

NON-ISOTHERMAL CRYSTALLIZATION OF ETHYLENE-VINYL ACETATE COPOLYMER CONTAINING A HIGH WEIGHT FRACTION OF GRAPHENE NANOSHEETS AND CARBON NANOTUBES*

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Abstract The effect of the different geometrical dimensionality of two dimensional graphene nanosheets (2D GNSs) and one dimensional carbon nanotubes (1D CNTs) on the non-isothermal crystallization of an ethylene-vinyl acetate (EVA) copolymer at high loading (5 wt%) was studied. Transmission electron microscopy indicated a homogeneous dispersion of GNSs and CNTs in EVA obtained by a solution dispersion process. Fourier-transform infrared spectroscopy and differential scanning calorimetry measurements showed that 1D CNTs and 2D GNSs acted as effective nucleating agents, with a noticeably increased onset crystallization temperature of EVA. A high weight fraction of nano-fillers slowed the overall crystallization rate of composites. At the same crystallization temperature, the crystallization behavior of GNS/EVA composites was slowed compared to that of the CNT/EVA ones owing to larger nucleus barrier and activation energy of diffusion. Dynamic mechanical relaxation and rheology behavior of CNT/EVA and GNS/EVA composites demonstrated that the planar structure of the GNSs had an intensively negative effect on EVA chain mobility due to interactions between nano-fillers and polymer chains, as well as spatial restriction.

Keywords: Non-isothermal crystallization; Ethylene-vinyl acetate; Graphene nanosheet; Carbon nanotube.

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INTRODUCTION

Carbon nanotubes (CNTs) and graphene nanosheets (GNSs), owing to their intriguing mechanical and physical properties, have attracted enormous attention as excellent candidates for the fabrication of CNT- and GNS-based polymer composites with outstanding performances^[1–6]. Because of the quasi-one-dimensional structure, large aspect ratio and enormous surface energy of CNTs, it has been extensively accepted that CNTs could act as effective nucleating agents for the crystallization of various polymers^[7–13]. For instance, the onset crystallization temperature of isotactic polypropylene containing a relatively low CNT loading of 0.1 wt% was increased from 122°C for neat polypropylene to 131°C^[11]. GNS, as a latest carbon-based nano-filler, consists of two-

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dimensional (2D) graphite layers of one or several atoms thick, which possesses remarkable mechanical and electrical properties, a high lateral thickness ratio and a low cost compared with one-dimension (1D) CNTs^[4, 6]. In recent years, it has been reported that GNSs can induce polymer crystallization as nucleating agents^[14, 15]. Xu *et al.* studied GNS-induced isotactic polypropylene crystallization under shear flow. They found that the half crystallization time ($t_{1/2}$) of composites containing 0.05 wt% GNSs was reduced to at least 50% of that of the neat isotactic polypropylene^[15]. Although GNSs and CNTs have similar surface morphology and sp^2 carbon basic units, a significant topological difference exists between these two types of nano-fillers, *i.e.* nano-line-like CNTs are regarded as curled graphite layers with two half-fullerenes capping either end of the tube, while nanoplate-like GNSs are made of one or several carbon atom layers. This difference may result in a discrepancy in the crystallization behavior of semi-crystalline polymers induced by GNSs and CNTs.

For the purpose of highlighting the prominent nucleating effect of CNTs and GNSs, in our most previous work, the nanoparticle concentration used was selected to be as low as possible, basically below 2 wt%. However, it has been well known that a relatively high filler loading and good dispersion are necessary to achieve composites with superior mechanical properties^[16, 17]. Different from low nano-filler concentration systems, the high loading of nano-fillers not only offers a larger amount of heterogeneous nucleating sites, but also means marked restrains for chain mobility during nucleation and crystal growth, and consequently results in a higher nuclei barrier and activation energy of diffusion, especially when the loading is high enough to construct a crowded network. Thereby, the results obtained from polymer composites at a low nano-filler loading may not represent the results obtained for the same polymer composites at a high nano-filler loading, especially for the polyamide system^[7, 18]. Meanwhile, the distinct difference in geometrical morphology of 1D CNTs and 2D GNSs could also lead to the variation of crystallization behavior in such high nano-filler loading composites.

In our previous work, we studied a semi-crystalline thermoplastic ethylene-vinyl acetate (EVA) copolymer, which is widely used for various applications because of its promising properties, such as in packaging films, adhesives/paper coatings, wire and cable insulation, barrier sheets, *etc*^[19], to reveal its non-isothermal crystallization behavior induced by a high content (*ca.* 10 wt%) of CNTs through differential scanning calorimetry (DSC)^[8]. Although the CNT/EVA composites possessed a higher onset and peak crystallization temperature, the incorporation of CNTs reduced the overall crystallization rate of the EVA matrix, indicating that a high loading of CNTs played two inconsistent roles in EVA crystallization: first as heterogeneous nucleating agents to facilitate crystallization, and simultaneously as physical obstacles to retard crystallization. Based on our pre-existing research, we identified the following questions:

How do EVA chains undergo nucleation in the presence of GNSs?

How do GNSs affect EVA crystallization at the stage of crystal growth compared with CNTs at a high loading?

How does the topological structure of the nanoparticles impact on the diffusion of EVA chains and retarding EVA nucleation or crystal growth?

To explore the answers, a comparative study on non-isothermal crystallization of CNT/EVA and GNS/EVA composites was performed by FTIR, DSC, dynamic mechanical analysis (DMA) and stress controlled rheometry. It was found that the 2D GNSs, compared with 1D CNTs, exhibited a notable negative effect on the mobility of the EVA molecular chains, leading to less heterogeneous nucleation activity and retarded crystal growth in EVA.

EXPERIMENTAL

Materials and Sample Preparation

The commercially available EVA with 18 wt% of vinyl acetate used in this study was purchased from Beijing Dongfang Petroleum Chemical Co., Beijing, China. The preparation of GNSs can be obtained in supporting information. CNTs were purchased from Chengdu Organic Chemicals Co. Ltd. and the Chinese Academy of Sciences R&D Center for Carbon Nanotubes. The properties of fillers and sample preparations were reported in

supporting information.

X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy Studies

XPS measurements were performed with an XSAM800 (Kratos Company, UK) using $AlK\alpha$ radiation ($h\nu = 1486.6$ eV); an XPSpeak41 software was used to perform curve fittings to calculate the atomic concentrations. FTIR measurements were performed with a Nicolet-iS10 spectrometer. The nano-filler powders were ground with KBr and then pressed to prepare KBr disks for FTIR measurements.

