

## Vulcanization Kinetics of Graphene/Styrene Butadiene Rubber Nanocomposites\*

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**Abstract** This paper presents the influence of graphene on the vulcanization kinetics of styrene butadiene rubber (SBR) with dicumyl peroxide. A curemeter and a differential scanning calorimeter were used to investigate the cure kinetics, from which the kinetic parameters and apparent activation energy were obtained. It turns out that with increasing graphene loading, the induction period of the vulcanization process of SBR is remarkably reduced at low graphene loading and then levels off; on the other hand, the optimum cure time shows a monotonous decrease. As a result, the vulcanization rate is suppressed at first and then accelerated, and the corresponding activation energy increases slightly at first and then decreases. Upon adding graphene, the crosslinking density of the nanocomposites increases, because graphene takes part in the vulcanization process.

**Keywords:** Graphene; Styrene butadiene rubber; Vulcanization kinetics.

### INTRODUCTION

As we all know, the mechanical properties of rubbers strongly rely on the vulcanization state. Therefore, the vulcanization reactions and kinetics of unfilled rubbers had been intensively investigated and well established decades of years ago<sup>[1]</sup>. However, with the rapid development in nanocomposites, some recent studies have shown that the vulcanization kinetics of rubbers could be changed significantly by the incorporation of nanofillers. Octadecylamine modified clay was found to behave as an accelerator for natural rubber (NR) vulcanized with sulfur, due to the fact that octadecylamine could accelerate the vulcanization process, but unmodified clay had little effect on the vulcanization process<sup>[2]</sup>. Moreover, the activation energy of the vulcanization process was also reduced by the presence of modified nanoclays, indicating an easier crosslinking of clay containing compounds<sup>[3]</sup>. Sahoo and coworkers<sup>[4]</sup> found that Zn-ion coated nano silica in styrene butadiene rubber (SBR) played dual roles, *i.e.* vulcanizing activator for sulfur and reinforcing filler, the former of which was attributed to the presence of Zn-ion on the nano silica surface. Carbon nanotubes (CNTs) were also reported to have strong influence on the vulcanization kinetics of rubber. Zhou *et al.*<sup>[5]</sup> showed that the induction period ( $t_{10}$ ) and the optimum time ( $t_{90}$ ) of vulcanization increased with the increment additions of CNTs. Thus, CNTs decelerated the vulcanization reaction of the SBR composites, which was attributed to the added functional groups of CNTs with acid treatment that prevented the formations of free radicals. However, with the increase of CNTs content, the cross-linking degrees of the vulcanizates increased gradually. In summary, the

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vulcanization kinetics in the rubber based nanocomposites is rather complicated, and some works even lead to controversial conclusions. Moreover, different nanofillers have different influences on the vulcanization kinetics of rubbers<sup>[6–9]</sup>.

In recent years, graphene (GE) has attracted tremendous attention in polymer nanocomposites. Many works have been done to improve the mechanical properties, electrical conductivity, gas permeability and thermal stability of thermoplastic polymers<sup>[10–16]</sup>. There are increasing works that incorporate graphene into elastomers<sup>[17–21]</sup>. The prominent potential of graphene in improving the mechanical and gas barrier properties of elastomers has been demonstrated. However, few works reported the influence of graphene on the vulcanization kinetics of rubbers, which is of primary importance to GE/rubber nanocomposites<sup>[22, 23]</sup>. In our previous work<sup>[24]</sup>, it was found that on adding graphene the induction period of the sulfur vulcanization process of GE/NR nanocomposites was remarkably depressed, whereas the vulcanization rate was enhanced at low graphene loading and then suppressed. As a result, the optimum cure time decreases dramatically at first and subsequently showed a slight increase with increasing graphene loading. At the same time, the crosslinking density of NR increased monotonically, because graphene took part in the vulcanization process. The work shed some light on the influence of graphene on the vulcanization kinetics of sulfur curing system. Peroxide is another widely used curing agent for rubbers. It is also important to study the effect of graphene on the peroxide vulcanization kinetics of GE/rubber nanocomposites.

In the present work, a new latex mixing method was developed to prepare GE/SBR nanocomposites, for which dicumyl peroxide was used as the curing agent. The vulcanization kinetics of the resulting nanocomposites was studied in detail.

