A comparative investigation on strain induced crystallization for graphene and carbon nanotubes filled natural rubber composites

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Abstract. Natural rubber containing graphene and carbon nanotubes (CNTs) composites were prepared by ultrasonically-assisted latex mixing. Natural rubber filled by both graphene and CNTs show significant enhanced tensile strength, while graphene exhibits a better reinforcing effect than CNTs. Strain-induced crystallization in natural rubber composites during stretching was determined by synchrotron wide-angle X-ray diffraction. With the addition of CNTs or graphene, the crystallization for natural rubber occurs at a lower strain compared to unfilled natural rubber, and the strain amplification effects were observed. The incorporation of graphene results in a faster strain-induced crystallization rate and a higher crystallinity compared to CNTs. The entanglement-bound rubber tube model was used to analyze the chain network structure and determine the network parameters of composites. The results show that the addition of graphene or CNTs has an influence on the molecular network structure and improves the contribution of entanglement to the conformational constraint, while graphene has a more marked effect than CNTs.

Keywords: rubber, strain-induced crystallization, tube model, graphene, carbon nanotube

1. Introduction

Natural rubber (NR) is used extensively in a variety of applications, due to its outstanding elastic property and good cracking resistance, arising from its ability to crystallize upon stretching [1–4]. The addition of nanoparticles offers the opportunity to render versatility in NR and extend its applications that unlikely to achieve by using NR alone. Graphene (GE) and carbon nanotubes (CNTs) are among the most fascinating nanoparticles, which have received numerous studies because of their intrinsic excellent properties [5, 6], such as high modulus [7], tensile strength [8], thermal [9, 10] and electrical conductivity [11, 12]. GE has been used to prepare NR nanocomposites by an ultrasonically assisted latex mixing and *in-situ* reduction process [13–15], the

mechanical properties were significantly improved at a low content of GE [14]. The reinforcement effect of graphene is believed to be related to its effect on strain induced crystallization (SIC).

Synchrotron X-ray diffraction (WAXD) allows the *in-situ* examination of SIC in NR composites during stretching [13, 16–20]. Results from extensive studies demonstrated the preferred chain orientations and prominent enhancement of SIC upon elongation in the filled rubber composites. Song *et al.* [19] investigated the SIC of natural rubber containing various amounts of CNTs and carbon black (CB) by synchrotron X-ray scattering. It was found that the rubber containing CNTs shows early onset point of SIC and CNTs helps to orient the chains and SIC during the uniaxial stretching. However, the CB in rubber

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act to interrupt the SIC. Ozbas *et al.* [20] compared the effect of graphene and CB on the SIC by synchrotron X-ray scattering. The results showed that the onset of crystallization occurs at significantly lower strains for GE-filled NR samples compared with CB-filled NR. Neat-NR exhibits SIC around a strain of 2.25, while incorporation of 1 and 4 wt% GE shifts the crystallization to strains of 1.25 and 0.75, respectively. In contrast, loadings of 16 wt% CB do not significantly shift the critical strain for crystallization. Despite many studies conducted on the SIC of NR, a comparative study on the influences of GE and CNTs on the SIC and rubber network parameters is still missing.

The established molecular statistical theories of crosslinked and entangled polymers assume that the restricted phase space (due to the entanglements) available to the chains only affects crosslink fluctuations. Nevertheless, these theories give no insight into the relationship between the configurational constraint of entire network chain and stress-strain behavior of crosslinked network. Edwards [21, 22] developed the concept of the tube model by conceiving that the entanglements act along the entire contour length of network chain segments. The introduction of tube model not only allows to reveal non-isotropic crosslink fluctuations to all chain segments of the network via constraining virtual tubes around the network chains, but also enables proper crosslink separation and constraint contribution to stress-strain behavior. Although the tube model has reliability in investigating stress-strain behavior to determine the network parameters of the unfilled rubber, it is not applicable in depicting the filled rubber network because of its complexity [23]. Funt [24] first proposed an entanglement bound rubber tube (EBT) model to describe the contribution of entanglement, which extends tube model to the filled system. Thereafter, EBT model has been used to describe the effect of carbon black [25] and clay [26] on the mechanical behavior of rubber. However, few works concerned on the influence of GE and CNTs on the NR network structure through the EBT model.

