

Thermooxidative Degradation of Natural Rubber/Clay Composite

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ABSTRACT: The clay is treated with a reducing agent and an acid so as to obtain a clay containing various metal components with a variable-valence state. Then, the clay is coprecipitated with natural rubber (NR) latex to prepare a vulcanized NR/clay composite. The degradation process of the NR/clay composite under hot air condition was studied dynamically by using a Fourier transform infrared spectrometer attaching an in situ sample cell and was also investigated using the TGA method. The test result obtained from the infrared spectrometry indicated that under low decomposition temperature, the decomposition products of the test samples mainly are ethylene, low molecular olefinic hydrocarbon, and carbonyl compounds. As the decomposition temperature rises, the low molecular olefinic hydrocarbon content decreases, the olefine with longer chain is formed, and a lot of alkane decomposition products are formed at the same time. When the content of the metal components with a variable-valence state in clay such as Cu, Mn, Co, and Fe increases, the oxidation products containing the carbonyl group, the olefinic hydrocarbon, and CO₂ in the

decomposition product of the test sample also increase. The TGA result clearly shows a shoulder peak that appears by the side of the main peak on the DTG curve of NR/clay composite. With the increase in the content of metal components with variable-valence state in clay, the initial degradation temperature of the test sample (T_0), the degradation peak temperature (T_{p1}), and the final degradation temperature (T_{f1}) in first-stage reaction, as well as the degradation peak temperature (T_{p2}) and the last final degradation temperature (T_f) in second-stage reaction of all the test samples more or less shift to the direction of low temperature; besides, the activation energy (E) of the reaction of the test samples more or less decreases. This means that the metal components with variable-valence state promote the oxidative degradation of the clay-rubber masterbatch. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3809–3815, 2006

Key words: NR/clay composite; metal components with variable-valence state; in situ infrared spectrum; TGA; thermooxidative degradation

INTRODUCTION

Heat sensitivity of the polymeric materials such as rubber is always a commonly concerned problem of researchers and technicians, in the scope of high molecular weight materials. Hot circumstances can greatly promote oxidation and degradation of the rubber material, and so its properties deteriorate significantly. It has been proved that the metal ions that existed originally in natural latex or carried into latex by ingredients will promote oxidation and thermooxidation of the rubber and other high polymers.¹ The mechanism and kinetics of degradation of the rubber during heating, and other factors are extensively investigated,² which suggests a positive action to protect rubber and other materials.

Red clay (clay for short) is a cheap and rich mineral distributed extensively in the rubber plantations of South China and Southeast Asia. Clay possesses a satisfactory reinforcing action and can replace or partly replace HAF (high abrasion furnace black), GPF (general purpose furnace black), and SRF (semireinforcing furnace black) for manufacturing bicycle tires, soles, and hoses. The properties of the products conform to national standard.³ Clay is a natural product, and its physical and chemical properties are complicated. Previous research has proved that the metals with variable-valence state such as Cu, Mn, and Fe contained in clay can exert an adverse effect on the aging resistance of the natural rubber (NR)/clay composite.^{4,5} However, the effect of variation of the content of these metal components on heat decomposition products has not been introduced yet.

In this article, it is attempted for the first time to find out a method for changing the content of metal components with a variable-valence state in clay using a reducing agent and an inorganic acid, and the corresponding vulcanized NR/clay composite was pre-

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pared. The degradation products and the thermodegradation process of the NR/clay composite at different temperatures were dynamically studied by use of in situ infrared spectrometry and TGA. The effect of metal components with a variable-valence state on thermodegradation of the clay-rubber masterbatch is explored.

EXPERIMENTAL

Raw materials

The clay was obtained from Nanhua state farm (Guangdong province). The natural rubber latex was obtained from Qianjin state farm (Guangdong province). The dispersion agent and coagulant are of AR or CP grade. The reducing agent and inorganic acid are commercial chemicals.

