Research Article

Thermal Property Studies of In Situ Blended Graphene/Nature Rubber Nanocomposites

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In this work, graphene/nature rubber (GE/NR) composites with filler content from 0 wt% to 1 wt% were prepared by an in situ reduction process. Thermal properties of the nanocomposites were studied by thermogravimetric (TG) analysis and thermogravimetric difference (ΔTG). Composites with higher GE content evidenced stronger thermal stability-enhancing effect. Kinetic analysis showed that the activation energies ($E_a$) during degradation of composites were always higher than pure NR. However, $E_a$ reached its maximum at 0.1 wt% GE content and started to decrease with further increase in GE loading. The changes in the thermal properties were attributed to the chemical structure and heat transfer properties of graphene sheets.

1. Introduction

Due to easy processing, low cost, and steerable mechanical properties, rubber is irreplaceable in many industrial fields, such as automobile, aerospace, and military [1]. Nevertheless, the existence of many unstable “C=C” bonds and active ally hydrogens in rubber chains results in the diene rubber product degradation readily during the service periods [2]. Among diene rubbers, including nature rubber (NR), styrene butadiene rubber, and butadiene rubber, NR has been widely applied in automotive, laboratory, and medical industries, given its excellent comprehensive performance [3]. However, NR contains numerous side methyl groups that are more susceptible to degradation in contrast to other general-purpose rubbers, which seriously deteriorate the physical and mechanical properties and even lose the use value.

The incorporation of filler into the polymer matrix is a common way to improve desired properties. Among which, graphene (GE), a two-dimensional monolayer composed of $sp^2$ hybridized carbon atoms, has attracted huge interest due to its superior mechanical, thermal, and electronic properties [4]. Unlike traditional fillers, such as carbon black, silica, and clay, the conjugated chemical structure confers graphene-based composites many unique characters, which makes them widely used in electronic circuits and sensors [5–7], supercapacitor electrodes [8, 9], electric conductive composites [10–12], mechanically reinforced materials [13–15], and so on.

The improved thermal properties of graphene-containing composites have been widely evidenced in various polymer matrices. However, most of the studies merely compare the thermal stability between composites and virgin polymers; little work has been done to date the kinetic changes during the degradation process [16, 17]. To this end, thermal properties and degradation kinetics of GE/NR composites have been studied by using TG experiments. In addition, with the help of multiple heating rate experiments in TG analysis, various kinetic approaches that differ in theory background could be introduced to study the complexity of thermal degradation [18]. Therefore, in this study, two methods (Kissinger-Akahira-Sunose (KAS) [18, 19] and Friedman [20, 21] methods) were carried out to determine the degradation kinetics of multiple heating rate experiment. Theoretically, interpreting the kinetic triplets
(preexponential factor $A$, activation energy $E_a$, and reaction function $f(a)$) from model-fitting procedures could provide us more information about thermal degradation and the concrete improving mechanism of graphene-containing composites. In addition, to achieve better dispersion of fillers in the matrix, ultrasonically assisted latex mixing and in situ reduction process of graphene oxide (GO) were introduced. It is believed that the mechanism of enhanced thermal properties could be studied more profoundly analyzed by degradation kinetics.

2. Experimental

2.1. Materials. Raw materials of graphite flakes (purity is 99.99%) were purchased from Qingdao Ruisheng Graphite Company, China. NR latex (60 wt% of NR content) was obtained from the Chinese Academy of Tropical Agricultural Sciences, Hainan, China. To prepare vulcanized rubber, sulfur, zinc oxide (ZnO), N-cyclohexyl-2-benzothiazolesulfenamide (CZ), and stearic acid (SA) are adopted as curing agents and are all kindly provided by Sichuan Haida Rubber Group Co., Ltd. Other common chemical reagents were all of analytical grade and commercially available.

2.2. Preparation of GE/NR Nanocomposites. GE/NR nanocomposites were prepared by in situ blended method [22]. Generally, GO was synthesized by Hummers’ method [23]; different amounts of GO powders were redispersed in water at a concentration of 1 mg/ml and blended with nature rubber latex. The mixture was cocoagulated with saturated NaCl solution to obtain particle suspension. Hydrazine hydrate was added to the suspension with a ratio of 30 ml per 1 mg of GO, which was allowed to stir for 24 h at 100°C to reduce GO in situ. The solids were filtrated and washed with deionized water and then vacuum dried in an oven at 60°C for 48 h. The obtained composites were filtrated and washed by deionized water and then dried in a vacuum oven.