In this study, the influences of GE and CNTs on the strain-induced crystallization were investigated by synchrotron WAXD measurements. EBT model was used in combination with stress-strain experiments to calculate the network parameters, and then to assess the contribution of entanglement to the mechanical

property. The results provide new insight into the discrepancy of the reinforcing effect between GE and CNTs.

2. Experimental

2.1. Materials

The commercial used natural rubber (NR) in this study was NR (SCR 5) from Yunnan Natural Rubber Industry Co., Ltd, Kunming, China. NR latex (NR content: 60 wt%) was purchased from Chengdu Fangzheng Co., Ltd (China). Flake Graphite with an average thickness of $\sim 75\ \mu\text{m}$ was obtained from Qingdao Dahe Graphite Co., Ltd (China). Hydroxyl multi-walled carbon nanotubes (CNTs, $\sim 3\ \text{wt}\%$) with a diameter of 10–20 nm were obtained from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. Formic acid was purchased from Tianjin Bodi Chemical Reagent Co., Ltd (China). Other reagents were obtained from Chendu Kelong Chemical Reagent Company (China).

2.2. Preparation of the NR composites

NR composites containing 1.76 wt% CNTs or GE were prepared through the previous route called ultrasonically assisted latex mixing and *in-situ* reduction process [14, 15]. Firstly, natural flake graphite was oxidized to graphene oxide (GO) according to the Hummer's method [27]. Then, 2.5 mg/mL GO aqueous solution was prepared by bath sonication (KQ-250DE, 40 kHz, Kunshan Ultrasonic Instrument Co., Ltd, China) at 40°C for 1 h. Then an appropriate quantity (16.6 g) of NR latex was sequentially dispersed into the GO solution by sonication for 1 h. After the coagulation and drying process, the NR/GO latex mixture was obtained. Then hydrazine hydrate was added into the GO/NR latex and the mixture was subjected to sonication. After the coagulation and drying process, the NR/GE masterbatch was obtained. Vulcanized NR samples were prepared in an open twin roll mill at room temperature according to the recipes outlined in Table 1. The resultant compounds were compression molded into sheets at a curing temperature of 150°C and a pressure of 10 MPa for 5 min, and then cooled for 3 min under pressure at room temperature.

For a comparative purpose, the natural rubber/carbon nanotubes (CNTs/NR) composites with 1.76 wt% filler content were also prepared by a latex mixing route.

Table 1. Recipes for preparing NR and NR composites containing 1.76 wt% CNTs or GE

Samples	NR	CNTs/NR	GE/NR
Raw NR	80	80	80
NR masterbatch containing 10 wt% GE or CNT	0	20	20
Zinc oxide	5	5	5
Stearic acid	2	2	2
Sulfur	3	3	3
Antioxidant (4010NA)	2	2	2
Accelerator (CBS ^a)	1.5	1.5	1.5
Accelerator (MBT ^b)	0.1	0.1	0.1

^aCBS, N-cyclohexyl-2-benzothiazole-sulfenamide^bMBT, 2-mercaptobenzothiazole

2.3. Characterization

Synchrotron wide-angle X-ray diffraction (WAXD) measurements were carried out at room temperature using a U7B beam-line in the National Synchrotron Radiation Laboratory, Hefei, China. The wavelength was 0.154 nm. The specimen was symmetrically stretched at a strain rate of 10 mm/min to the predetermined elongation, allowing the X-ray to irradiate almost the same specimen position. The exposure time for each image was 180 s. The two-dimensional (2D) WAXD patterns were recorded by a Mar CCD 165 X-ray detector system and analyzed by the Fit2D software package.

The tensile strength was tested using an Instron (5567) universal test machine at room temperature. The deformation rate was 500 mm/min. The initial width and thickness of those samples were 4 and 2 mm, respectively. All tests were carried out on a minimum of five samples and the reported results are average values.