Preparation of test samples

The raw clay sample (20% dispersion of clay in water) is extracted from clay through dispersion, filtration, and settling.

The raw-clay sample (sample a) is treated with the following process: adding sodium dithionite, heating, settling, and washing (sample b) and adding nitric acid, warming, settling, and washing (sample c).

The content of metal components with a variable-valence state in clay samples a, b, and c were determined by using a US made SP-6 plasma emission spectrometer.

The natural rubber (NR)/clay composite samples A, B, and C (the ratio of NR/clay is 60 : 40 m/m) were prepared from clay samples a, b, and c, respectively, through coprecipitation with natural latex, sheeting, drying, and vulcanization.

Instrument and method

1. The degradation gas products of the clay-rubber masterbatch were determined at four different temperature stages, i.e., room temperature to 270°C, 270–380°C, 380–500°C, and 500–600°C using a 6DX Fourier transform infrared spectrometer and attaching an in situ infrared sample cell developed by the Chemical Department of Shamen University, China. The temperature rising rate was 10°C/min. After the temperature rose to the lowest value of one of the temperature stages, the degradation products formed were extracted away, and then the temperature programming was carried out further.
2. The thermooxidative degradation of the samples was studied using a Seiko TG-DTA 320 thermoanalyzer made in Japan; the temperature

TABLE I
Metal Component Content of Raw Clay Sample and Treated Clay Sample

Clay samples	Cu	Mn	Co	Fe
a	0.0091	0.0934	0.0040	16.9317
b	0.0084	0.0374	0.0031	11.3512
c	0.0085	0.0179	0.0023	6.8170

rising rate used was 10°C/min and the air flow was 50 mL/min.

Data processing of kinetics of thermooxidative degradation reaction

The TG data of the test sample were processed with the method of integration according to Coats and Redfern's⁶ equation to find out the corresponding data of the reaction kinetics of the test sample. After mathematical processing of the reaction kinetics equation,

$$d\alpha/dt = k(1 - \alpha)^n \quad (1)$$

and Arrhenius' equation,

$$k = A e^{-E/RT} \quad (2)$$

the following equation was obtained:

$$\begin{aligned} \ln\{[1 - (1 - \alpha)^{1-n}]/[T^2(1 - n)]\} \\ = \ln[(1 - 2RT/E)AR/\beta E] - E/RT \quad (n \neq 1) \end{aligned} \quad (3)$$

where n is the reaction order, α is the reaction degree, T is the absolute temperature, β is the temperature rising rate, E is the activation energy of reaction, R is the gas constant, and A is the frequency factor. When $n \neq 1$, a straight line is obtained from the diagram using $\ln\{[1 - (1 - \alpha)^{1-n}]/[T^2(1 - n)]\}$ and $1/T$ as coordinates, and the intercept of the line is $\ln[(1 - 2RT/E)AR/\beta E]$. When the maximum correlation coefficient r is obtained using least square fit method with a different n value, then the n is the reaction order sought and the corresponding E is the activation energy of the reaction sought. According to the intercept of the straight line, A is found out.

RESULTS AND DISCUSSION

Metal components in clay

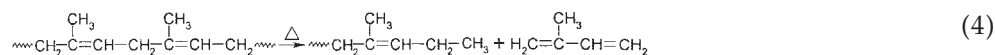
Four metal components contained in three test samples are listed in Table I. It can be seen from Table I, that four metal components with a variable valence state in the treated clay samples b and c vary more or less, and especially the Fe and Mn contents obviously decrease.