Curing agents were mechanically blended with rubber composites on a laboratory open two-roll mill (SK-160B, Shanghai Huaxiong Machinery Co., Ltd., China). The recipe was as follows: NR 100 phr, sulfur 2 phr, ZnO 5 phr, CZ 0.9 phr, steric acid 1 phr, and 4010NA 1 phr (phr means parts per hundred of rubber). After that, the rubber stock was cured under 10 MPa with a temperature of 143°C according to the vulcanization time ($t_{90}$) measured on a moving die rheometer (Scarabaeus V-50, Germany). The nomenclature of composite with different GE loading (0.1, 0.3, 0.5, and 1 wt%) was noted as NR/GE-n, where $n$ is the mass fraction of GE.

2.3. Characterization. The dispersion morphologies of the GE sheets in the NR matrix were examined on a Tecnai G2 20 transmission electron microscope (TEM) under an accelerating voltage of 200 kV (Hong Kong FEI). Thermogravimetric analysis (TGA) was performed using a Q20 equipment (TA Corporation, America). About 7 mg samples were cut from the rubber sheets and analyzed at the temperature between 30°C and 800°C with a heating rate of 5, 10, and 15°C·min$^{-1}$ and a gas flow rate of 50 ml·min$^{-1}$ under nitrogen. The differential thermogravimetric analysis (DTG) and mass loss curves were recorded on an Origin 8.0 software. All the TG lines of the same sample have been collected three times to ensure the reproducibility.

3. Results and Discussion

3.1. The Dispersion of GE in the NR Matrix. GE is a typical two-dimensional sheet structure; TEM can intuitively observe the peeling or dispersion state of graphene in a rubber matrix. Moreover, the dispersion state of the filler in the matrix will affect various properties of the composite material, such as thermal stability, mechanical properties, thermal conductivity, and electrical conductivity. As shown in Figure 1, the dark line is the GE nanosheets and the gray background is the NR matrix. From the TEM image, we can see that GE is well dispersed in the NR matrix which indicates that the in situ blended method is an effective way to get GE/NR nanocomposites.

3.2. Characterization and Thermostability of GE/NR Composites. To compare the thermal stability of GO, GE, and GE/NR composites, TG analysis was performed in the temperature range of 30-800°C. Figures 2(a) and 2(b) show the TG and DTG curves of different samples recorded under the heating rate of 5°C·min$^{-1}$, respectively. The temperatures for weight loss of 10% ($T_{10\%}$), weight loss of 90% ($T_{90\%}$), and maximum weight loss rate ($T_m$) were listed in Table 1, which are obtained from Figures 2(a) and 2(b). From Figure 2(a), the thermal degradation of GO could be clearly divided into two steps. The first step occurring below 100°C is ascribed to the release of residue water in GO. The second step in the temperature region between 160 and 240°C is assigned to the thermal decomposition of oxygen-containing functional groups which originated from the oxidation step of graphite flake [17]. $T_m$ was at 213.3°C. In contrast, because
of the removal of unstable moieties, GE exhibits single-step degradation during heating. The residue weight at 600°C is 87.50%, showing the excellent thermal stability of this material. Similar to GE, only one successive process is evidenced in the degradation of composites irrespective of filler contents. With increasing amount of GE, $T_{10\%}$, $T_{90\%}$, and $T_m$ steadily shift to higher temperature. After the addition of 1 wt% GE, $T_{10\%}$, $T_{90\%}$, and $T_m$ display 9.2°C, 18.7°C, and 8.7°C increments, respectively, compared to those of pure NR.

To investigate the eventual increase in thermal stability for filled polymers, Li [21, 24] has proposed a facile method based on the subtraction between theoretical and experimental TG ($\Delta$TG) curves, which is performed as follows: $M_{\text{the}} = C_{\text{NR}}M_{\text{NR}} + C_{\text{GE}}M_{\text{GE}}$, where $M_{\text{NR}}$ is the TG curves of nature rubber, $M_{\text{GE}}$ is the TG curves of graphene sheets, $M_{\text{exp}}$ is the experimental TG curves of NR/GE nanocomposites, and $M_{\text{the}}$ is the theoretical TG curves of NR/GE nanocomposites. $C_{\text{NR}}$ is the mass content of nature rubber in the composites, and $C_{\text{GE}}$ is the content of graphene sheets.