Transmission Electronic Microscopy (TEM) Observations

The morphologies of as-prepared CNTs (GNSs) and CNT (or GNS)/EVA composites were characterized by TEM with an acceleration voltage of 200 kV (FEI Tecnai F20). Sample films were prepared with a thickness of 80 nm using a Leica EMUC6/FC6 microtome.

Differential Scanning Calorimetry Studies

The non-isothermal crystallization behaviors of CNT (or GNS)/EVA composites were determined on a TA DSC Q20 differential scanning calorimeter according to the following standard procedure: the samples (*ca.* 3–5 mg) were first annealed at 150°C for 8 min to erase any thermal history and then cooled to 0°C at predetermined cooling rates (2, 5 and 10 K/min) for the non-isothermal crystallization studies under a nitrogen atmosphere.

Time-resolved Fourier-Transform Infrared Spectroscopy

In situ IR spectra were collected over the wave-number range 400–4000 cm^{-1} using a Nicolet 6700 FTIR spectrometer equipped with a DTGS detector in transmission mode. A Nicolet TH32 hot stage controlled to within 0.1°C was employed. Two ZnSe plates were used as IR windows to enclose membranes of the EVA composites. The samples were kept at 160°C for 5 min to erase any thermal history and then cooled to 20°C under a 2 K/min cooling rate. During the cooling process, the data collection process was started and was continued until the temperature reached 20°C. According to the same standard, the baseline of each spectrum was linearly corrected, and the intensities of the characteristic bands were used to follow the crystalline band changes and crystallization kinetics for both EVA composites and neat EVA samples. Moreover, because of the limitation of the apparatus and the time required to collect FTIR data, the cooling rate for the non-isothermal crystallization by time-resolved FTIR must be kept low. Here, we chose a cooling rate of 2 K/min. Sample films were prepared with a thickness of 10 μm using hot compaction.

Dynamical Mechanical Analysis

DMA analyses were carried out with a Q800 DMA instrument (TA Instruments, USA) at a heating rate of 5 K/min. The testing temperature range was from –100°C to 80°C.

Dynamical Rheology Tests

The viscoelastic properties of the CNT/EVA and GNS/EVA composites were studied with a stress controlled dynamic rheometer AR2000ex (TA, USA), using a parallel plate geometry. The dynamic rheological tests of these samples were then conducted at 160°C. The strain and oscillation frequency range used were 1.0% and 0.01–70 Hz, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the different geometrical morphologies of the CNTs and GNSs used in the current work. CNTs are curved and coiled, which suppress the surface energy (Fig. 1a). The aspect ratio of CNTs is more than 400, as estimated by dividing their length (10–20 μm) by the o.d. (30–50 nm), which allows the CNTs to be considered as one-dimensional nano-lines with large surface curvature. A TEM image of the GNSs used reveals a layered graphite structure with a large radius/thickness ratio (Fig. 1b). The CNTs were observed to entangle with each other, while the GNSs showed their large lateral dimensions on the micron scale with a typical wrinkled structure^[4, 20]. Additionally, the specific surface area of GNSs is larger than that of CNTs, since the carbon thickness of CNTs is 12–15 nm and the thickness of GNSs is *ca.* 1–2 nm (see Supporting Information). From the FTIR spectra shown in Fig. 1(c), it was found that epoxide groups (*ca.* 1105 cm^{-1}) and hydroxyl

groups (*ca.* 3430 cm^{-1}) exist in both CNTs and GNSs, indicating that these two typical nano-fillers possess a similar surface structure. Furthermore, the quantified XPS results show that the O/C atom ratios of the CNTs and GNSs are *ca.* 0.012 and *ca.* 0.065, respectively. The total amount of oxide groups present in the nano-fillers is extremely low compared with the amount of carbon groups, which allows us to consider that the influence of the surface groups is not of critical importance, compared to the different structural dimensionality of these nano-particles. Therefore, the comparative study of 1D CNTs and 2D GNSs that induced non-isothermal crystallization of EVA can reveal the effect of the structural dimensionality of carbon-based nano-fillers on EVA crystallization.

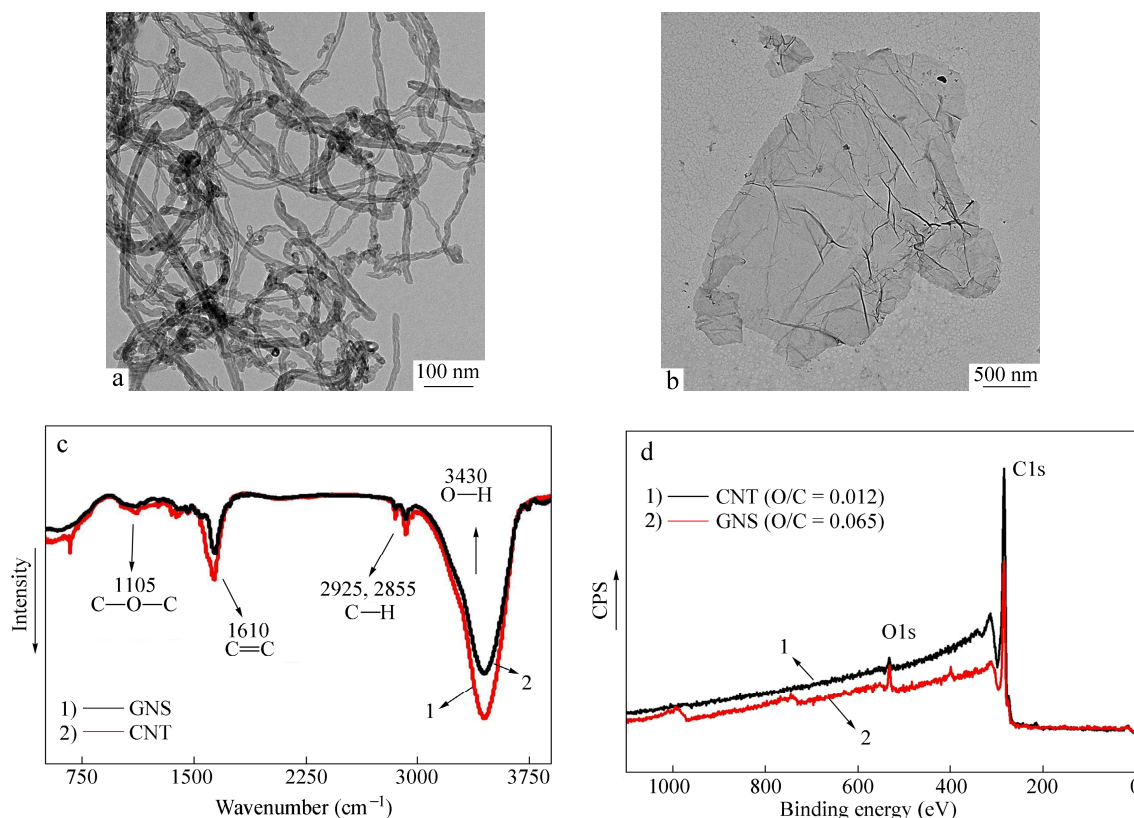


Fig. 1 TEM images of as-purchased CNTs (a) and as-prepared GNSs (b), FTIR spectra (c) and XPS curves (d) of CNTs and GNSs