## EXPERIMENTAL

### Chemicals

Highly-purified graphite flakes (99.99%) were purchased from Qingdao Ruisheng Graphite Company, China). SBR latex (21wt% of SBR content) was obtained from PetroChina Lanzhou Petrochemical Company. Curing reagent dicumyl peroxide (DCP) is provided by Sinopharm Chemical Reagent Co., Ltd. Other reagents were all of analytical-grade and commercially available.

### Preparation of Graphite Oxide

Graphite oxide (GO) was synthesized by Hummers' method from graphite flakes<sup>[25]</sup>, and then dispersed in water by ultrasonic-treatment. The suspension was centrifugated at 10000 r/min for 15 min to remove any unexfoliated graphite, thus fully exfoliated GO suspension was obtained and subsequently placed in a vacuum oven at 70 °C for several days to remove the remaining water.

### Preparation of GE/SBR Nanocomposites

Graphite oxide was re-dispersed in water to obtain aqueous GO suspension at a concentration of 1 mg/mL by bath sonication. Styrene butadiene rubber latex was mixed with different amounts of aqueous GO suspension by mechanical stirring to produce nanocomposites with different GE loading. After 30 min of stirring, the homogeneous mixture was co-coagulated with saturated NaCl solution and saturated calcium chloride solution to form a particles' suspension. Hydrazine hydrate was added to the suspension with a ratio of 3 mL per 0.01 g of GO, which was allowed to stay for 24 h at 100 °C to reduce GO *in situ*. The solids were filtrated and washed with deionized water and then was vacuum dried in an oven at 60 °C for 48 h. For comparison, a sample of unfilled SBR was prepared from styrene butadiene rubber latex subjecting to the same procedure that was used to prepare GE/SBR nanocomposites. The curing agents were added in an open twin-roll mill at room temperature with a friction ratio of 1:1.2 and nip gap of *ca.* 1 mm. The formula of the curing agents is as follows: SBR 100 phr, DCP 2 phr.

### Characterization

The vulcanization process was analyzed with a curemeter produced by Beijing Youshen Electronic Apparatus

Factory (Beijing, China) at 150 °C. Measurements of differential scanning calorimeter (DSC) at different heating rates (5, 10, 20, and 30 K/min) were performed on Q200, TA instruments. The weights of the samples were in the range of 5–8 mg.

The equilibrium swelling measurement was performed at room temperature in toluene for 7 days. After equilibrium swelling, the solvent was gently wiped off the sample surface with filter paper,  $w_2$  was determined by deducting the weight of graphene from the overall weight of swollen sample. After drying the swollen sample at 70 °C until a constant weight was achieved,  $w_1$  was determined by deducting the weight of graphene from the overall weight of deswollen sample.

## RESULTS AND DISCUSSION

### *Vulcanization Kinetics of GE/SBR Nanocomposites Studied by Curemeter*

To illustrate the influence of graphene loading on the vulcanization kinetics of SBR, the curing curves of SBR and GE/SBR nanocomposites with dicumyl peroxide were measured. The representative curing curves are shown in Fig. 1. It is clear that the curing curves are systematically shifted toward the short time side with increasing graphene loading, suggesting that the vulcanization process of SBR is accelerated. At the same time, the presence of graphene increases both the minimum and maximum torque values of the curing curves. To get more specific information, some important vulcanization parameters, including  $t_{10}$  cure time (which can also be used to measure scorch safety),  $t_{90}$  cure time (*i.e.*, optimum cure time), the difference between  $t_{10}$  cure time and  $t_{90}$  cure time ( $t_{90} - t_{10}$ ), and the difference between minimum and maximum torques ( $\Delta S$ ) are determined from the curing curves, as shown in Fig. 2.