Relation between metal component content in clay and thermodegradation of clay-rubber masterbatch

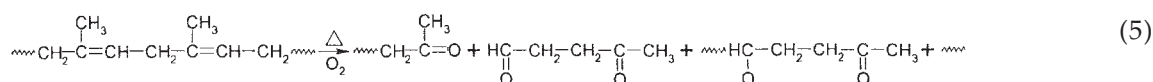
Hot air infrared analysis

The heat decomposition product of NR is very complicated; it includes the heat decomposition product

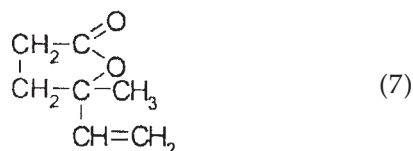
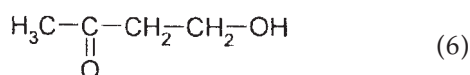
Heat decomposition



Thermooxidative decomposition



Therefore, the decomposition product includes aldehyde, ketone, ester, olefinic hydrocarbon, and alkane,⁸ but different results were obtained by different studies. The study carried out by Gross⁹ indicates that no absorbing band higher than 1800 cm⁻¹ exists on the infrared spectrum of the decomposition product of pure natural rubber at 200°C and 500–600°C. Bevilacqua¹⁰ found that the decomposition product includes ethylene, propaldehyde etc. Morand¹¹ further proved, besides the above-mentioned products, that there exist also the products 6 and 7, given below:



Usually, the main expression of the infrared absorbing peak of NR is the characteristic extended vibration of C=CH₂ at 885 cm⁻¹, the absorbing bands of terminal olefinic groups at 3054, 1631, 966, 910, and 837 cm⁻¹, the double band concentration at 1663 and 837 cm⁻¹, as well as the absorbing band of CH₃ at 1449 and 1376 cm⁻¹.¹² The increase of C=O and —OH and the decrease of double bond during oxidation of NR is also proposed. It is also proved that the chain scission and the crosslinkage of diolefinic polymer can happen simultaneously under thermooxidation.¹³

Figures 1–3 are the thermooxidative degradation infrared spectrograms of test samples A, B, and C respectively. It can be seen, that the main gas products of degradation of the test samples at lower temperature stages are ethylene (1588 cm⁻¹), low molecular

and the oxidation product. The heat decomposition process and the oxidation process can be shown as follows⁷:

olefinic hydrocarbon (1414 cm⁻¹), CO₂ (2360 cm⁻¹), water (3402 cm⁻¹), and carbonyl compound (1711 cm⁻¹) as well as other oxidation products. As the temperature increases, formation of ethylene and other low molecules olefine decreases gradually, at the same time a lot of alkane is formed (2867–2927 cm⁻¹). This phenomenon is most clearly seen at the temperature stage of 380–500°C, but the alkane, olefinic hydrocarbon, and oxidized product decrease again at higher temperatures; it can be said that at this time the rubber hydrocarbon has been decomposed completely. It can be noticed further, that as the temperature increases, the peak at 1700 cm⁻¹ disappears gradually. The absorption peak that appeared around 1700 cm⁻¹ is mainly the oxidized carbonyl product of the rubber hydrocarbon.¹¹ Therefore, it can be considered that the decomposed products obtained by us are different from those obtained in previous studies; that is, at low temperature, the decomposed products include olefinic hydrocarbon, alkane, and oxidized products such as olefine, ketone, and acid; at the same time, water is formed. Because of the decomposition effect of water on oxidized products,¹⁴ these products will vary accordingly. At high temperature, rubber decomposes rapidly and gives out olefinic hydrocarbon and alkane, but the concentration of oxygen in the in situ sample cell is lower than 100 Torr. Because the oxidation rate is related to oxygen pressure,¹⁵ the decomposed products have not enough time to be oxidized, but instead, the thermodegradation reaction happens. Therefore, none of the oxidized products such as aldehyde and hydroxyl compound are formed. As the temperature rises, the amount of alkane and olefine also increases, but the amount of oxidized products such as aldehyde and ketone decreases. It can be noticed further, that the variation of the amount of metal components with variable-va-