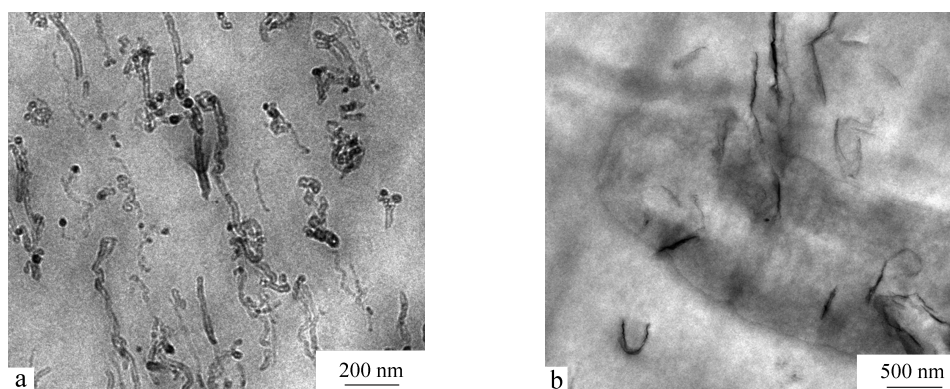
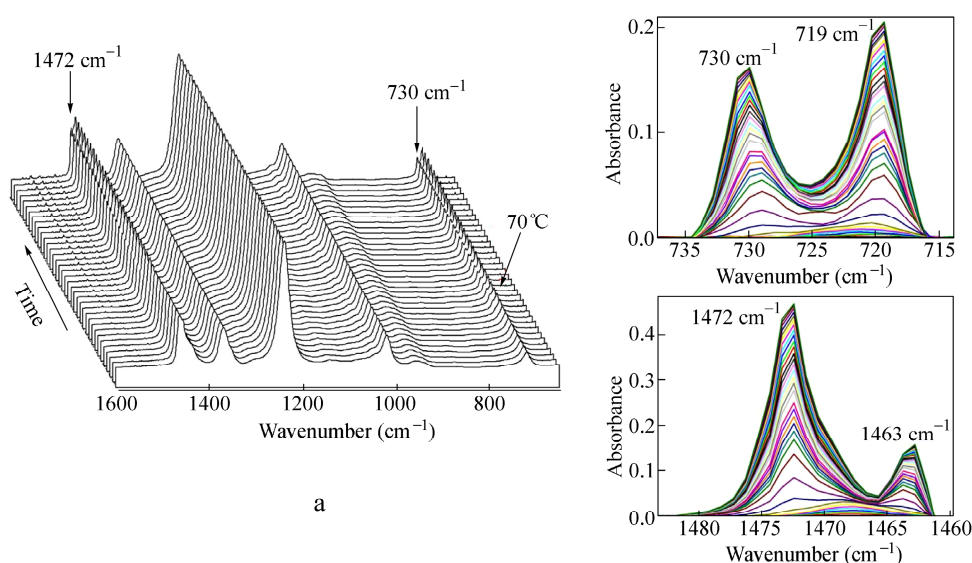


Fig. 2 TEM images of EVA composites containing 5 wt% CNTs (a) and GNSs (b)

Figure 2 shows the TEM images of CNT/EVA and GNS/EVA composites. For the CNT/EVA composite (Fig. 2a), one can clearly see that the CNTs were homogeneously dispersed in the EVA copolymer at such a high loading without any agglomerates and any obvious entanglement. Analogous to the CNT/EVA composites, most of the GNSs (disordered dark lines) with a layer thickness of 5–10 nm are homogeneously dispersed in the EVA matrix (Fig. 2b), which proves that the GNSs were well exfoliated and dispersed in the EVA matrix. Additionally, both the CNTs and GNSs form an integrated network and the gaps formed between the carbon nano-fillers are less than 50 nm for the CNTs and around 100–200 nm for the GNSs. As shown in Fig. 2, the GNSs occupy a relatively sealed space in the network compared with that of the CNTs. As the EVA crystalline lamellae have a thickness of *ca.* 10 nm to 20 nm, the process of nucleation and growth that controls the EVA crystallization kinetics may be profoundly affected by the presence of CNTs and GNSs within the copolymer matrix.

FTIR measurements were utilized to characterize the specific group vibrations related to the crystallization and molecular chain conformation of polymers. Through probing the intensity and shape changes of peaks online by *in situ* FTIR, one can obtain detailed information on the conformational ordering and crystallization behavior of semi-crystalline polymers, making it a powerful method for investigating the crystallization process, in particular at the molecular level and in the early stages^[21–25]. Here, the non-isothermal crystallization of neat EVA and its CNT and GNS composites was detected by *in situ* FTIR from 160°C to 20°C at a cooling rate of 2 K/min, as shown in Fig. 3.

It can be found that the band at 1463 cm⁻¹ for all samples studied splits into two bands at 1472 and 1463 cm⁻¹. Similarly, the band at 719 cm⁻¹ splits into two bands at 730 and 719 cm⁻¹ during the non-isothermal crystallization process. The bands at 1472 and 730 cm⁻¹ are considered to be the infrared crystalline bands, and specifically, related to the orthorhombic modification of ethylene chains^[26], which can also be confirmed from their difference spectra in Fig. 3 due to their intensities over the standard zero line. The infrared crystalline bands (1472 and 730 cm⁻¹) of the CNT/EVA and GNS/EVA composites appear some 6 K and 4 K earlier than that of neat EVA, respectively. This result demonstrates that CNTs and GNSs can act as effective nucleating agents for EVA crystallization. Although polyethylene chains are present in EVA, the conformational bands at 1340, 1308, and 1352 cm⁻¹, corresponding to the conformers of –t_mg, –gtg– (–gtg'–) and –gg–, respectively, are not apparent^[26]. This may be ascribed to the introduction of vinyl acetate chains disordering the conformational order of the ethylene chains.