The swelling behavior was tested as follows: the cured samples were cut into strips with dimensions of 30 mm×5 mm×2 mm, and then immersed in toluene at 25°C for 48 h to reach their equilibrium swelling. Afterward, the samples were dried at 60°C until constant weights were obtained. The toluene uptake per gram of rubber (Q) was determined using Equation (1):

$$Q = \frac{w_s - w_d}{w_o \cdot \phi_{\text{rubber}}} \quad (1)$$

where w_s is the swollen weight, w_d is the dried weight, w_o is the original weight and ϕ_{rubber} is the mass fraction of the rubber in the composites. The filler-rubber interaction in the composite was evaluated by the Q_f/Q_g (Q_f and Q_g are the toluene uptakes per gram

for filled and neat rubber respectively) [28]. The lower Q_f/Q_g value means the higher interaction extent between the filler and matrix [29].

The bound rubber content was tested based on the method reported by Leblanc and Hardy [30]. Uncured sample (0.5 g) was cut into small pieces and placed into a steel wire net (m_1). The net was closed and weighed (m_2), and then immersed in toluene at room temperature for 72 h during which the sample was washed with fresh solvent every 24 h. The net was slowly removed from the solvent and dried at 40°C under vacuum for a few hours until a constant weight (m_3) was achieved. The amount of bound rubber (as the weight percent, wt%) of the initial rubber content of the uncured sample was given by Equation (2):

$$BdR[\%] = \frac{m_0 - (m_2 - m_3)}{m_0} \cdot 100 \quad (2)$$

where m_0 is the rubber content in the sample given by $m_0 = (m_2 - m_1) \cdot \phi_{\text{rubber}}$ (m_1 is the mass of the empty net and ϕ_{rubber} is the mass fraction of the rubber in the composites.), m_2 is the mass of the net plus the unextracted sample, and m_3 is the mass of the basket plus the extracted dried sample.

3. Results and discussion

3.1. Stress-strain behavior

The stress-strain curves for the unfilled NR and NR nanocomposites with GE or CNTs are shown in Figure 1. The NR exhibits marked increase in tensile strength with low contents of GE or CNTs. The tensile strength was increased by 98.4% from 12.4 MPa for unfilled NR to 24.6 MPa for the nanocomposite with 1.76 wt% GE. The NR/CNTs containing 1.76 wt% of CNTs showed a tensile strength of 18.6 MPa. It is clear that GE shows an evidently

Figure 1. The stress-strain curves of filled and unfilled NR

better reinforcing effect on NR than CNTs. Additionally, both GE and CNTs at low contents exhibit the comparable reinforcing effect to the conventional filler at high loading, indicating the reinforcing advantages of nanoparticles.

In order to understand the reinforcing effect of GE and CNTs, we compared the crosslink density, bound rubber content and filler-rubber interaction of the rubber nanocomposites. The crosslink chains density (v_c) can be obtained according to Equation (3) [31]:

$$\sigma = v_c k T (\alpha - \alpha^{-2}) \quad (3)$$

where σ is the force per unit area, v_c is the crosslink chains density, k is the Boltzmann constant, T is the absolute temperature, and α is the elongation ratio ($\alpha = l/l_0$, in which l_0 is the initial length of the sample and l is that of the elongated sample). The bound rubber content was tested based on the method reported by Leblanc and Hardy [30] (Equation (2)). The filler-rubber interaction in the composites was evaluated by Q_f/Q_g . The crosslink density, bound rubber content and filler-rubber interaction are listed in Table 2. The crosslink chains density for GE/NR is more than twice higher than that of NR, also much higher than that of CNTs/NR. In addition, the GE/NR composite has a very high bound rubber content, nearly three times higher than the CNTs/NR composite, which suggests stronger interaction between GE and NR. The lower Q_f/Q_g value of NR/GE also indicates a stronger interaction between GE and NR matrix. From those data on the crosslink density, bound rubber content and filler-rubber interaction of the rubber nanocomposites, it can be understood why graphene has a much better reinforcing effect on natural rubber. In order to get deeper understanding into the reinforcing mechanism, further investigations were conducted experimentally by Synchrotron Wide-angle X-ray Diffraction and theoretically through the entanglement-bound rubber tube model.