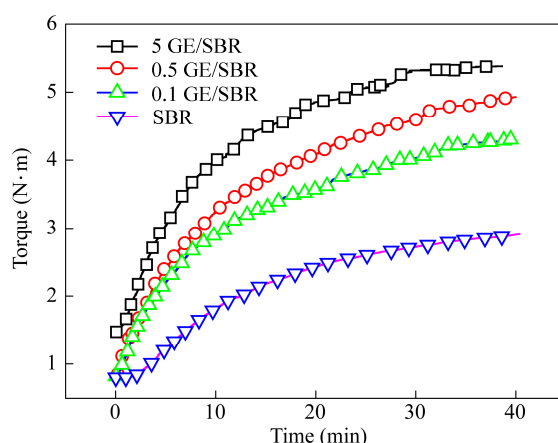


**Fig. 1** Representative curing curves of SBR and GE/SBR nanocomposites with different graphene loadings

The scorch time,  $t_{10}$ , is the time at which the torque equals to  $\Delta S \times 10\% +$  the value of minimum torque. It can be used to characterize the induction period. It is clear in Fig. 2(a) that  $t_{10}$  decreases rapidly when the graphene loading is lower than 0.5 phr, and then levels off. It suggests that the presence of a small amount of graphene greatly reduces the induction period of the vulcanization process, but incorporation of more than 0.5 phr of graphene does not lead to further reduction of the induction period. The optimum cure time,  $t_{90}$ , is the time to increase the torque 90% above the minimum torque. During this process, the organic peroxide splits into 2 radicals:  $R-O-O-R \rightarrow 2RO\cdot$ . The next step is the abstraction of a hydrogen atom from an allylic position on the polymer molecule, or the addition of the peroxide-derived radical to a double bond of the polymer molecule, converting them into free radicals. Subsequently, the resulting radicals react with each other to form cross-linked structure<sup>[1]</sup>. On adding graphene,  $t_{90}$  shows a monotonic decrease trend, as shown in Fig. 2(a). Thus, incorporating graphene reduces the optimum time of SBR. As a result,  $t_{90} - t_{10}$  increases at first then inversely decreases. Actually,  $CRI = 100/(t_{90} - t_{10})$  can be used to evaluate the vulcanization rate, where higher

vulcanization rate leads to higher CRI. It can be inferred from Fig. 2(a) that the vulcanization rate is suppressed at low graphene loading ( $< 0.5$  phr), whereas it is promoted subsequently. Therefore, the vulcanization rate of the GE/SBR nanocomposites with the graphene loading lower than 0.5 phr is even slower than that of unfilled SBR, although the overall cure time is reduced due to shorter induction period.

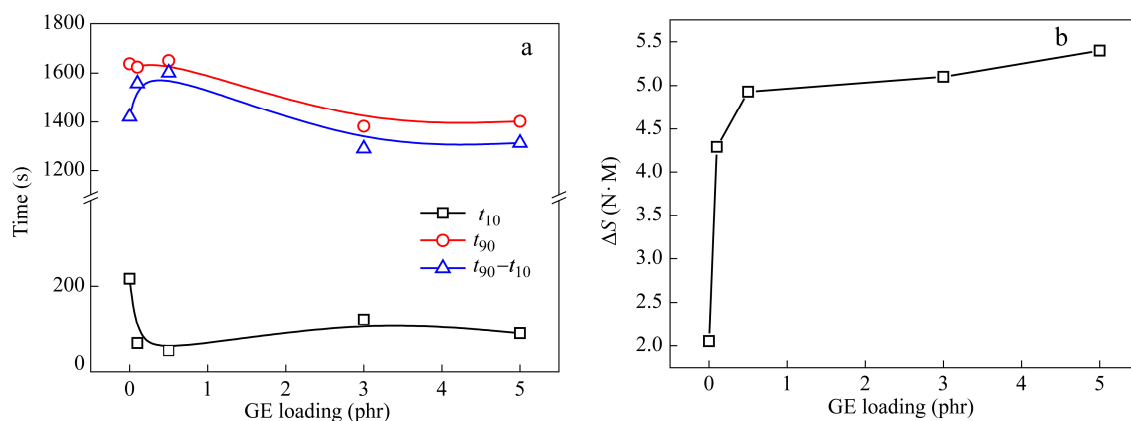


**Fig. 2** The effect of graphene loading on the vulcanization parameters determined from the curing curves: (a)  $t_{10}$ ,  $t_{90}$  and  $t_{90}-t_{10}$  and (b)  $\Delta S$