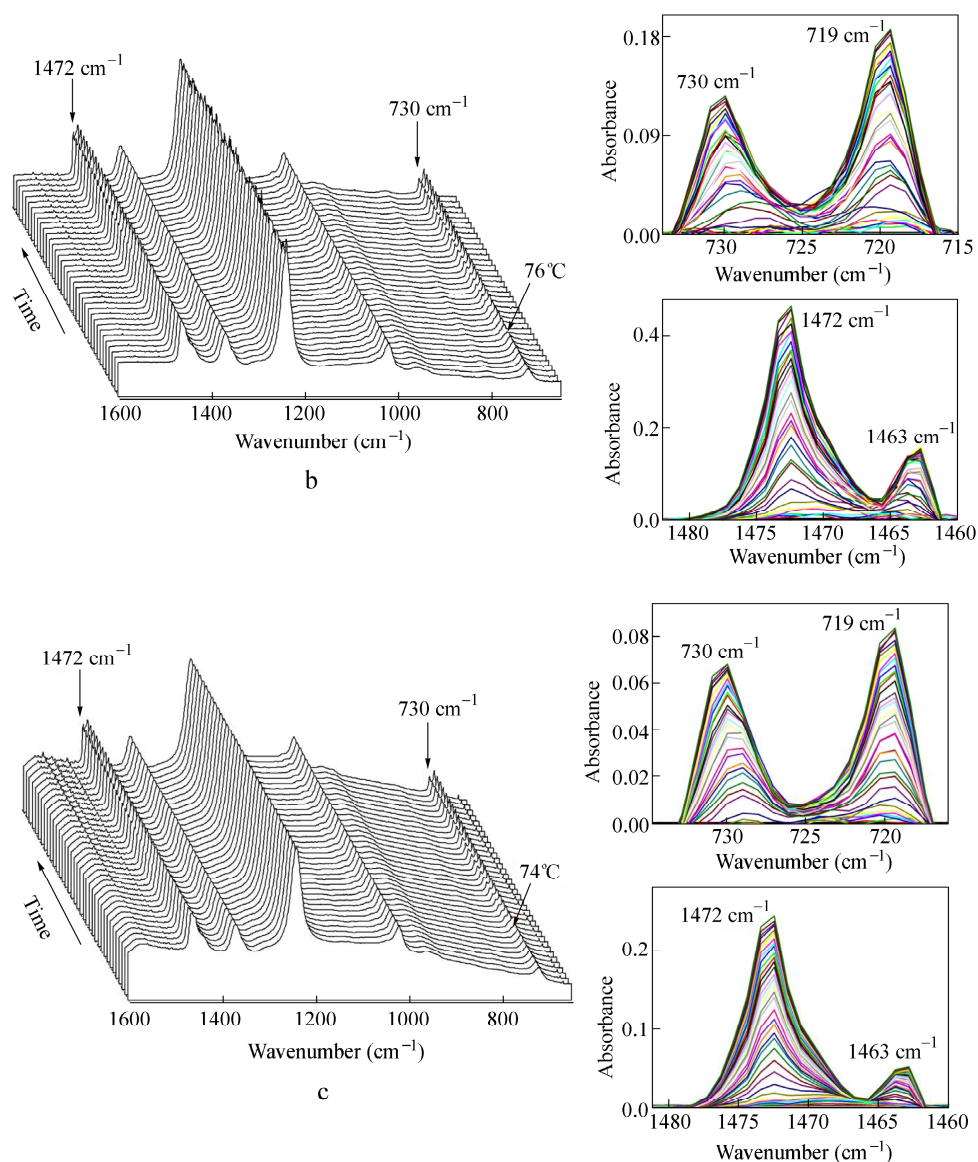


Fig. 3 Time-resolved spectra and difference spectra in the range 1600–650 cm^{-1} obtained for neat EVA (a), 5 wt% CNT/EVA (b) and 5 wt% GNS/EVA (c) non-isothermally crystallized from 160°C to 20°C at a cooling rate of 2 K/min

Since the high CNT and GNS loading can sharply decrease the absorbance intensity in the FTIR spectra, the sensitivity of the crystalline bands at 730 and 1472 cm^{-1} cannot be inevitably influenced, especially for the 730 cm^{-1} band. Therefore, in the following we discuss the intensity changes of the stronger crystalline bands at 1472 cm^{-1} originating from the intermolecular forces of the orthorhombic form of the ethylene chains of EVA^[26]. The normalized intensity of the crystalline band of 1472 cm^{-1} as a function of temperature is illustrated in Fig. 4. It is clearly found that the normalized intensity of the 1472 cm^{-1} band for both the CNT/EVA and GNS/EVA composites starts increasing at a higher temperature than that of neat EVA. Furthermore, at the same crystallization temperature, the 1472 cm^{-1} band associated with the CNT/EVA and GNS/EVA composites possesses a stronger normalized intensity. However, when the normalized intensity rises beyond 0.3, the curves of the neat EVA and its CNT and GNS composites almost overlap, indicating that the growth of EVA crystals is possibly retarded by the CNT and GNS networks.

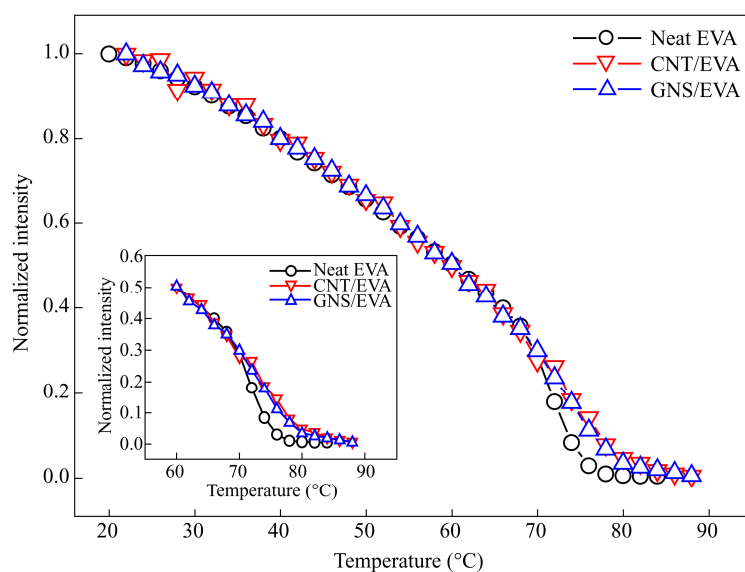


Fig. 4 Normalized peak intensities at 1472 cm^{-1} as a function of the non-isothermal crystallization temperature for neat EVA, 5 wt% CNT/EVA and 5 wt% GNS/EVA composites

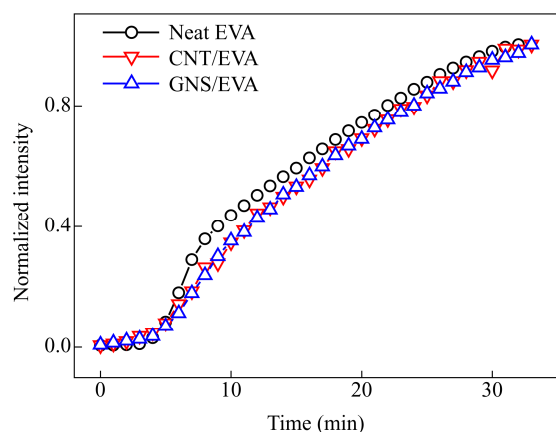


Fig. 5 Normalized peak intensities at 1472 cm^{-1} as a function of the non-isothermal crystallization time for neat EVA, 5 wt% CNT/EVA, and 5 wt% GNS/EVA composites
The onset crystallization temperature (Table 1) corresponding times were chosen as the onset times.