Table 2. The crosslink density, bound rubber content and filler-rubber interaction for the filled and unfilled NR

Sample	NR	CNTs/NR	GE/NR
$v_c \cdot 10^4$ [mol/cm ³]	0.79±0.01	0.92±0.01	1.72±0.03
BdR [%]	0	11.4±0.2	30.3±0.4
Q_f/Q_g	–	0.89±0.01	0.85±0.01

3.2. Strain induced crystallization during stretching

It has long been recognized that the excellent tensile properties of NR originate from its strain-induced crystallization ability. It is of great significance to explore the relation between nanoparticles and strain induced crystallization. SIC was studied via *in-situ* synchrotron wide-angle X-ray diffraction. The 2D WAXD patterns for unfilled NR and NR containing GE or CNTs during stretching are shown in Figure 2. All images were normalized with respect to the sample thickness change, sample absorption, and beam fluctuation. The intensities of these reflections increase with strain during stretching. NR/GE composite has stronger diffraction intensity compared to unfilled NR and NR/CNTs at the same strain. The evolution of strain-induced crystallization can be identified by the linear diffraction profiles taken along the equator from the 2D WAXD patterns collected at different strains during stretching (Figure 3). The resultant peaks on the equatorial diffraction profiles were fitted with a Gaussian function (Equation (4)):

$$I(x) = h \cdot \frac{\exp[-(x - x_c)^2]}{2w^2} \quad (4)$$

where $I(x)$ is the intensity at position x , x_c is the position at the scattering maximum, and h and w are the parameters related to the peak height and peak width, respectively. It can be seen that two distinct diffraction peaks located at $2\theta \sim 15.3^\circ$ corresponding to the 200 plane and $2\theta \sim 19^\circ$ corresponding to the 120 plane increase with strain, and the crystallization occurred at a lower strain for GE/NR compared to that for unfilled NR and CNTs/NR composites. The equatorial reflection peak intensities of $I_{eq}(200)$ and $I_{eq}(120)$ were used to assess the crystallinity via quantitative evaluation in mass fractions of crystal and amorphous phase. The crystallinity calculation from the resultant Gaussian peak is described as Equation (5) [32]:

$$X_c = \frac{A_c}{A_c + A_a} \quad (5)$$

where A_c and A_a represent the integrated intensities of the crystalline and amorphous part, respectively. Figure 3b shows the variation of crystallinity with strain for unfilled NR, GE/NR and CNTs/NR com-

Figure 2. Sequential changes of WAXD patterns of neat NR, CNTs/NR and GE/NR

Figure 3. (a) Equatorial diffraction profiles taken from 2D WAXD patterns at selected extension ratios of GE/NR; (b) the crystallinity as a function of extension ratio for unfilled and filled NR composites

posites respectively. The crystallinity for three kinds of materials increase with respect to strain, and CNTs or GE filled NR composites exhibit higher crystallinity compared to unfilled NR at the same strain. GE/NR composite has the highest crystallinity among the three kinds of material. The crystallites formed along the chains during stretching can be regarded as quasi-fillers or alternatively as additional cross-links in the rubber network, which plays a crucial role in enhancing mechanical properties of NR.

The onset extension ratio of crystallization (α^0) was obtained by the interception of the linear regression lines derived in the plot of crystallinity against strain. The calculated α^0 value for the unfilled NR, CNTs/NR and GE/NR are 3.5, 3.0 and 2.5 respectively. It is clear that SIC occurs at a lower α^0 value in the filled NR samples, and GE/NR exhibits the lowest α^0 value among the three samples. The low α^0 value in GE/NR is thought to correlate with the high strain amplification effect of GE on NR matrix. The

Table 3. Onset extension ratios of crystallization for unfilled NR and filled NR

Samples	α^0	$\alpha_r^0(\varphi)$	$\alpha_r^0(b)$
NR	3.5	3.5	3.5
CNTs/NR	3.0	3.0	3.3
GE/NR	2.5	2.5	3.2

α^0 : the experimental values, $\alpha_r^0(\varphi)$: the corrected values considering the filler volume fraction, and $\alpha_r^0(b)$: the corrected values considering the volume fraction of the fillers plus bound rubber.

effective strain of rubber portion in GE/NR is higher than the nominal macroscopic one by assuming GE un-deformable.