$\Delta M$ is the eventual changes in thermal properties of composites after the addition of GE. Positive $\Delta M$ value corresponds to the improvement while negative value corresponds to the decrement of thermal stability. $\Delta M = M_{\text{exp}} - M_{\text{the}}$.

Figure 3 displays the $\Delta$TG curves collected under 5°C·min$^{-1}$ for GE/NR composites with different GE loading. The dotted line indicates the temperature of maximum $\Delta$TG values.

Table 1: Degradation temperatures of GE/NR composites.

|        | $T_{10\%}$ (°C) | $T_{90\%}$ (°C) | $T_m$ (°C) |
|--------|-----------------|-----------------|------------|
| 0 wt% GE/NR | 343.3           | 441.8           | 370.3      |
| 0.1 wt% GE/NR | 346.5           | 446.0           | 373.0      |
| 0.3 wt% GE/NR | 350.5           | 449.0           | 376.0      |
| 0.5 wt% GE/NR | 351.0           | 454.0           | 376.5      |
| 1.0 wt% GE/NR | 352.5           | 460.5           | 379.0      |
The thermal stability of NR upon heating has been substantially enhanced after the addition of GE as evidenced from the above results. This improvement of thermal properties in graphene-based nanocomposites can be related to the “tortuous effect” which precludes the volatilization of gaseous components generated during heating. Kuila [16] indicated that the homogenously distributed GE layers could effectively inhibit both the emission of small gas molecules produced by pyrolysis and the diffusion of oxygen from the sample surface. Although the thermogravimetric analysis performed in this work does not involve the use of oxygen, the former effect is believed to be significant due to the increased decomposition temperature. In addition, some researches [25, 26] also contribute the enhancement of thermal stability to the less mobility of polymer chains and the ability of capturing free radicals generated during pyrolysis after the incorporation of GE sheets. This is also helpful in understanding the improved thermal stability of the composites studied in this work because most of the carbon-backboned polymers follow the basic auto oxidation scheme [27]. Finally, the increased char yield shown in Figure 2 can be related to the superior thermal stability of GE.

3.3. Kinetic Analysis Performed on the Multiple Heating Rate Experiments. For a single-step degradation process of NR and GE/NR composites, the reaction rate is well-known to be the functions of conversion and temperature, expressed by the following equation [18]:

\[ \frac{da}{dt} = K(T)f(\alpha), \]  

(1)

where \( \alpha \) is the degree of conversion, \( t \) is the time, \( k(T) \) is the function of temperature, and \( f(\alpha) \) is the reaction model. Based on the Arrhenius equation \( k(T) = A \cdot \exp\left(-\frac{E_a}{RT}\right) \) and taking the logarithm form of both sides, equation (1) is transformed to the commonly used Friedman method:

\[ \ln \frac{da}{dt} = \ln Af(\alpha) - \frac{E_a}{RT}, \]  

(2)

where \( A \) is the preexponential factor, \( E_a \) is the activation energy, and \( R \) is the gas constant. When \( \alpha \) is fixed, the value of reaction function \( f(\alpha) \) will be constant consequently. Then, the activation energy \( E_a \) can be calculated by the straight line slope of \( \ln \left[\left(\frac{da}{dt}\right)^{-1}\right] \) versus \( 1/T \). By varying \( \alpha \), the evolution of \( E_a \) versus \( \alpha \) could be obtained, showing the overall kinetic profile of degradation. Figure 4 displays the representative plot obtained by the Friedman method for pure NR with conversion ranging from 0.1 to 0.9. At each \( \alpha \), a straight line is fitted by the least-square method to the group of four data points (with four different heating rates). The calculated \( E_a \) values together with that from other composites are gathered in Figure 5. From this figure, an increasing trend of \( E_a \) is evidenced until the end of degradation (\( \alpha > 0.8 \)) for all the samples except 0.1 wt% GE/NR composite. At a constant \( \alpha \), \( E_a \) is the lowest for pure NR and the highest for 0.1 wt% GE/NR sample. It is interesting that further increase in GE amount reduces the activation energy values, although the values are still higher than \( E_a \) of pure NR. Composites with 0.3, 0.5, and 1 wt% GE amounts almost display the same activation energy when the degree of conversion is below 0.6. However, GE/NR composites with higher GE content have a greater activation energy while the degree of conversion is greater than or equal to 0.6.

