



# Crystallization and melting behavior of poly (ethylene succinate) in presence of graphene nanoplatelets



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## ABSTRACT

In this study, poly (ethylene succinate)/graphene nanoplatelets composites were prepared via solution casting method in different compositions and analyzed via differential scanning calorimetry. Crystallization and melting characteristics in both dynamic (non-isothermal) and isothermal modes were investigated at various cooling rates and isothermal temperatures. It was confirmed that graphene, while being incompatible with the matrix polymer, could act as nucleating agent so that hot (melt) crystallization rates, intensities, and positions were increased in the dynamic mode. However, the overall crystallinity remained almost unchanged. Cold crystallization was also decreased to lower temperatures on graphene addition; however its enthalpy was also reduced. Similar findings were observed for the isothermal mode, but to a lesser extent. The presence of graphene changed the perfection of crystals as their thermodynamic stability against heating and recrystallization behavior varied.

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## 1. Introduction

Graphene has very recently drawn vast interest in both fundamental and applied fields on account of extraordinary physical, chemical, and mechanical properties. It is a new class of several-atom-thick layer of sp<sup>2</sup>-hybridized carbon atoms arranged in a two-dimensional nanostructured lattice and is considered to be the thinnest and the strongest material to date. The discovery of graphene with its combination of outstanding properties has created a new class of polymer nanocomposites and expanded the application window of homopolymers [1–4].

Biodegradable polymers based on aliphatic polyesters have attracted a great deal of attention since the commercial non-degradable plastics usually pose critical environmental problems [5–7]. Poly (ethylene succinate) (PES) is an aliphatic polyester of biodegradable feature which exhibits excellent processability; however, as a potential candidate for industrial applications, PES suffers from insufficient thermal and mechanical properties [8–10].

Graphene seems to be an attractive choice to be incorporated into the PES matrix via blending in purpose of properties improvement by virtue of its outstanding reinforcing performance. This lies behind the motivation of blending graphene with thermoplastic polymers. Since the final performance of the nanofilled polymer hinges on its crystallization evolution during processing, the effect of the nanofiller on the polymer crystallization behavior must be well drawn into focus [11,12]. Graphene has been reported to impose different effects on the crystallization degree depending on the identity of the polymer [13–18]. It can increase [13–16], decrease [17], or make no change [18]. As an instance, Wang et al. [19] reported that graphene had no remarkable influence on the crystallinity of poly (butylene succinate), a homologue of PES. They ascribed the improvement of the nanocomposite performance to the uniform dispersion of the nanoscale filler in the matrix combined with strong interfacial interactions. Zhao et al. [20] studied the crystallization and melting behavior of PES/graphene oxide nanocomposite in low amounts and reported no melt crystallization due to the slow crystallization rate of the polymer. They only observed multiple cold crystallization exotherms which not only decreased in magnitude, but also shifted to lower temperatures on adding graphene ascribed to the nucleating role of the graphene entities. However, beyond 0.2 wt% graphene, the nucleation effectiveness of the nanofiller became limited. A high

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amount of graphene confined the mobility of polymer chains which led to the formation of imperfect crystals of depressed melting points compared with pure polymer. Elsewhere, Papageorgiou et al. [21] prepared PES/graphene oxide nanocomposites of relatively much higher nanofiller content (2.5 wt%) using solution casting and examined the thermal and morphological properties. They reported no change in crystal morphology of PES after incorporation of the nanofiller, while faster crystallization rate was realized due to the nucleating activity of the nanofiller on account of reduced activation energy. Also, cold crystallization peak was shifted to lower temperatures after adding graphene and the overall crystallization degree decreased. The polymer/filler interactions as well as great specific surface area provided by the filler were believed to be the key parameter in controlling the crystallization kinetics. They also compared the activity of carbon nanotubes with graphene and reported that carbon nanotubes influenced the crystallization and melting behavior much more than graphene did [21].

In this effort, as an extension to our previous report [22] published on the effect of unmodified carbon nanotube on the crystallization and melting behavior of PES, we aim to contribute to the discussions surrounding the influence of neat graphene nanoplatelets (GnP) in very low amounts on crystallization and melting behavior of PES as the crystallizable matrix under both isothermal and dynamic regimes. PES/GnP nanocomposites are prepared based on solution casting method and analyzed via differential scanning calorimetry (DSC). What makes this contribution distinguished from previously published, similar ones is that the former papers used graphene oxide rather than neat graphene to examine the properties to attain a better dispersion, while we intend to explore the effect of pure GnP.

## 2. Experimental

### 2.1. Materials

PES with an average molecular weight of 10 kDa as well as chloroform of 99.0% purity was supplied from Sigma-Aldrich (USA). GnP Grade M with an average thickness of around 7 nm and particle diameter of approximately 15  $\mu\text{m}$  having less than 1.0 wt% oxygen content was obtained from XG Sciences (USA). The materials were used as received without any pretreatment.