The relationship between the effective extension ratio and volume fraction (φ) of the filler is formulated as Equation (6) [33]:

$$\alpha_r^0(\varphi) = \frac{\alpha^0 - \varphi}{1 - \varphi} \quad (6)$$

The α^0 values are converted in terms of Equation (6), and listed in Table 3. Because of the low filler content, the corrected value $\alpha_r^0(\varphi)$ does not change compared with the experimental values (α^0). In filled rubber, the bound rubber layer around un-deformable filler particles is regarded as immobile, because of the intense physical and chemical interactions. The variation of the strain amplification effect in GE/NR and CNTs/NR composites were interpreted in terms of different bound rubber contents in the two composites. On the basis of Leblanc and Hardy's methods [30], the measured bound rubber contents for CNTs/NR and GE/NR samples are 11.4 and 30.3% (Table 2), respectively. The corrected onset strain $\alpha_r^0(b)$ considering the filler plus bound rubber volume fraction are shown in Table 3. The corrected $\alpha_r^0(b)$ values for filled NR are closer to the uncorrected values α^0 , but still much smaller than the onset

strain of unfilled NR. The addition of filler can dominate the rubber network structure and strain amplification effect. Also the GE or CNTs particles can act as nucleation centers of the NR crystallites. Raul *et al.* [34] thought that the addition of GE or CNTs makes the chains overstrained, and the crystallization was accelerated around particles.

3.3. Lateral crystallite size

Crystallite size is an important parameter in characterizing the crystallization behavior of rubber. The widths of peaks I_{eq} (200) and I_{eq} (120) were estimated and width (w) value was converted into the half-width β_{hkl} (represented by radian) according to the procedure described by Tosaka *et al.* [35]. The crystallite size was estimated using the Scherrer equation (Equation (7)):

$$L_{hkl} = \frac{k\lambda}{\beta_{hkl}\cos\theta} \quad (7)$$

where L_{hkl} is the crystallite size in the direction perpendicular to the (hkl) plane which is parallel to the drawing direction, λ is the wavelength, and θ is the Bragg angle (half of the scattering angle). The Scherrer factor k is 0.89 when β_{hkl} is the half width of the (hkl) reflection in the radial direction [36]. Figure 4 shows the variations of the L_{200} and L_{120} crystallite sizes during stretching. Both I_{eq} (200) and I_{eq} (120) decrease with strain, this is because the mean distance between the stretched chains acting as precursor of crystallite decreases, resulting in a decrease in the average crystallite size [36]. Since both GE and CNTs can act as the nuclei to induce the formation of crystallites during stretching, the filled NR samples show smaller crystallite sizes compared to the unfilled NR at the same strain. GE/NR

Figure 4. Variation of lateral crystallite size: (a) L_{120} and (b) L_{200} during stretching

has the smallest crystallite size among the three samples, because of the stronger interaction between GE and rubber.

3.4. Entanglement-bound rubber tube (EBT) model

EBT model was used to analyze the rubber network microstructure, to gain insight into the reinforcing effect of GE or CNTs on NR materials on molecular level. In EBT model, the packing effect arising from the inability of molecular chains to pass through their neighborhood imparts topological constraint acting on the entire network chains, and restricts the chains from fluctuating within small length scale. The EBT model allows an appropriate separation of crosslinks and constraint contribution to the stress-strain behavior, and enables the determination of crosslink density.

Based on the EBT model, the elastic free energy w_f that considers the finite extensibility of the chain together with the tube constraint can be expressed by two elastic moduli G_c and G_e , which are closely related to the constants C_1 and C_2 in the Mooney-Rivlin equation [37]. The nominal stress σ is obtained by differentiation $\sigma = \partial w_f / \partial \alpha$ [38]. Based on the model, the constitutive equation of an incompressible sample can be expressed as Equations (8) and (9):

$$\sigma^* = \frac{\sigma}{\alpha - \alpha^{-2}} = G_c + G_e \cdot f(\alpha) \quad (8)$$

$$f(\alpha) = \frac{2(\alpha^{\beta/2} - \alpha^{-\beta})}{\beta(\alpha^2 - \alpha^{-1})}, \quad f(\alpha = 1) = 1 \quad (9)$$