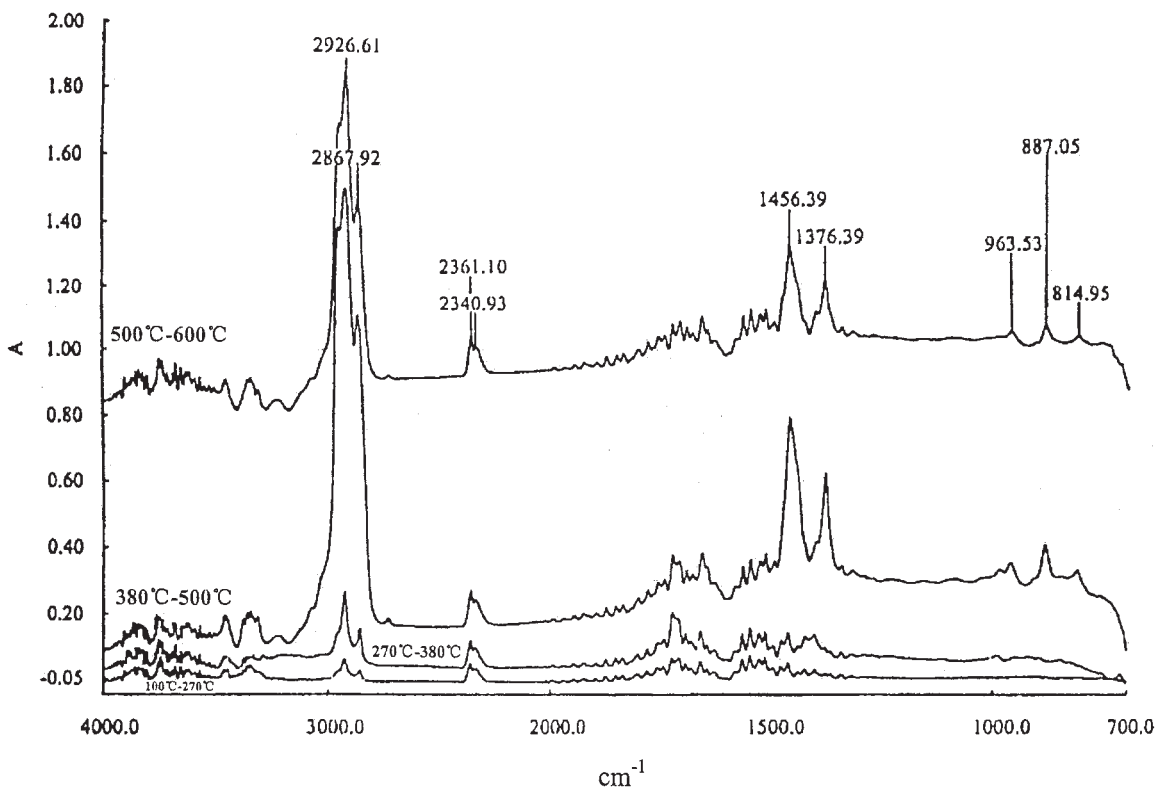


Figure 1 Infra-red spectrogram of test sample A.