The difference between minimum and maximum torque,  $\Delta S$ , is generally assumed to be proportional to the final number of crosslinks<sup>[26]</sup>. Thus it can be deduced from Fig. 2(b) that the crosslinking density of the GE/SBR nanocomposites increases with increasing graphene loading. The conclusion can be confirmed by the swelling measurements in toluene, as shown in Fig. 3. It can be found that the equilibrium swelling ratio (which is defined as  $w_2/w_1$ ,  $w_1$  is the weight of rubber in the deswollen sample and  $w_2$  is the weight of rubber and solvent in the swollen sample) decreases with increasing graphene loading, indicating that the addition of graphene raises the crosslinking density of SBR. On the basis of the Flory-Rehner equation, the crosslinking density was determined from equilibrium swelling measurements<sup>[27]</sup>:

$$-\ln(1-v_r) + v_r + \chi v_r^2 = V_0 n (v_r^{1/3} - v_r / 2) \quad (1)$$

where  $v_r$  is the volume fraction of the rubber in the swollen sample,  $V_0$  is the molar volume of the solvent ( $106.2 \text{ cm}^3$  for toluene),  $n$  is the number of active network chain segments per unit of volume (crosslinking density), and  $\chi$  is the Flory-Huggins polymer-solvent interaction term. The value of  $\chi$  for SBR in toluene is  $0.391$ <sup>[28]</sup>. The value of  $v_r$  was attained according to:

$$v_r = \frac{w_2 / \rho_2}{w_2 / \rho_2 + (w_1 - w_2) / \rho_1} \quad (2)$$

where  $\rho_1$  and  $\rho_2$  are the densities of the solvent and the rubber, respectively. Calculated by Eq. (1), the crosslinking density of the unfilled SBR and GE/SBR nanocomposites is also presented in Fig. 3. It can be seen that the crosslinking density of unfilled SBR is  $2.15 \times 10^{-3} \text{ mol/cm}^3$ , and it increases rapidly when the graphene content is lower than 0.5 phr and then shows a gentle increase.

Like many classical chemical reactions, the vulcanization kinetics can be modeled by a differential equation related to time and temperature, regardless of the reaction mechanism<sup>[2, 29]</sup>. The equation can be written as follows:

$$d\alpha / dt = K(T)f(\alpha) \quad (3)$$

where  $\alpha$  is the conversion,  $d\alpha/dt$  is the vulcanization rate,  $t$  is the time,  $K$  is a kinetic constant at temperature  $T$ , and  $f(\alpha)$  is a function corresponding to the phenomenological model.

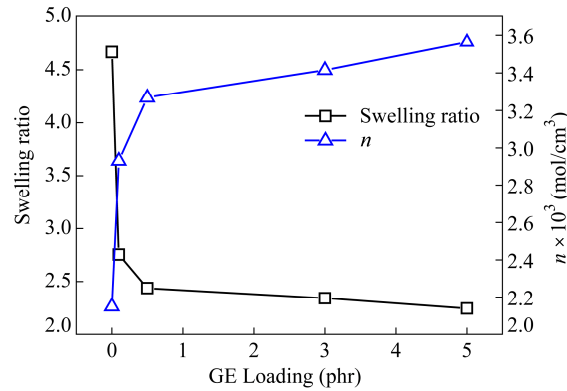


**Fig. 3** The effect of graphene loading on the equilibrium swelling ratio and crosslinking density of unfilled SBR and GE/SBR nanocomposites

When a curemeter is used to study the vulcanization kinetics,  $\alpha$  is defined as follows<sup>[30]</sup>:

$$\alpha = \frac{M_t - M_0}{M_\infty - M_0} \quad (4)$$

where  $M_0$ ,  $M_t$ , and  $M_\infty$  are the torque values at time zero, at a given curing time and at the end of the vulcanization process, respectively.

It has been generally realized that the vulcanization process is an autocatalytic reaction, thus  $f(\alpha)$  is given as<sup>[2, 7, 27]</sup>:

$$f(\alpha) = a^m (1 - \alpha)^n \quad (5)$$

where  $0 \leq m \leq 1$  and  $n \geq 1$  are both the orders of reaction.

Thus, Eq. (3) can be given as:

$$d\alpha / dt = K(T) a^m (1 - \alpha)^n \quad (6)$$

As shown in Fig. 4, the experimental data can be well fitted with Eq. (6). The resulting fitting parameters are listed in Table 1.  $m + n$  decreases at first and then shows an increasing trend by adding graphene loading, which indicates that the reaction order is slightly changed when graphene takes part in the curing reaction of SBR.

