Kinetics of the Thermal Degradation and Thermal Stability of Conductive Silicone Rubber Filled with Conductive Carbon Black

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ABSTRACT: The kinetics of the thermal degradation and thermal stability of conductive silicone rubber filled with conductive carbon black was investigated by thermogravimetric analysis in a flowing nitrogen atmosphere at a heating rate of 5°C/min. The rate parameters were evaluated by the method of Freeman–Carroll. The results show that the thermal degradation of conductive silicone rubber begins at about 350°C and ends at about 600°C. The thermal degradation is multistage, in which zero-order reactions are principal. The kinetics of the thermal degradation of conductive silicone rubber has relevance to its loading of conductive carbon black. The activation energies are temperature-sensitive and their sensitivity to temperature becomes weak as temperature increases. In addition, the conductive silicone rubber filled with conductive carbon black has better thermal stability than that of silicone rubber without any fillers. Also, conductive silicone rubber filled with conductive carbon black has better thermal stability than that of silicone rubber filled with the same amount of silica. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1548–1554, 2003

Key words: kinetics (polym.); degradation; conducting polymers; silicones; thermogravimetric analysis (TGA)

INTRODUCTION

Compared with general organic rubber, silicone rubber has outstanding heat resistance. Research on the thermal stability of silicone rubber has attracted considerable attention.[1–8] Kinetic analysis is used to study the process of thermal degradation quantitatively and to determine the mechanism of thermal degradation of silicone rubber. Feng et al.[1] studied the kinetics of the thermal degradation of silicone rubber using polyvinyltetraphenylphenylsiloxane as a crosslinker and determined the rate parameters using the method of Freeman–Carroll. The results manifested why polyvinyltetraphenylphenylsiloxane could improve the thermal stability of silicone rubber. Henry[2] deduced the kinetics of high-temperature degradation of silicone rubber in a silicone oil environment and calculated the activation energy for the process. Zhou et al.[7] reported the effect of dimaleimides in improving the thermal stability of silicone rubber by kinetic analysis.

Conductive silicone rubber, whose conductivity is imparted by the addition of conductive fillers, has been the most popular conductive rubber due to the inherent advantages of silicone. At present, most research on it is focused on the formation of conductive pathways[9,10] and its electrical properties.[11–14] No research on its kinetics of thermal degradation has been found. However, the ever-increasing need for thermally stable conductive composites is creating a demand for more information on the pyrolysis kinetics of such materials. In this article, the kinetics of the thermal degradation of conductive silicone rubber filled with conductive carbon black was studied by thermogravimetric analysis (TGA) in a flowing nitrogen atmosphere at a heating rate of 5°C/min. The method of Freeman–Carroll[15–17] was used to evaluate the rate parameters. To study the effects of conductive carbon black on the thermal stability and the kinetics of conductive silicone rubber, four samples with different loadings of conductive carbon black and one sample with a loading of silica were used.

EXPERIMENTAL

Materials

Methylvinylsilicone gum (M_n, 5.8×10^5; mol content of vinyl group, 0.15%), VXC-72 conductive carbon black, 4 SiO_2 (specific surface area, 176 m²/g, and treated with octamethylcyclotetrasilazane), and 2,5-bis(*tert*-butyl peroxy)-2,5-dimethylhexane (DBPMH), were supplied by the Institute of Medical Apparatus and Instrument of Shandong Province (Jinan, China), Cabot China Ltd. (Shanghai, China), and Chenguang

TABLE I
Formulation and Volume Resistivity of TGA Samples

Sample no.	Silicone gum (wt parts)	Conductive carbon black (wt parts)	DBPMH (wt parts)	Volume resistivity (□ cm)
1	100	0	1.5	—
2	100	20	1.5	253.1
3	100	30	1.5	52.28
4	100	40	1.5	32.76
5	100	40(silica)	1.5	—

Institute of Chemical Industry (Chengdu, China), respectively.

The formulation of the samples and their volume resistivity are listed in Table I. In referring to the literatures,[18,19] materials were compounded and then vulcanized at 170°C for 20 min under 9.8 MPa. The samples were postcured at 190°C for 3 h.