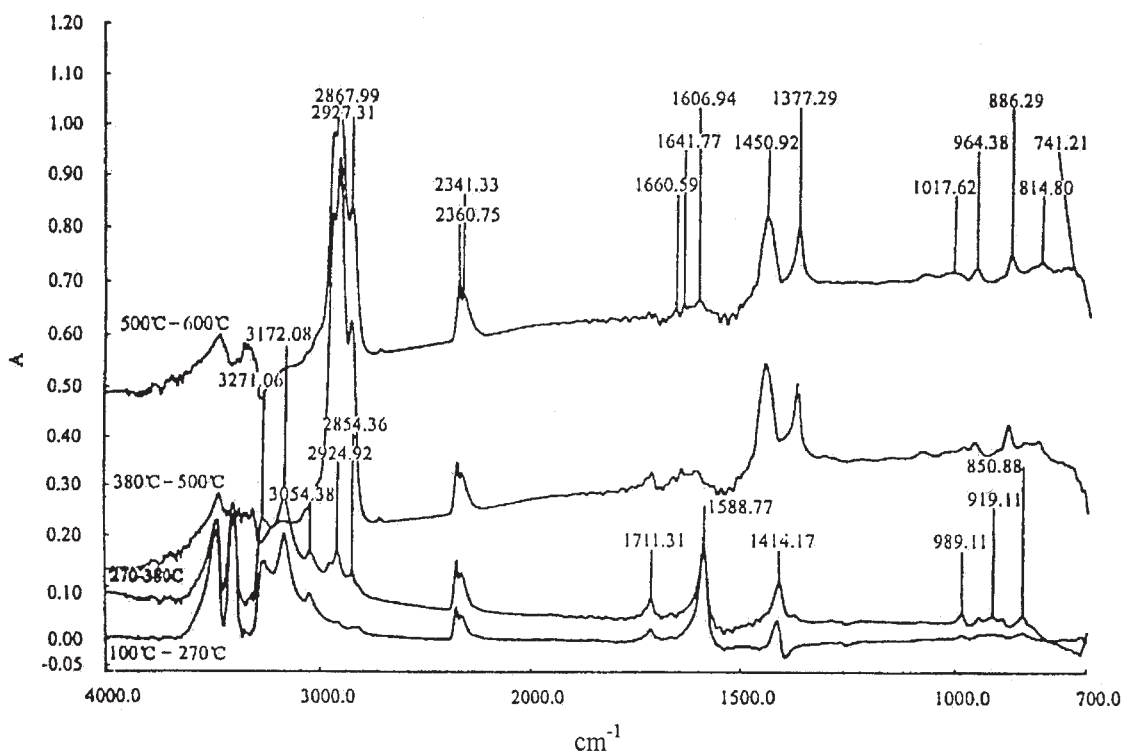


Figure 2 Infra-red spectrogram of test sample B.