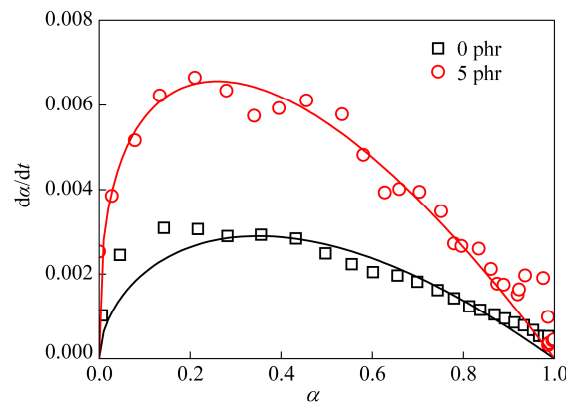


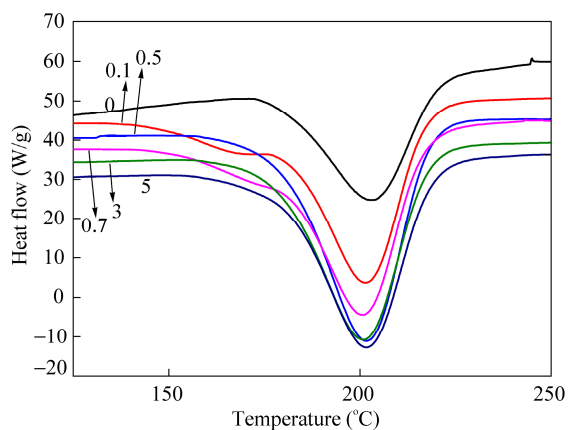
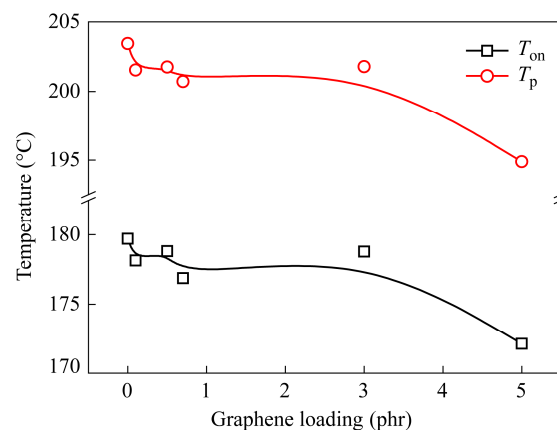
**Fig. 4** Representative plotting of the derivative of  $\alpha$  as a function of  $\alpha$  for the GE/SBR nanocomposites at 150 °C (The lines are the results predicted from Eq. (6).)

**Table 1.** Kinetic parameters obtained by fitting the experimental data in Fig. 4 with Eq. (6)

| GE loading (phr) | $K$   | $M$   | $n$ | $m+n$ |
|------------------|-------|-------|-----|-------|
| 0                | 0.008 | 0.548 | 1   | 1.548 |
| 0.1              | 0.099 | 0.508 | 1   | 1.508 |
| 0.5              | 0.017 | 0.293 | 1   | 1.293 |
| 3                | 0.016 | 0.323 | 1   | 1.323 |
| 5                | 0.014 | 0.350 | 1   | 1.350 |

### Vulcanization Kinetics of GE/SBR Nanocomposites Studied by DSC

DSC is another widely used technique to study the vulcanization kinetics, through monitoring the change in heat flow upon crosslinking. The influence of graphene loading on the vulcanization kinetics of the GE/SBR nanocomposites was also studied by DSC under dynamic conditions. The representative heat flow curves of unfilled SBR and GE/SBR nanocomposites subjected to a heating process are shown in Fig. 5. For quantitative discussion, two characteristic temperatures of the vulcanization process, including onset temperature ( $T_{on}$ ) and peak temperature ( $T_p$ ), are shown in Fig. 6. It is evident that  $T_{on}$  decreases with increasing graphene loading, which well coincides with the result of curemeter that shows reduced induction period. Meanwhile,  $T_p$  shifts to lower temperatures with the addition of graphene.