where σ^* is the reduced stress. σ is the nominal stress. α is the extension ratio. G_c is the elastic modulus resulting from the crosslink constraint, and G_e is related to the topological tube-like constraint. β is an empirical constant which describes the relation between the deformed tube in the stretched state and an undeformed tube corresponding to the equilibrium state, β is generally taken as 1 [25]. G_e correlated with the tube lateral dimension within bulk rubber can be calculated by Equation (10):

$$G_e = \frac{v_s l_s^2 k_B T}{4\sqrt{6} d_0^2} \quad (10)$$

where v_s is the density of the statistical segments taken as 3.85 nm^{-3} [26], l_s is the average length of Kuhn's statistical segment (0.88 nm for NR). k_B is the Boltzmann constant. The lateral tube dimension (d_0)

Figure 5. Mooney-Rivlin plots of the unfilled NR and NR composites. The red lines were obtained by linear fitting for the Mooney-Rivlin plots in the region of intermediate deformation

with a relationship with the mean number of statistical segments between successive entanglements (n_e) is expressed as Equation (11):

$$d_0 = l_s \sqrt{n_e} \quad (11)$$

According to the Equation (8) and (9), the stress-strain curves in Figure 1 are converted into the form of a Mooney-Rivlin plot, σ^* vs. $f(\alpha)$, as shown in Figure 5. Considering that EBT model is not fulfilled at large strains on the basis of molecular statistical theory [39], our analysis is limited in the intermediate deformation region. The parameters G_e (related to the topological tube like constraint) and G_c (contributed by the chemical crosslink) in Equation (8) can be determined from the slope and y-axis interception of the linear part of intermediate deformation, as shown in the Mooney plot σ^* vs. $f(\alpha)$ (Figure 5), and the results are shown in Table 4. Given the fact that stress-strain behaviors of NR composite show strong dependence on both chemical crosslink and topological constraints contributions, the initial decrease in stress with increasing strain α can be ascribed to the slippage of entanglement [25]. At high strains, however, Mooney-Rivlin curves exhibit a noticeable upturn related to the rapidly increase of stress, which can be attributed to the strain induced crystallization [40] and the finite extensibility of chains [39]. As shown in Table 4, with the addition of filler, both network parameters G_c and G_e increase. Also it can be noted that the G_c and G_e values for GE/NR composite are higher than those for CNTs/NR composite. As shown in Figure 5, GE/NR composite

Figure 6. Schematic diagram of the entanglement bound rubber tube model, (a) GE/NR (b) CNTs/NR (c) NR

shows an upturn at a smaller strain than CNTs/NR composites, indicating that GE is more helpful for strain induced crystallization.

The average molecular mass of the network chains (M_c) is related to G_c according to the equation of $M_c = \rho_p RT / G_c$, ρ_p is the polymer density, R is the gas constant. The decrease of M_c with increasing GE content is equal to an increase in the formation of polymer-filler couples and short bridging chains between filler particles which enlarges the extension of the filled network or the highly bounded clusters of filler particles [26]. Because of the stronger interfacial interactions between GE and rubber, GE/NR composites exhibit more increase in the parameters G_c and G_e than CNTs/NR composites. To understand the effect of fillers on the rubber chain network, EBT model is schematically represented in Figure 6. The EBT model assumed that a number of entanglements, which are believed to dominate the rubber property, are formed in the transition zones between the tightly adsorbed bound and bulk rubbers far from the filler surface phases [25]. The parameters G_c and G_e values shown in Table 4 increased due to the strong interaction between fillers and rubber matrix in the transition zones. With the addition of filler, the tube dimension d_0 decreases, also the mean number of Kuhn's statistic chain segments between two successive entanglements (n_e), as well as the average molecular mass of the chain (M_c) decrease. Our results are similar with those for rubber network filled with clay reported by López-Manchado *et al.* [26].