Table 1. Onset crystallization temperature (T_c^0) and half crystallization time ($t_{1/2}$) of the non-isothermal crystallization of neat EVA, CNT/EVA and GNS/EVA composites (5:95 by weight) measured by *in situ* FTIR

Sample	T_c^0 ($^{\circ}\text{C}$) of 730 cm^{-1}	T_c^0 ($^{\circ}\text{C}$) of 1472 cm^{-1}	$t_{1/2}$ (s) of 730 cm^{-1}	$t_{1/2}$ (s) of 1472 cm^{-1}
Neat EVA	70	78	306	714
CNT/EVA	76	86	312	846
GNS/EVA	74	86	342	894

To further clarify the effect of CNTs and GNSs on the crystal growth of EVA, we transformed the abscissa of temperature (T) to time (t) to show the normalized intensity development in Fig. 5. The normalized intensity of neat EVA is always stronger than those of its composites, and the normalized intensity of the CNT/EVA and GNS/EVA composites exhibits a similar evolution. Furthermore, from Table 1, it can clearly be observed that the $t_{1/2}$ value of the CNT/EVA composite (846 s) is unexpectedly larger than that of neat EVA (714 s), while the

$t_{1/2}$ value of the GNS/EVA composite (894 s) is larger than that of the CNT/EVA composite. These results clearly indicate that both CNTs and GNSs effectively induce EVA nucleation at the early stage of non-isothermal crystallization, while the crystal growth of EVA may be affected at a high weight fraction of carbon nano-filler and higher crystallization temperatures. The 2D GNSs exhibit a more negative effect on the crystal growth of EVA than the 1D CNTs.

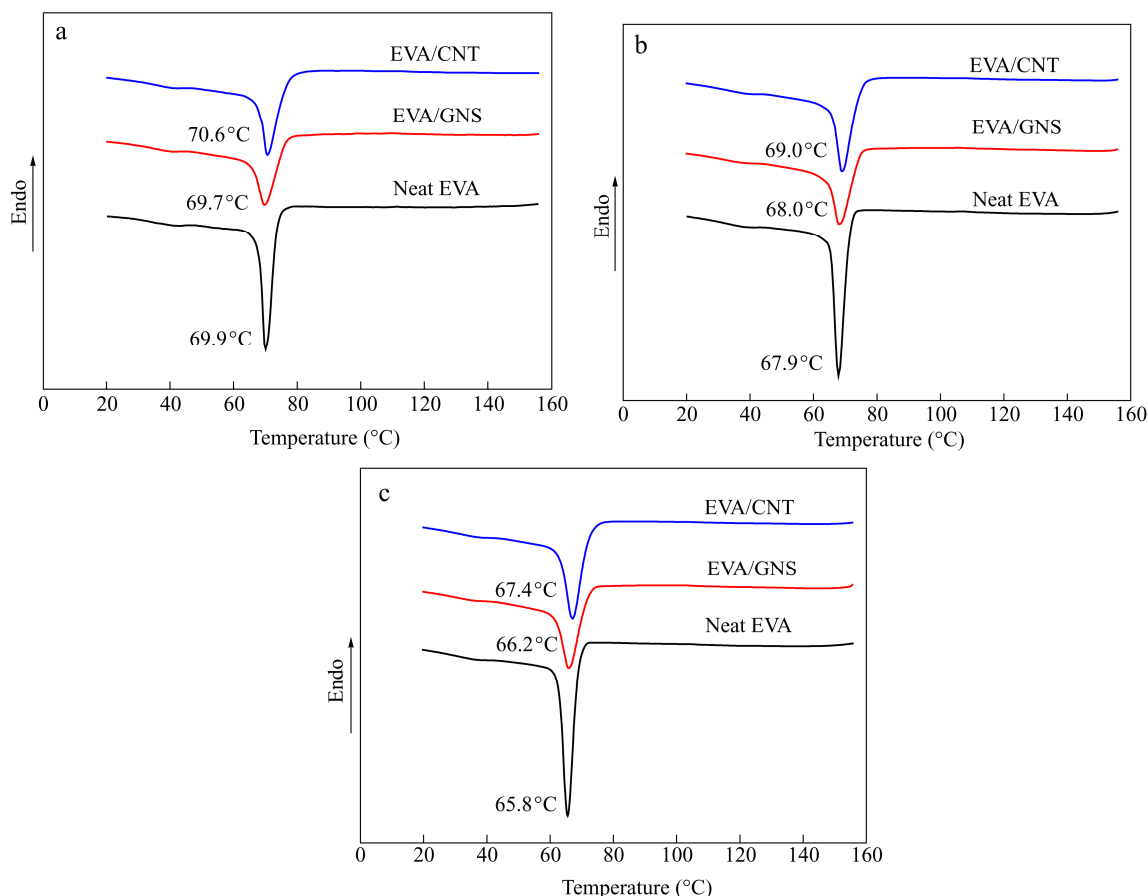


Fig. 6 Non-isothermal crystallization thermograms of neat EVA, CNT/EVA and GNS/EVA composites (5:95 by weight) at different cooling rates: 2 K/min (a), 5 K/min (b) and 10 K/min (c)

The crystallization is dependent on supercooling, which is directly related to the cooling rate for non-isothermal crystallization. FTIR measurements ordinarily take 60 s to collect experimental data per frame. As the cooling rate is more than 2 K/min (*e.g.*, 10 K/min), the temperature span of a FTIR frame is too large to accurately elucidate the non-isothermal crystallization behavior of composites. Thus, differential scanning calorimetry (DSC) was further employed to study the effect of CNTs and GNSs at a higher loading on the non-isothermal crystallization of EVA at different cooling rates. Figure 6 shows the DSC curves of neat EVA and its composites at various predetermined cooling rates of 2, 5, and 10 K/min. Each DSC curve exhibits one prominent crystallization peak, but, interestingly, the peaks of the CNT/EVA and GNS/EVA composites are flat and broad compared with those for the neat EVA, which is indicative of a low crystallization rate. To describe the non-isothermal crystallization evolution, the relative crystallinity $[X(T)]$ as a function of temperature is expressed as^[8]:

$$X(T) = \int_{T_0}^T \left(\frac{dH}{dt} \right) dt / \int_{T_0}^{T_2} \left(\frac{dH}{dt} \right) dt \quad (1)$$

where T_0 and T_2 are the onset and end crystallization temperatures, respectively, and dH/dt is the heat-evolution rate. Using Eq. (1), $X(T)$ as a function of temperature at different cooling rates is plotted in Fig. 7 based on the DSC crystallization curves of the EVA composites (Fig. 6).