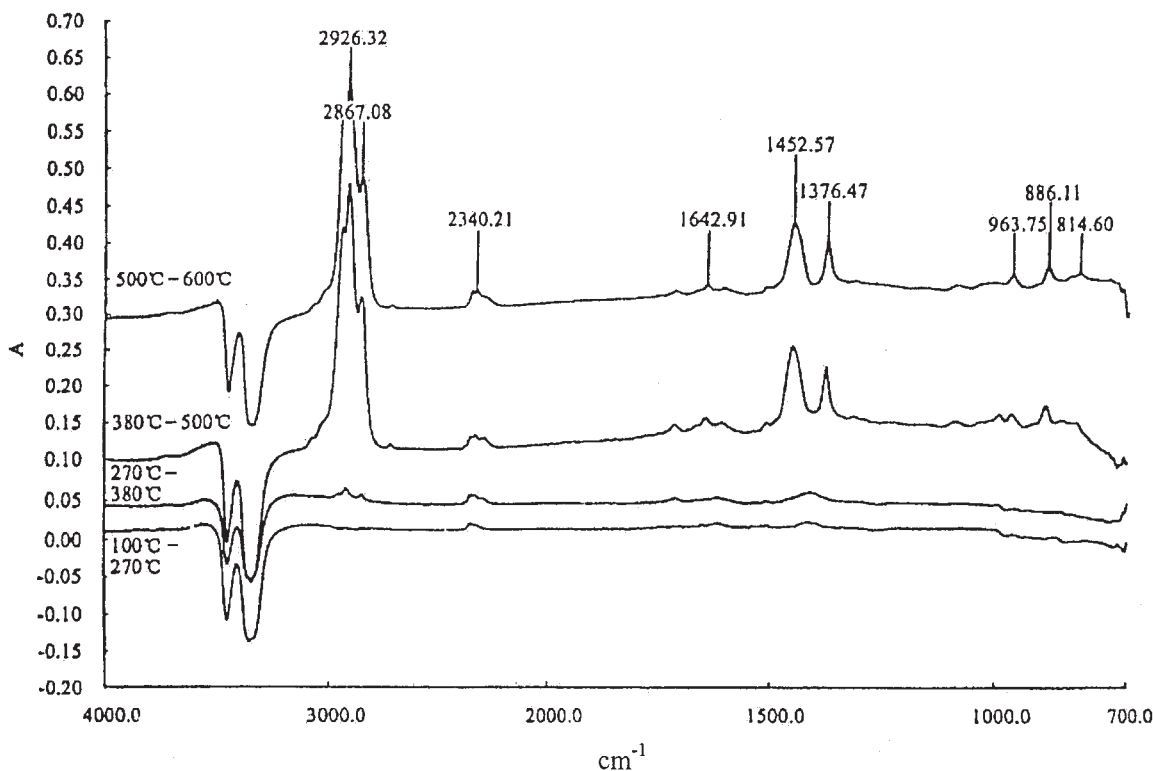


Figure 3 Infra-red spectrogram of test sample C.

lence state in clay has little effect on the kind of thermodegradation products of NR/clay composite, but they certainly affect the decomposition rate, that is to say the speed of formation, and the quantity of thermodegradation products are obviously different. At low temperature (lower than 380°C), almost no decomposition happens in test sample C, in which the metal components content is the lowest, and only a small amount of CO₂ is formed; but when the temperature rises above 380°C, the alkane, olefinic hydrocarbon with long chain and water are formed, but almost no oxidized products and ethylene are produced. In the test samples A and B, when the metal components' content increases, the oxidized carbonyl compound and ethylene are formed at a lower temperature (lower than 270°C), and the amount of decomposed product, olefinic hydrocarbon, increases as well, which indicates that the thermodegradation of the NR/clay composite is affected by the metal components with a variable-valence state contained in clay. The existence of these components makes the rubber hydrocarbon degrade to form olefinic hydrocarbon more easily under heating condition.

It has been found that the metal components with variable-valence state have a catalytic action for oxidative decomposition of high polymer.¹⁶ These metal components are not only the medium for production of the nascent oxygen during oxidation, but also make the oxidative reaction of nascent oxygen to be carried

out under a more favorable condition, and thereby the decomposition of the polymer is promoted. Even though the concentration of the metal components with a variable-valence state is only $5 \times 10^{-3} - 4 \times 10^{-4}\%$, they can still exert an influence on the procedure stated above. But under anaerobic condition, not all the metal ions with a variable-valence state play a part in positive catalysis; the existing form of the metal ions also determines the catalytic effect, and the influence exercised by easy ionized metal components is bigger.⁴ The test results stated in this article indicate further that even though at very low concentration of oxygen, all metal ions with a variable-valence state exert a catalytic action over heat decomposition of NR/clay composite; but when the temperature rises, the oxidized products decrease, and the absorption of carbonyl and hydroxyl groups does not increase significantly, but a lot of olefine and alkane are produced. This is because the rubber hydrocarbon has not enough time to be oxidized, and the decomposition happens owing to the rapid heat decomposition.

Hot air thermogravimetric analysis

Figure 4 shows the TG and DTG curves (100–600°C) of the test samples A, B, and C in air atmosphere, and the temperature rising rate β is 10°C/min. From Figure 4 it can be seen that during the thermodegradation process, two stages appear clearly on the TG curves of all