**Fig. 5** Heat flow curves of SBR and GE/SBR nanocomposites at a heating rate of 30 K/min**Fig. 6** Effect of graphene loading on  $T_{on}$  and  $T_p$  at a heating rate of 30 K/min

The activation energy ( $E_a$ ) of the vulcanization reaction can be determined from the non-isothermal cure reactions with different heat rates, while avoiding the use of any specific model. Frequently, the Ozawa method<sup>[31]</sup> and the Kissinger method<sup>[32]</sup> are used to calculate  $E_a$  with the following equations:

Ozawa method:

$$E_a = -R \frac{d \ln \beta}{d(1/T_p)} \quad (7)$$

Kissinger method:

$$E_a = -R \frac{d \ln(\beta / T_p^2)}{d(1/T_p)} \quad (8)$$

where  $\beta$  is the heating rate,  $T_p$  is the peak temperature of the exothermal peak, and  $R$  is the gas constant. According to Eqs. (7) and (8), the plots of  $\ln \beta$  versus  $1000/T_p$  and  $\ln(\beta / T_p^2)$  versus  $1000/T_p$  are shown in Figs. 7(a) and 7(b), respectively. By fitting these plots with linear functions, we can calculate  $E_a$  from the slopes of these plots. The results are shown in Table 2. Both the Ozawa method and the Kissinger method indicate that  $E_a$  of the reaction increases slightly at low graphene loading and then shows a decrease, which is in coincident with the previous observation that the vulcanization rate decreases at low graphene loading and then shows an increase.

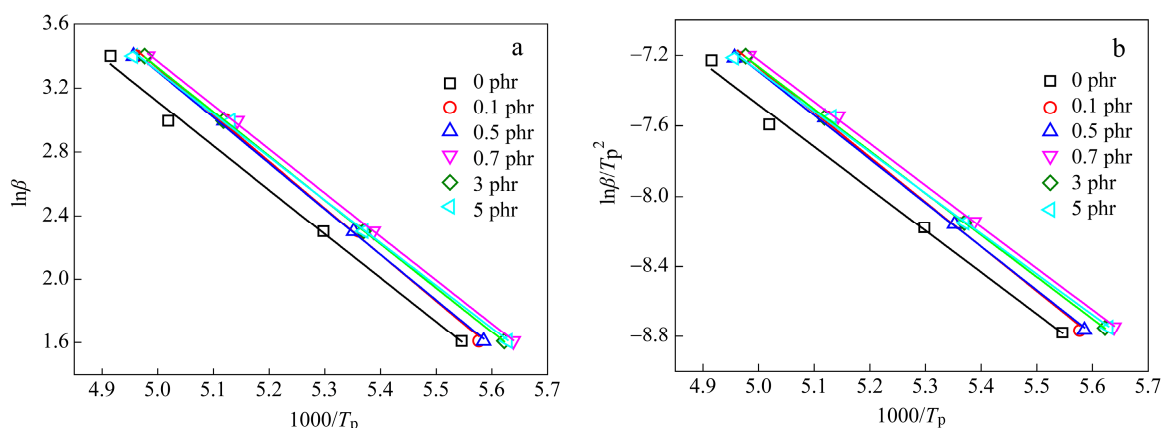


**Fig. 7** Dynamic DSC for calculating  $E_a$  by (a) the Ozawa equation and (b) the Kissinger equation

**Table 2.** The activation energy of the vulcanization reaction of the GE/SBR nanocomposites

| GE loading (phr) | $E_a$ (kJ/mol) |           |
|------------------|----------------|-----------|
|                  | Ozawa          | Kissinger |
| 0                | 22.95          | 19.81     |
| 0.1              | 24.27          | 21.12     |
| 0.5              | 23.86          | 20.70     |
| 0.7              | 22.83          | 19.70     |
| 3                | 23.02          | 19.88     |
| 5                | 22.37          | 19.26     |