### 2.2. Samples preparation and characterization

Polymer granules and nanofiller particles were thoroughly dried beforehand in an oven for 3 h at 40 °C. Certain amount of PES was weighed and solved in chloroform under stirring at room temperature until homogenous solution was obtained. Then, defined weights of GnP was dispersed well in chloroform under stirring at room temperature so that a fine dispersion was obtained. PES solution was then added slowly to GnP dispersion in an ultrasonic stirrer at 40 °C followed by magnetic mixing at 70 °C for an hour to render a fine dispersion assisted by gradual evaporation of the solvent. The dispersion was then transferred into petri dishes, held in room temperature overnight for complete drying. The samples have been designated by special codes of PES/GnP-0.0 (pure polymer), PES/GnP-0.1, PES/GnP-0.2, and PES/GnP-0.5 where the numbers refer to the weight percentage of the nanofiller incorporated.

Crystallization and melting behavior was studied using DSC Q1000 (TA Instruments) in nitrogen atmosphere. Non-isothermal crystallization and melting behaviors were recorded as follows. First, the sample of approximately 5 mg weight was equilibrated at  $-80\text{ }^{\circ}\text{C}$  for 5 min followed by heating at  $10\text{ }^{\circ}\text{C}/\text{min}$  up to  $140\text{ }^{\circ}\text{C}$  held for 5 min to produce a uniform thermal history. The sample

was then cooled down to  $-80\text{ }^{\circ}\text{C}$  at different rates of 2, 5, 10, and  $20\text{ }^{\circ}\text{C}/\text{min}$  to study crystallization behavior. After keeping the sample at  $-80\text{ }^{\circ}\text{C}$  for 5 min the sample was reheated back to  $140\text{ }^{\circ}\text{C}$  through the same ramp to record cold crystallization and melting behavior. Crystallization in isothermal mode was performed as follows. First, the sample was equilibrated at  $-80\text{ }^{\circ}\text{C}$  for 5 min followed by heating at  $10\text{ }^{\circ}\text{C}/\text{min}$  up to  $140\text{ }^{\circ}\text{C}$  held for 5 min. Rapid cooling at  $40\text{ }^{\circ}\text{C}/\text{min}$  was done down to temperatures of 20, 30, 40, 50, and  $60\text{ }^{\circ}\text{C}$ , where the sample was kept for 120 min denoted as  $t_{\text{iso}}$  in the text). Cooling was then continued down to  $-80\text{ }^{\circ}\text{C}$  at  $10\text{ }^{\circ}\text{C}/\text{min}$  and held there for 5 min. The subsequent heating run was carried out back to  $140\text{ }^{\circ}\text{C}$  at  $10\text{ }^{\circ}\text{C}/\text{min}$  to record the melting behavior. Crystallinity was calculated using the value of fully crystalline PES which is equal to 180 J/g [23].

## 3. Results and discussion

### 3.1. Non-isothermal mode

Fig. 1a–d illustrates the DSC cooling scans carried out at various cooling rates on the neat polymer as well as nanocomposite samples. The crystallization peak shifts down to lower temperatures with increasing cooling rate. All figures have identical scale to allow for comparison of the behavior as a function of filler content. The highest extent of overall crystallization is found for PES/GnP-0.1. A further increase in content leads to lower crystallinity, which is produced during cooling.

As for the subsequent heating run of the non-isothermally crystallized sample, a multiple crystallization and melting behavior is observed and shown in Fig. 2a–d with comparable scale. Two exothermic crystallization peaks (except for the sample crystallized at  $2\text{ }^{\circ}\text{C}/\text{min}$  which only shows one) are observed. The intensity of the first crystallization peaks generally increases on speeding up the cooling rate at which the samples have been crystallized. The observations are in agreement with the literature except with Zhao et al. [20] who did not report crystallization on cooling. It is surmised that since they used PES of much higher molecular weight than the commercial, low molecular weight PES we used, the crystallization rate was reduced so that no crystallization during cooling took place.

The occurrence of two crystallization peaks during subsequent heating is a special phenomenon of the non-isothermal procedure and is dependent on cooling rate as well as filler content. The higher the cooling rate, the larger the first peak is that can be termed as cold crystallization. The second crystallization peak during heating should be a post-crystallization and/or reorganization event because it takes place independent of the previous cooling rate.

The data of non-isothermal crystallization and of melting are summarized in Table 1. Since the main objective of this effort is to highlight the influence of GnP on thermal characteristics, a discussion on this subject should also be presented. Based on Table 1, the presence of GnP influences the crystallization parameters significantly. It is generally observed that the crystallization peak shifts to lower temperatures with increasing cooling rate. The addition of low GnP content (0.1 wt%) leads to a maximum of cold crystallization peak at all cooling rates and the highest crystallinity at  $2\text{ }^{\circ}\text{C}/\text{min}$ . This is translated to the contributing impact of nanofiller on crystallization onset of the polymer meaning shorter induction time due to lower nucleation barrier energy [24]. Interestingly, on adding the nanofiller, the crystallinity is slightly decreased for all GnP-containing samples suggesting that the existence of GnP confines the chain mobility and makes the PES crystal smaller and less perfect. This is in harmony with the finding reported earlier [20,21]. The effect is more pronounced for GnP rather than graphene oxide being highly disposed to form aggregates which normally possess

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