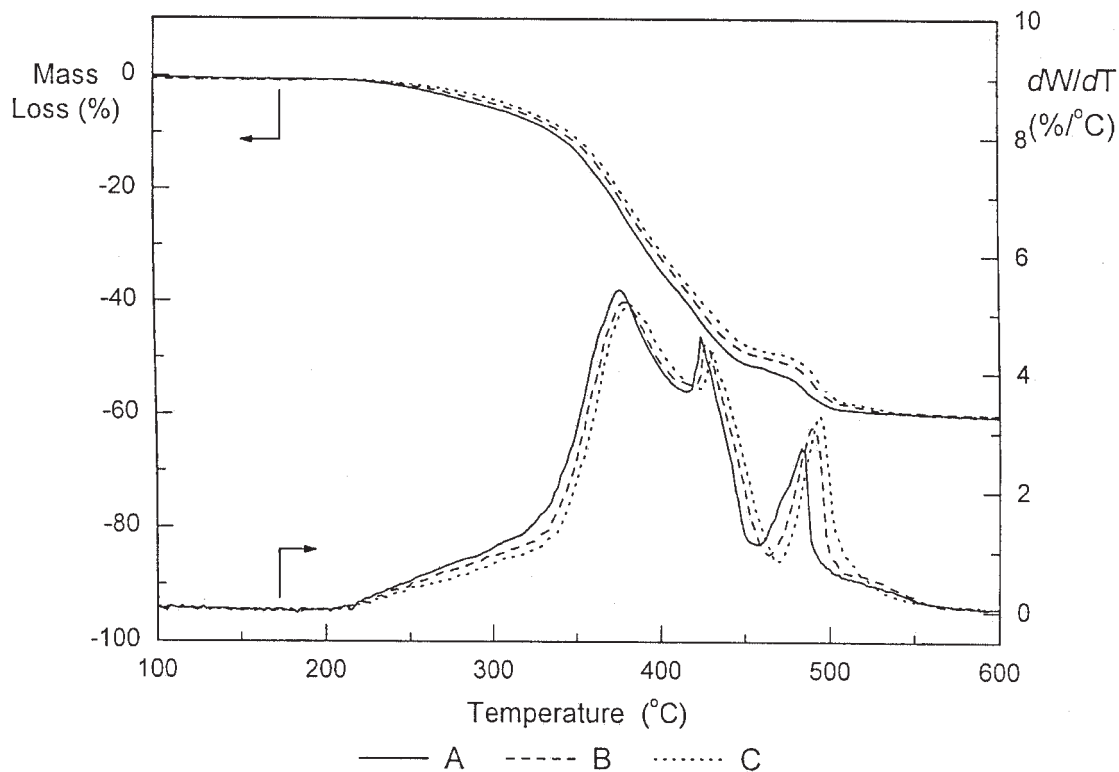


Figure 4 TG-DTG curves of test samples.

test samples, and two corresponding peaks also appear on the DTG curves, which indicates that test samples A, B, and C all possess a two-stage oxidative degradation reaction.^{17,18} The first-stage reaction appears at 209.5–458.5°C, then the second-stage reaction appears at 458.5–600°C. The characteristic features of the TG or DTG curves of the test samples are similar. Up to 600°C, the degradation rate of three test samples is from 60.1 to 60.4%, and almost all the residue is clay.

From the DTG curves of the test samples, it can be seen further, that a main peak appears at 376.1–381.5°C, and a shoulder peak appears at 424.4–431.6°C, which is different from the DTG curve of thermooxidative degradation of NR pure gum vulcanizate. On the DTG curve of NR pure gum vulcanizate, there is no shoulder peak by side of the main peak,¹⁹ which indicates that the thermooxidative degradation of the test samples is more complicated than the thermooxidative degradation of NR. It is inferred that the appearance of the shoulder

peak is possibly caused by the following fact: at higher temperature, the metal components in the test samples accelerate the degradation of rubber hydrocarbon, which conforms substantially to the result of the infrared spectrogram stated above.

The initial degradation temperature (T_0), the final degradation temperature in the first-stage reaction (T_{f1}) and the last final degradation temperature (T_f) of the test samples are obtained from the TG curves in Figure 4 using an extrapolation of the double tangent method. The degradation peak temperature T_{p1} and T_{p2} are obtained from the DTG curves in Figure 4 and are listed in Table II.