#### Discussion on the Mechanism of Accelerating Effect of Graphene

To further demonstrate the accelerating effect of graphene, we performed DSC measurements directly on pure DCP, pure GE and DCP with GE, in which SBR is not involved. It is shown in Fig. 8 that the onset temperature ( $T_{on}$ ) of pure DCP decomposition appears at 144.77 °C, while with the addition of graphene (1/2 the weight of DCP) the temperature is depressed to 142.06 °C, suggesting the decomposition reaction takes place at lower temperature. Moreover, another important feature in Fig. 8 is that addition of graphene significantly increases the enthalpy of reaction,  $\Delta H$ , from 193.9 J/g of DCP to 684.4 J/g of DCP containing graphene. Besides, pure GE shows an endothermic peak, which may correspond to evaporation of a small amount of water or the further removal of oxygen containing groups on GE. The exothermic thermal behavior of GE does not contribute to the more than three-fold increase in the exothermic  $\Delta H$ , thus the only reason for which is the violent reaction between DCP and graphene. We propose that graphene even after reduction also bears a few epoxy groups, which could react with DCP to give free radicals groups, *i.e.*,  $-O\cdot$ . What's more, we use hydrazine to reduce GO, which brings more double bonds to graphene<sup>[14]</sup>, DCP could also react with the double bonds of graphene to produce free radicals. As a result, the graphene-based radicals can react with the macroradicals which derive from the abstraction of a hydrogen atom from an allylic position on the polymer molecule or the addition of the peroxide-derived radical to a double bond of the polymer molecule<sup>[1]</sup>. Thus crosslinks may be generated between graphene and SBR molecules in this way.

To sum up, graphene probably takes part in the vulcanization process, the resulting network structure of GE/SBR nanocomposites is different from that of unfilled SBR. As shown in Scheme 1, graphene may provide additional crosslinks, leading to higher crosslinking density of the GE/SBR nanocomposites, which is confirmed by the curemeter and swelling measurements. Meanwhile, graphene is likely to stabilize the peroxide-derived radical to some extent, which could also improve the crosslinking efficiency of DCP.

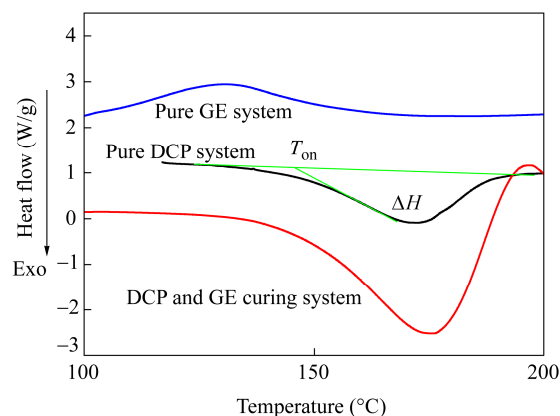
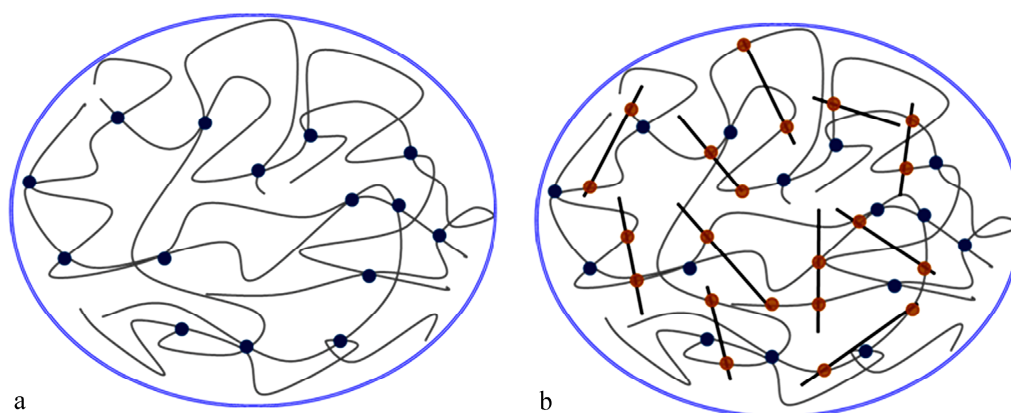


**Fig. 8** The heat flow curves of DCP curing system and DCP-GE curing system at a heating rate of 10 K/min



**Scheme 1** Schematic representation of the network structures of unfilled SBR (a) and GE/SBR nanocomposites (b)

## CONCLUSIONS

In this work, the vulcanization kinetics of GE/SBR nanocomposites was studied with curemeter and DSC measurements. It is found that addition of GE accelerates the vulcanization process of SBR with dicumyl peroxide as the curing agent. With the increase of GE loading, the optimum cure time shows a monotonous decrease, while the induction period of the vulcanization process of SBR is noticeably reduced at low graphene loading and then levels off. As a result, the vulcanization rate is decreased in the beginning and improved later. Meanwhile, the corresponding activation energy increases slightly at first and then decreases. At the same time, the crosslinking density of the nanocomposites remarkably increases, owing to the fact that graphene is involved in the vulcanization process.

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