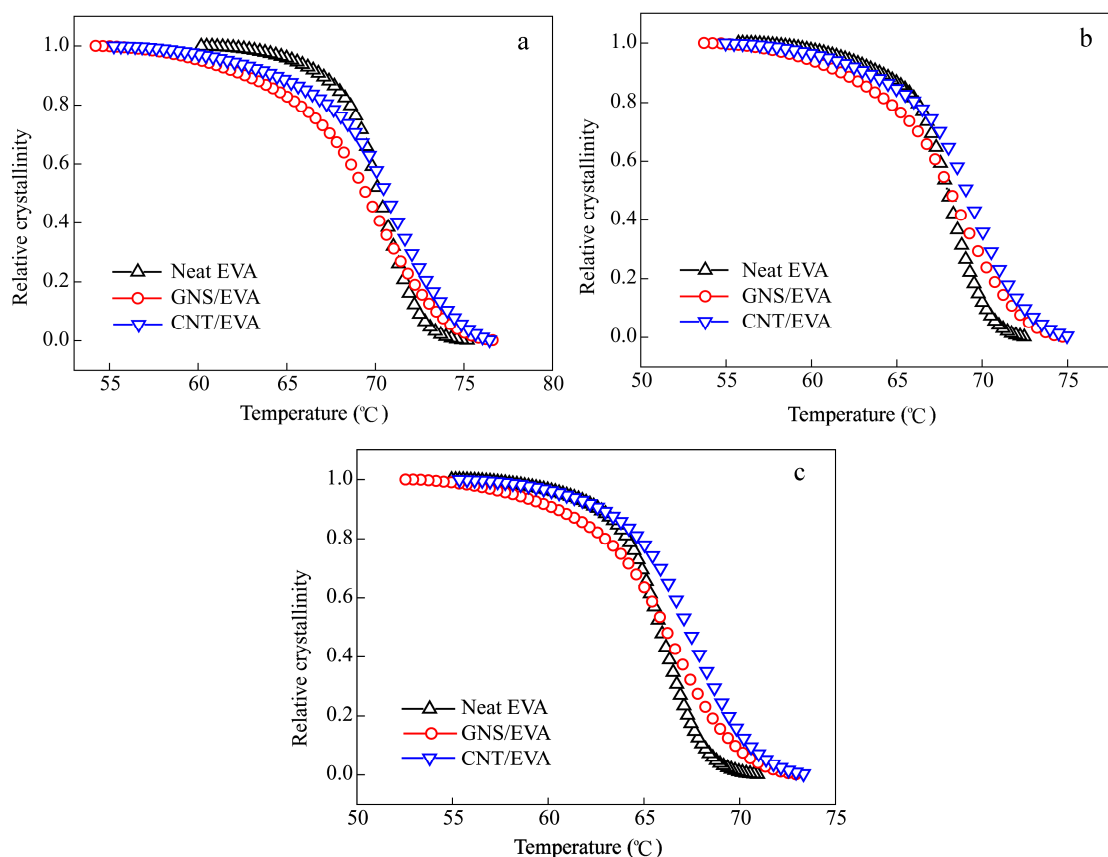


Fig. 7 Relative crystallinity versus temperature for the non-isothermal crystallization of neat EVA and CNT/EVA and GNS/EVA composites at different cooling rates: 2 K/min (a), 5 K/min (b) and 10 K/min (c)

As shown in Table 2, compared with neat EVA at a given cooling rate, The T_c^0 value of both GNS/EVA and CNT/EVA composites shifts to a high temperature (*ca.* 3 K higher than neat EVA). The T_c^p value of the CNT/EVA composite increases by *ca.* 1.5 K, while the T_c^p value of the GNS/EVA composite remains at almost the same value as neat EVA. These results definitely indicate that both CNTs and GNSs act as nucleating agents and 1D CNTs are more effective in promoting heterogeneous nucleation growth. Although crystallization time of neat EVA would be expected to be shorter due to the effect of the low initial crystallization temperature, the overall crystallization rate of EVA and its composites can be manifested by $t_{1/2}$. At the same cooling rate, the $t_{1/2}$ value of the CNT and GNS/EVA composite systems is always larger than that of neat EVA (more than 5 s). In addition, it is worth noting that the $t_{1/2}$ value of the GNS composite is constantly 10–66 s longer than that of the CNT/EVA composite. In addition, ΔH_c can further unravel the relationship of the overall crystallization rates of the three materials, as shown in Table 2. The neat EVA has a larger ΔH_c value (*e.g.* 29.05 J/g at the cooling rate of 10 K/min) than the CNT/EVA (*e.g.* 24.35 J/g) and GNS/EVA (*e.g.* 21.72 J/g) composites. Both the $t_{1/2}$ and ΔH_c values suggest that CNTs and GNSs have a negative effect on the EVA crystal growth. In addition, 2D GNSs retard polymer crystal growth more strongly than 1D CNTs. As depicted in Fig. 8, at the same crystallization time, neat EVA has the highest relative crystallinity after the nucleation stage, and the relative crystallinity of the CNT/EVA composite is higher than that of the GNS/EVA composite. These results

demonstrate that a high loading of nano-fillers possesses a negative effect on the crystal growth of EVA, and the layered structure of the GNSs exhibits more distinct restrains on the crystal growth of EVA than the tubular structure of CNTs^[7, 8, 27–29], which is in agreement with the results of the FTIR measurement. Therefore, the reasons for the differences in the crystallization behaviors of CNT/EVA and GNS/EVA composites may be attributed to the dimension of the carbon nano-fillers, and will be discussed in the next part.