KAS method was also introduced in this work to give further insight into the degradation kinetics. The differences of the theory background between KAS and Friedman methods are that the former takes its origin from the integral isoversional principle [28]. After some simple rearrangement...
and integrating procedures of equation (1), under linear heating rate condition, it can be easily derived that

\[
g(a) = \int_{0}^{a} da \frac{d\alpha}{f(a)} = A \int_{0}^{t} \exp \left( -\frac{E}{RT} \right) dt = \frac{A}{B} \int_{0}^{T} \exp \left( -\frac{E}{RT} \right) dT,
\]

where \( g(a) \) is the temperature integral and \( \beta \) is the heating rate. Analytical solution of the above equation is impossible. Thus, many efforts based on solving the temperature integral by various approximations have been made, yielding different integral isoconversional methods. Among which, the KAS method is the relatively accurate one; the mathematical formula is given as follows:

\[
\ln \left( \frac{B}{T^2} \right) = \text{Const} - \frac{E_a}{RT}.
\]

Parameters in this equation have common meaning. Obviously, plotting \( \ln \left( \beta/T^2 \right) \) versus \( 1/T \), from the slope of the straight line, \( E_a \) can be obtained. When \( \alpha \) is fixed, the number of data pairs \( (1/T, \ln (\beta/T^2)) \) is in accordance with the number of heating rates used in the experiment. Figure 6 gives the representative KAS plot of pure NR with \( \alpha \) ranging from 0.1 to 0.9. Every group of four data points was fitted by the least-square procedure analogous with that of the Friedman method. Subsequently, derived \( E_a \) from the fitting lines are collected in Figure 7. It could be seen that the development of activation energies computed by the KAS method is smoother and shows smaller fluctuations over the whole \( \alpha \) range. \( E_a \) monotonously increases with \( \alpha \) at all the GE loading. The highest \( E_a \) value is also observed for 0.1% GE/NR sample. \( E_a \) values from other samples lie between those derived from pure NR and 0.1% GE/NR systems irrespective of conversion degree, which is consistent with the results from the Friedman method.

Unlike the monotonously increased decomposition temperature in Figure 2(a), the degradation activation energies of the composites obtained from the Friedman and KAS methods evidence a maximum value at 0.1 wt% filler loading. \( E_a \) values of GE-containing samples are always higher than those of pure NR. The increased \( E_a \) values are contributed to the following reasons: barrier effect and the ability of scavenging free radicals of GE sheets, which hinder the degradation process to occur. Firstly, compared with pure NR, the migration ability of polymer degradation products in the composites is seriously confined due to the lamellar structure and larger specific surface area of GE, which results in the inability to quickly migrate to the surface of the material. At the same time, after the polymer cracks to generate free radicals, the free radicals will be removed when they migrate to the GE surface, thereby reducing the probability of degradation within the composites. However, \( E_a \) values do not change monotonically with increasing the GE content in the NR matrix. The declining trend of \( E_a \) after further increase in the GE content is explained by the migration ability of polymer chains and faster heat transfer rates of composites with high GE content, which facilitates thermal degradation [17, 29]. Due to the addition of fillers, part of the polymer chains will be adsorbed on the surface of GE, which decreased the migration ability of polymer chains [29]. Moreover, the mobility may be further decreased by increasing the GE content, so the ability of scavenging free radicals of GE will be seriously damaged. Meanwhile, the reduced migration ability of polymer chains is also conducive to the thermal transfer in composite [29]. In addition, it is reported that lower maximum mass loss temperature of GE nanosheets (GNS) filled poly(butylene succinate) (PBS) than that of pure polymer matrix when the GNS amount reached 2 wt% [17]. At low GE loading, the gas-inhibiting and radical-eliminating effects are more prominent in the composite, resulting in the increasing \( E_a \). After further increase in filler loading, the improved thermal conductivity and the reduced migration ability of polymer chains offset partly the former effect, which leads to lower \( E_a \).
4. Conclusion

Thermal properties of in situ blended NR/GE nanocomposites with GE content ranging from 0.1 to 1 wt% have been investigated by thermogravimetric analysis from the kinetic point of view. Both of the initial degradation temperature and maximum mass loss temperature were increased with filler loading. The essential improvement in thermal stability of the composites was studied by thermogravimetric difference analysis. Composites with higher GE loading showed stronger enhancing effect. The Friedman and KAS methods were introduced to obtain activation energies during degradation; it was found that $E_a$ of composites was always higher than that of pure NR, which reached its maximum at 1 wt% GE content. This result was rationalized by the unique chemical structure and good heat transfer properties of graphene.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors’ Contributions

Zhenqiang Dong and Fei Cai contributed equally to this work.

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