According to the characteristic degradation temperature of test samples listed in Table II, the corresponding degradation rate C of test samples is obtained from the TG curves and listed in Table III.

It can be seen from Table II, that test samples A and C possess the lowest and highest degradation temperature, respectively. It can also be seen from Table III

TABLE II
Characteristic Degradation Temperature T (°C)
of Test Samples

Sample	T_0	T_{p1}	T_{f1}	T_{p2}	T_f
A	328.7	376.1	458.5	483.5	501.6
B	331.8	379.7	463.9	490.7	509.1
C	333.1	381.5	467.1	494.2	512.9

TABLE III
Degradation Rate C (%) Test Samples

Sample	C_0	C_{p1}	C_{f1}	C_{p2}	C_f
A	-8.41	-22.9	-51.6	-55.0	-58.7
B	-7.98	-22.7	-50.0	-54.6	-58.3
C	-7.52	-22.2	-49.1	-54.4	-58.1

TABLE IV
Kinetic Parameters of Thermooxidative Degradation of Test Samples

Sample	<i>n</i>	<i>E</i> (kJ/mol)	<i>A</i> (10 ⁻⁵)	<i>r</i>
First-stage reaction				
A	2.3	82.699	3.775	0.9994
B	2.3	85.883	6.215	0.9984
C	2.3	87.089	7.271	0.9986
Second-stage reaction				
A	2.3	36.172	894.148	0.9658
B	2.3	40.833	497.526	0.9746
C	2.3	50.593	127.897	0.9559

that the maximum and minimum degradation rate corresponding to degradation temperature also appears in the test samples A and C, respectively, which indicates that metal components with variable-valence state obviously exert an influence on the degradation of NR/clay composite. When ΔT is expressed as the temperature difference of degradation temperature of two out of three test samples listed in Table II, it can be seen that $\Delta T_f > \Delta T_{p2} > \Delta T_{f1} > \Delta T_{p1} > \Delta T_0$, which indicates that as the temperature rises, the promoting action of the metal components with variable-valence state on oxidative degradation of the NR/clay composite is more obvious.

The thermooxidative degradation data of test samples were processed, using Coats and Redfern's⁶ equation, and the kinetic parameters of thermooxidative degradation of the test samples were obtained and listed in Table IV.

It can be seen from Table IV, that the activation energy *E* of test sample C is maximum and the activation energy *E* of test sample A is minimum, which indicates that the thermooxidative stability of the test sample A is the poorest during the thermooxidative degradation reaction, and that of the test sample C is the best. This indicates further, that the metal components with variable-valence state accelerate the degradation of rubber hydrocarbon.

CONCLUSIONS

1. The thermodegradation products of NR/clay composite include olefinic hydrocarbon, alkane, and carbonyl compounds from various molecular weight, which is different with pure NR. Following the variation of the heat decomposition temperature, the amount of the heat decomposition gas product of NR/clay composite also varies.

2. All metal components with a variable-valence state such as Cu, Mn, Co, and Fe exert a catalytic action on heat decomposition of NR/clay composite. The metal components promote the decomposition of rubber hydrocarbon to gas olefinic products. The constituents of the thermodegradation product of NR/clay composite varies as the amount of metal components contained in clay increases.
3. The shoulder peak appears clearly by the main peak on the DTG curve of NR/clay composite, but on the DTG curve of pure NR no shoulder peak appears by the main peak. When the amount of the metal components with a variable-valence state such as Cu, Mn, Co, and Fe contained in the clay increases, the initial degradation temperature (T_0), the degradation peak temperature (T_{p1}) and the final degradation temperature (T_{f1}) in first-stage reaction, as well as the degradation peak temperature (T_{p2}) and the last final degradation temperature (T_f) in second-stage reaction of all the test samples more or less shift to the direction of low temperature, and the activation energy *E* of the reaction of the test samples also more or less decreases.

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