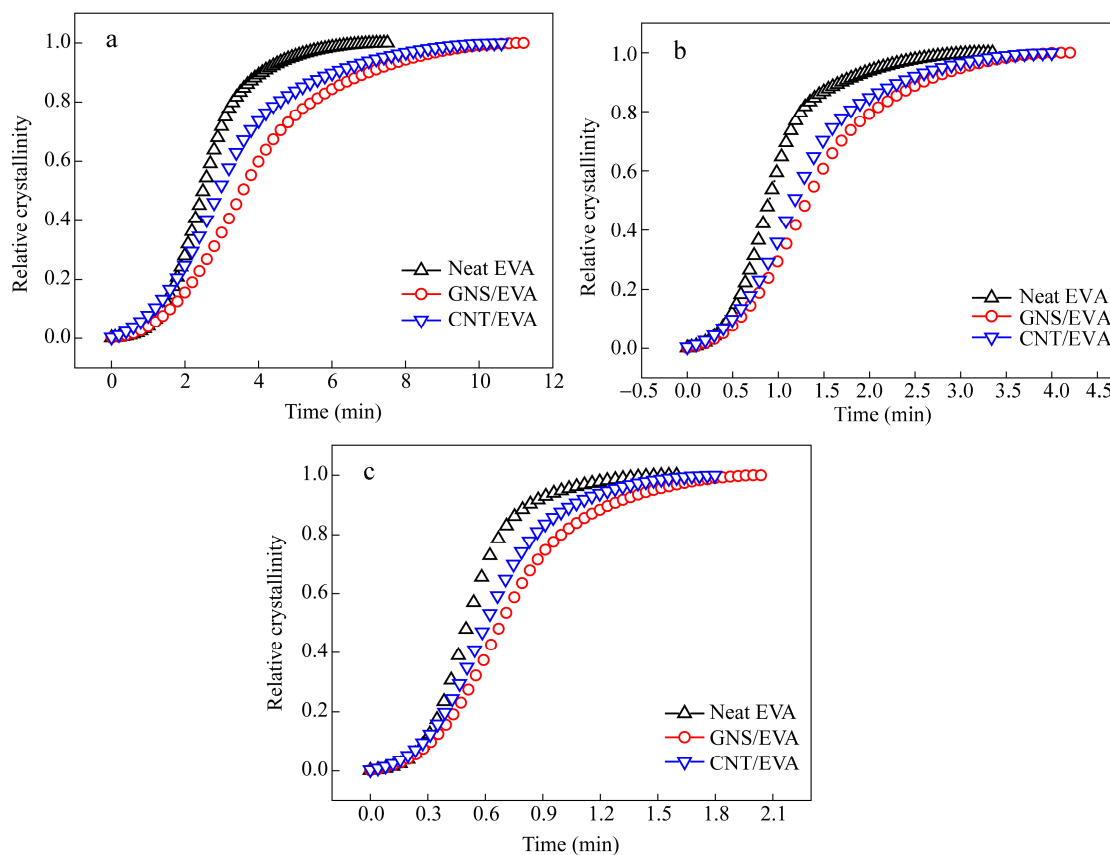


Fig. 8 Relative crystallinity versus time for the non-isothermal crystallization of neat EVA and CNT/EVA and GNS/EVA composites at different cooling rates: 2 K/min (a), 5 K/min (b) and 10 K/min (c). The onset crystallization temperature (Table 2) corresponding times were chosen as the onset times.

Table 2. Parameters of non-isothermal crystallization of neat EVA, CNT/EVA and GNS/EVA composites (5:95 by weight) measured by DSC

Sample	Cooling rate (K/min)	T_c^o (°C)	T_c^p (°C)	$t_{1/2}$ (min)	ΔH_c (J/g)
Neat EVA	–2	73.8	69.9	149	–24.24
	–5	71.4	67.9	54	–28.04
	–10	69.2	65.8	31	–29.05
CNT/EVA	–2	76.7	70.6	178	–20.99
	–5	74.7	69.0	71	–24.15
	–10	72.6	67.4	36	–24.35
GNS/EVA	–2	76.6	69.7	215	–19.87
	–5	74.8	68.0	81	–21.32
	–10	72.3	66.2	41	–21.72

T_c^o : onset crystallization temperature; T_c^p : peak crystallization temperature; $t_{1/2}$: half crystallization time; ΔH_c : enthalpy of crystallization

It is of necessity to discuss the mechanism of the 1D CNT- and 2D GNS-retarded crystallizations of EVA to rationalize the varying abilities of these two differently dimensional carbon nano-fillers to affect the EVA crystallization. According to the traditional point of view, the overall crystallization rate depends on two stages: nucleation and growth^[14]. Nucleation is the precondition for crystallization, and crystal growth involves the formation kinetics of a certain modification and growth space. In the EVA composites with a high nano-filler loading, the nano-fillers not only offer heterogeneous nucleating sites for the EVA chains to attach, but also form limited space for the mobility of the EVA chains^[30–32]. Chain mobility of EVA in the solid and melt state was evaluated by DMA and stress-controlled rheometry as shown in Fig. 9. Figure 9(a) shows the dynamic mechanical behavior of neat EVA and its composites in the solid state as a function of temperature. The neat EVA exhibits a T_g value of -6.2°C , while the addition of GNSs and CNTs increases the T_g value to -1.5°C and -5.5°C , respectively. The storage modulus (G') has the same tendency as T_g . These results imply that EVA needs more energy to trigger the movement of its chain segments under the influence of CNTs and GNSs. Figure 9(b) shows the viscoelastic properties of neat EVA and its composites in the melt state at 160°C . The GNS and CNT composites both display an elevated storage modulus in comparison to neat EVA. It is worth noting that the GNSs lead to a more considerable increase in the storage modulus than the CNTs. With the increase of frequency, neat EVA has a drastic sensitivity of storage modulus to frequency, while the CNTs and GNSs depress the frequency dependence of the storage modulus. Especially, the GNS/EVA composite is nearly independent of frequency. The lower frequency sensitivity indicates that GNSs and CNTs tend to construct a network structure^[33, 34]. In particular, the GNS composites form a more complete nano-network. The DMA and dynamic rheological data testify that a high fraction of CNTs and GNSs, which generate geometrical space confinement (GSC), do restrict the chain mobility of EVA, and more strongly for 2D GNSs. Thus, the GSC of the CNTs and GNSs logically depresses the crystallization rate of EVA, which is in good agreement with the *in situ* FTIR and DSC measurements. Moreover, according to the results obtained from the DMA and stress controlled rheometry studies, it seems reasonable to infer that different topological carbon-based nano-fillers may form different topological basic units in nano-networks. Considering the non-isothermal crystallization behavior as well as the EVA chain mobility in the EVA composites, we believe that there are two factors controlling the crystallization rate of EVA in the CNT/EVA and GNS/EVA composites. One is that the carbon-based nano-fillers have a nucleating effect in terms of non-covalent binding between the filler and EVA chains^[8, 15], resulting in an enhanced nucleation, which is a positive effect on the crystallization of EVA. The other is that the carbon-based nano-fillers hinder the migration and chain diffusion of the EVA chains as a result of the GSC effect^[35–37], which is in agreement with the results of the polyamide system^[7, 18]. Li *et al.* studied the non-isothermal crystallization behaviors of polyamide 6 (PA6)/multi-walled carbon nanotubes (MWNTs) composites by DSC and found the presence of MWNTs influenced the mechanism of nucleation and suppress the growth of PA6 crystallites at high CNT loadings^[7]. As low-dimensional carbonaceous fillers, 1D CNTs and 2D GNSs both possess large surface areas, which is favorable for adsorbing EVA chains^[38]. However, the DSC measurements indicate that the 1D CNTs possess a more effective nucleating ability and that the 2D GNSs retard EVA crystal growth intensively. These results may be caused by their markedly different geometrical morphologies. Namely, the surface-induced crystallization of EVA is probably slowed in the 2D space of the GNS topological basic unit in the nano-network, while the 1D CNTs could provide the whole space for EVA crystallization around them. Xu *et al.* studied the isothermal crystallization of poly(L-lactide) induced by GNSs and CNTs and found a similar phenomenon^[18]. Therefore, 1D CNTs may also be more effective at nucleating crystallinity compared with 2D GNSs.