The well dispersed GE or CNTs nanoparticles with high specific surface area have more chance, compared to the conventional filler with low specific surface, to interact with rubber matrix, and are capable of making majority of rubber confined even at a

Table 4. Network molecular parameters of unfilled and filled rubbers

	G_c^{*a} [MPa]	G_e^{*b} [MPa]	d_0 [nm]	n_e	M_c
NR	0.34	0.43	1.71	3.76	5389
CNTs/NR	0.44	0.45	1.67	3.59	4164
GE/NR	0.66	0.63	1.41	2.57	2776

lower content. TEM and SEM micrographs confirm the homogeneous dispersion of GE or CNTs in NR matrix in our previous report [14, 41]. So, as corroborated by molecular network parameters, the addition of GE or CNT reduces the tube dimensions, by the presence of adjacent chains, which restricts the movement of the rubber chains to a lower range. The chain is nanoscopically confined, forming a highly ordered and entangled structure due to the intense filler-rubber interactions, which limits the lateral fluctuation of the chain to a lower volume and reduces the number of possible chain configuration associated to the chain entropy [26]. In addition, the tube dimension for the GE/NR systems is smaller than that for CNTs/NR. This can be attributed to a more significant contribution of the entanglements in the transition zone due to the stronger filler-rubber interaction in the GE/NR composite. The lower Q_f/Q_g value and higher bound rubber content of GE/NR shown in Table 2, confirm the strong interaction between the GE and NR matrix.

It is known that strain induced crystallization of NR results from the entropy drop during stretching, and this allows a thermodynamic description for SIC. The melting temperature (T_m) of NR increases during stretching. When T_m exceeds the room temperature, NR molecular chains are overstrained and get into a supercooled state, and the onset of crystallization take place, as shown in Equation (12) [42]:

$$\frac{1}{T_{m,s}} = \frac{1}{T_{m,0}} + \frac{\Delta S_{\text{def}}}{\Delta H} \quad (12)$$

where $T_{m,s}$ is the melting temperature in the stretched state, $T_{m,0}$ the melting temperature in the unstretched state, ΔH the melting enthalpy, and ΔS_{def} the difference of the entropy between the stretched and unstretched states. The onset of SIC of NR composites is dependent on ΔS_{def} , which is a function of strain.

The entropy change of the filled rubber is consisted of two parts: (1) the entropy reduction caused by the addition of filler (ΔS_f), which was attributed to the interactions between rubber chains and the filler; (2) deformation entropy (ΔS_{def}) during stretching, as shown in Figure 7. ΔS_f of CNTs/NR and GE/NR composites are expressed as ΔS_1 and ΔS_3 , respectively. ΔS_{def} of CNTs/NR and GE/NR composites are expressed as ΔS_2 and ΔS_4 , respectively. On the assumption that the total entropy change required for the onset of SIC in the filled and unfilled rubber is the same, i.e. $\Delta S_0 \approx \Delta S_1 + \Delta S_2 \approx \Delta S_3 + \Delta S_4$, as ΔS_f of GE/NR composites is higher than that of CNTs/NR, i.e. $\Delta S_3 > \Delta S_1$ due to a more ordered structure for GE/NR composites, ΔS_{def} of GE/NR composites should be lower than that of CNTs/NR, i.e. $\Delta S_4 < \Delta S_2$, which means the onset of strain-induced crystallization of GE/NR composites appeared at a lower strain.

4. Conclusions

Natural rubber composites containing two kinds of fillers, CNTs and graphene were prepared by an ultrasonically-assisted latex mixing process. A significant improvement in tensile strength was achieved for both graphene and CNTs filled NR, while

graphene has a better reinforcing effect. The role of CNTs and graphene on strain-induced crystallization of NR was investigated by means of synchrotron WAXD. The addition of graphene in NR results in faster strain-induced crystallization rate and a higher crystallinity compared to CNTs, which contributes to a better reinforcing effect. The NR molecular network parameters of graphene/NR and CNTs/NR composites were determined by applying the EBT model in combination with Mooney-Rivlin plots. Due to the larger specific surface area, Graphene has more chance to interact with rubber than CNTs, resulting in the decreased tube dimension, and sequentially the reduction of configurational entropy of rubber molecular chains. Graphene/NR composites have lower deformation entropy during stretching than CNTs/NR composites.

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Figure 7. Schematic representation of structural evolution and entropy change of filled and unfilled rubber during stretching

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