crystallize into at least four crystalline modifications ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  forms) because of their polymorphic nature [1]. The mechanical strength of sPS samples is dependent on the crystalline modification and degree of crystallinity developed within the sample. Polymer composites containing nanoscaled fillers have elicited considerable attention in the field of nanotechnology. Among nanoscaled fillers, carbon nanotubes (CNTs) and their associated materials, such as fullerene and graphene nanosheets (GNS), are the most promising for advanced applications because of their exceptional thermal, mechanical, and electrical properties [2–7]. In general, CNT and graphene have large aspect ratios but different apparent geometries. CNTs are considered as 1D carbon nanoparticles, whereas GNSs are considered as 2D carbon nanoparticles. In composites, agglomeration of GNS is likely to occur because of the large area-to-volume ratio of the nanofiller. To characterize filler dispersion, a percolation scaling law is adopted to determine the minimum filler content (threshold), above which a significant enhancement of physical properties is expected [8,9]. For practical applications, electrical conductivity is the primary focus of property characterization in  $sp^2$ -carbon-filled polymer composites because only a small amount of CNT (or GNS) is sufficient to develop a conductive percolation path for enhanced electron transport within the insulating polymer matrix. These GNS-filled polymer composites show promising applications in electrostatic discharge and electromagnetic interference-shielding materials [4]. According to Stankovich et al. the lowest electrical conductivity threshold ( $\varphi_c$ ) of aPS/GNS composites is 0.1 vol% [4]. Despite extensive studies on the amorphous composite of aPS/GNS, the  $\varphi_c$  of semi-crystalline sPS/GNS composites has yet to be studied. We are interested to determine whether or not the crystallizability of the matrix (sPS and aPS) will affect the  $\varphi_c$  of GNS-reinforced composites. Our previous studies on CNT-filled composites of sPS and aPS [10,11] have disclosed that the overgrowing crystals at the CNT surface leads to higher  $\varphi_c$ . In this study, we aim to distinguish whether 2D GNS or 1D CNT is more effective in structuring the nanofiller network for electrical conductivity, and which has a lower  $\varphi_c$  for the sPS matrix.

The addition of GNS improves the electrical properties of polymers; however, it may also alter the crystalline modification, morphology, and crystallization kinetics of the polymers used. Crystallization and morphologies of GNS-filled polyethylene [12] and isotactic polypropylene [13] have been investigated. Results of these studies show that GNSs, like CNTs, act as effective nucleating agents and increase the overall crystallization rate significantly. Interestingly, 2D GNSs can accelerate the crystallite growth kinetics of poly(L-lactide) (PLLA), although their effect is less pronounced than that of 1D CNTs [14]. We have reported on the influence of CNT [11] and carbon nanocapsules (CNC) [15] on crystal morphology and crystallization kinetics of sPS; both nanofillers serve as good nucleating agents. To date, the crystallization kinetics of GNS-filled sPS composites has not been explored, and the mechanism underlying the nucleating ability of GNS remains unclear. In addition, whether or not 2D GNSs are a better nucleating agent for sPS chains than 1D CNTs for later crystal growth remains unknown. As part of our series of investigations on nanocarbon-reinforced sPS composites [10,11,15], the present study investigates in detail the effect of GNS with two different aspect ratios on crystal modification, crystallization kinetics, and melting behavior of the sPS matrix.

## 2. Experimental

### 2.1. Materials and composite preparation

The sPS pellets were obtained from Dow Chemical Co. The weight-average molecular weight and polydispersity were  $2.49 \times 10^5$  g/mol and 2.37, respectively. Two types of GNS with different thicknesses, coded by N002-PDR and N006-P, were purchased from Angstrom Materials, LLC. According to the manufacturer, both fillers have a density of  $2.20$  g/cm<sup>3</sup>; the former has an average thickness lower than 1 nm and was denoted as *G1*, whereas the latter has an average thickness of 10 nm–20 nm and was denoted by *G10*. Both *G1* and *G10* were used without any surface treatment. In producing well-dispersed GNS-filled sPS composites by solution blending, *ortho*-dichlorobenzene (*o*-DCB) is more appropriate than other solvents because of its higher solubility for sPS chains and the  $\pi$ – $\pi$  interactions between the graphene surface and the phenol group [16]. After sonication, GNSs in the sPS/*o*-DCB solution exhibited a uniform dispersion for days without visible precipitation or aggregation on the vial bottom. Thus, sPS/GNS composites with various compositions were prepared by dissolving the sPS pellets in *o*-DCB solvent at 140 °C and adding GNS to the homogeneous solution. This step was followed by sonication for 3 h. Subsequently, the uniform suspension with 1% (w/v) was precipitated dropwise into a 20-fold excess volume of methanol. Recovered powders were dried continuously in a vacuum oven until the residual solvent was removed. In this work, the code 99/1 represents the weight ratio of sPS to GNS, equivalent to a GNS weight fraction ( $\varphi_w$ ) of 0.01. The volume fraction of nanofillers ( $\varphi_v$ ) was calculated using the respective density of GNS and sPS ( $\sim 1.06$  g/cm<sup>3</sup>). Melt-quenched samples 20  $\mu$ m thick were obtained by holding the dried powders at 300 °C for 10 min in a hot stage (THMS600, Linkam), followed by quenching in liquid N<sub>2</sub>.

### 2.2. Composite characterization

Raman spectroscopy was used to probe the chemical difference between *G1* and *G10*. The Raman spectra of the as-received *G1* and *G10* nanofillers were obtained using DXR Raman Microscope (ThermoScientific). The surface and dimensions of the *G1* and *G10* particles were investigated through atomic force microscopy (AFM, MMAPM-2, Digital Instruments). Tapping mode imaging was conducted under ambient conditions. Suspensions of GNS were prepared in *o*-DCB at 0.5 mg/mL. After sonication at room temperature for 10 min or 3 h, the suspensions were deposited onto a mica substrate and a carbon-coated copper grid, respectively. The former was used for AFM study to measure the GNS dimensions, whereas the latter was used for the TEM observation to reveal the GNS morphology. The TEM micrographs shown in this work were obtained by using a Jeol JEM-2000FX electron microscope operated at 80 kV. To reveal the microstructure of GNS-filled sPS composites under TEM, ultrathin films (ca. 50 nm) were prepared by sectioning the samples at room temperature with an Ultracut UCT (Leica) microtome. The sPS lamellar morphology was observed by staining the ultrathin films to enhance the contrast between the amorphous and crystalline layers. Staining was carried out with ruthenium tetroxide (RuO<sub>4</sub>) vapor at room temperature. WAXD intensity profiles were obtained using a Bruker diffractometer (NanoSTAR Universal System, Cu K $\alpha$  radiation). The crystallization and melting behavior of sPS/GNS composites were investigated using a PerkinElmer DSC7 under N<sub>2</sub> atmosphere. The melt-quenched samples were heated to 300 °C at 10 °C/min for nonisothermal crystallization to reveal the cold-crystallization kinetics (first heating scan). After holding at 300 °C for 10 min, the samples were cooled to room temperature at a rate of 10 °C/min to disclose the melt-

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