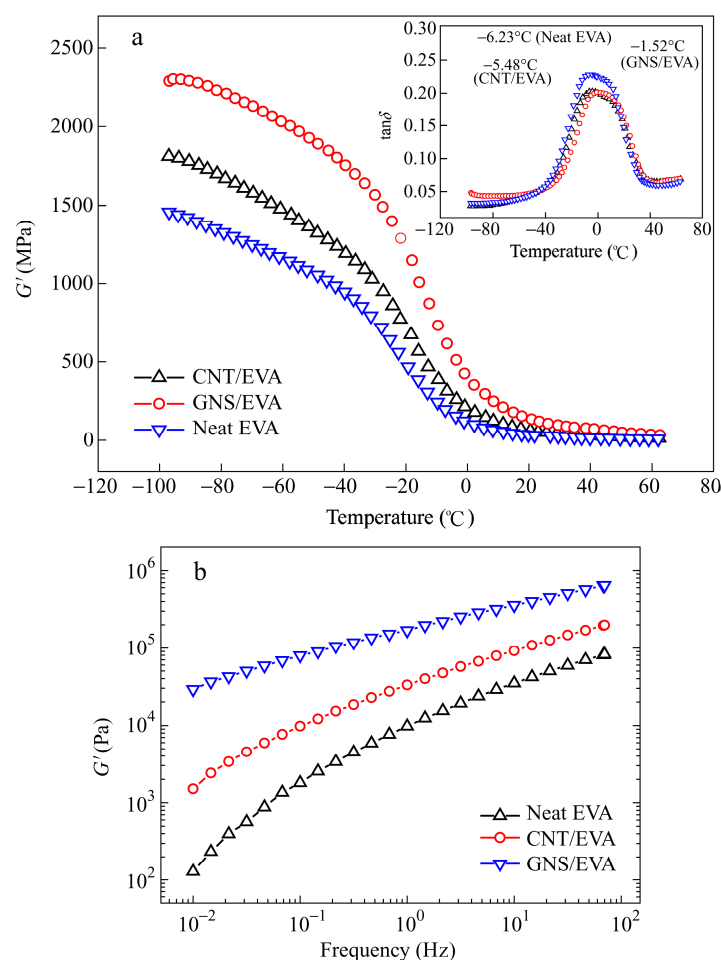


Fig. 9 Dynamic mechanical relaxation behaviors (a) and viscoelastic properties (b) of neat EVA and CNT/EVA and GNS/EVA composites

When the fraction of the second-phase fillers increases, the motion of the polymer chains will be affected. Gam *et al.* traced the motion of deuterated polystyrene in a polystyrene/silica nanoparticle matrix and found that the macromolecular motion was reduced in the crowded polymer composites^[39]. In the same way, it is rational to consider that the behaviors of polymers related to the macromolecular motion will also be influenced. In contrast with silica nanoparticles, the large surface area of CNTs and GNSs may lead to a more intensive confinement between the polymer matrix and the nanoparticles. As observed from the TEM images, CNTs and GNSs both form an integrated network and the gaps between the carbon nano-fillers are less than 50 nm for CNTs and around 100–200 nm for GNSs. Compared with an incompact nano-network of CNTs, GNSs form a relatively closed space. When the thickness of the polymer film in the closed space composed of GNS networks arrives at a critical value, the motion of the EVA chains will be retarded^[40–44]. The 2D GNSs form a limited nano-network, which can seriously hinder the movements of the EVA chains, since there is little space for the macromolecular chains to permeate through the layered and closed networks. The 1D CNTs weave a netted space where the thread-like CNTs leave relatively more space for the EVA chains to pass through. It is difficult to form a limited nano-network space for 1D CNTs to retard the macromolecular motion. According to the fact that 2D GNS nano-networks impede EVA chain movement more obviously than 1D CNT nano-networks, the negative effect of the 2D GNSs on crystallization became severe, resulting in the lowest crystallization rate.

CONCLUSIONS

A comparative study on the non-isothermal crystallization of EVA with a high 1D CNT and 2D GNS loading has been investigated by DSC and *in situ* FTIR. These results showed that the 1D CNTs and 2D GNSs act as nucleating agents, resulting in a noticeably increased crystallization temperature of EVA. However, due to the different geometrical morphology, the 1D CNTs and 2D GNSs revealed different GSC values for EVA. The overall crystallization rates of EVA in the carbon nano-filler composites were lower than that for neat EVA, and the lowest crystallization rate was observed in the GNS/EVA composite, indicating that 2D GNSs have less heterogeneous nucleation activity and more negative effect on the crystal growth of EVA than 1D CNTs. DMA and stress controlled rheometry were employed to explore the origin of the retarded crystallization in crowded carbon nano-filler composites. It is apparent that the 2D GNS networks result in stronger GSC values than the 1D CNT networks, namely, retarding the heterogeneous nucleation activity and suppressing crystal growth. These studies on the EVA crystallization in composites of different dimensional carbon nano-fillers inspire a series of further works including the isothermal crystallization and design of semi-crystalline polymer composites based on these experimental foundations. Such studies also provide new insight into the effect of the dimensions of nano-fillers on polymer crystallization in industrial composite systems.

SUPPLEMENTAL DATA

Details on the preparation of graphene nanosheets; Morphological analyses of nano-fillers; Isothermal crystallization behaviors of composites.

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