TGA

TGA was carried out using a Rheometric Scientific TGA instrument. Samples were heated at a rate of 5°C/min in an atmosphere of flowing oxygen-free nitrogen from ambient temperature to 700°C.

RESULTS AND DISCUSSION

From the thermogravimetric and derivative thermogravimetric curves, the kinetics of the thermal degradation of conductive silicone rubber can be analyzed. According to the method of Freeman–Carroll, the rate of thermal degradation of a polymer is usually written as[1,20]

$$-dw/dt = kw^n \quad (1)$$
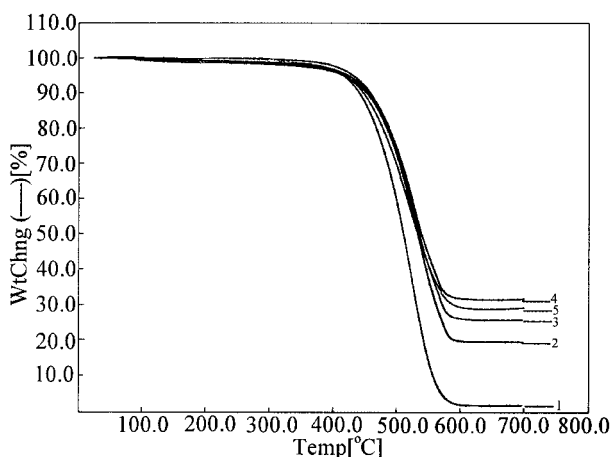
Figure 1 Thermogravimetric curves for the degradation of samples.
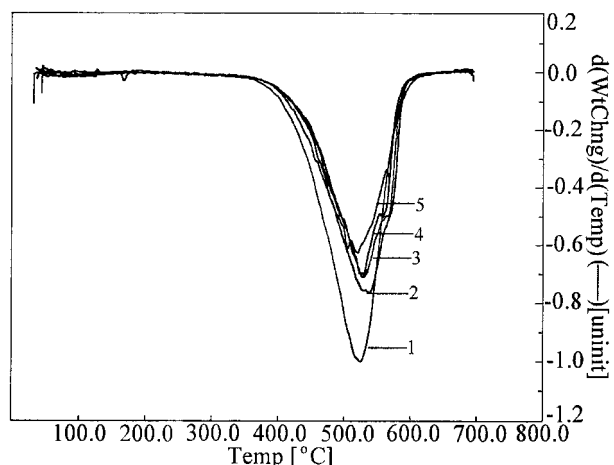
Figure 2 Derivative thermogravimetric curves for the thermal degradation of samples.

where $-dw/dt$ is the rate of thermal degradation; n, the order of the reaction; $w = (w - w_\infty)/(w_0 - w_\infty)$; w_t, the residual weight of the sample at the time t; w_∞, the residual weight of the sample when the thermal degradation is finished; w_0, the weight of the sample at the beginning of thermal degradation; k, the rate constant, which can be written by the Arrhenius equation as

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

where A is the frequency factor; E, the activation energy; R, the gas constant; and T, the absolute temperature. Substituting eq. (2) into eq. (1), we obtain

$$-dw/dt = Ae^{-E/RT}w^n \quad (3)$$

since $dT/dt = 5°C/min$, that is, $dt = dT/5$. Equation (3) can be changed to

$$-dw/dT = (A/5)e^{-E/RT}w^n \quad (4)$$

By making a logarithmic operation on eq. (4), it then becomes

$$\lg(-dw/dT) = n \lg w - E/2.303RT + \lg(A/5) \quad (5)$$

A difference equation will be obtained from eq. (5):

$$\Delta \lg(-dw/dT) = n \Delta \lg w - (E/2.303R) \Delta(1/T) \quad (6)$$

It can be seen from eq. (5) that if a linear relationship is obtained when $\lg(-dw/dT)$ is plotted against $1/T$ the order of the reaction is zero and the activation energy can be determined from its slope. If the order of reaction, n, is not zero, it and the activation energy can be determined by taking $\Delta(1/T)$ as a constant in eq. (6) and the linear relationship between $\Delta \lg(-dw/dT)$ and

TABLE II
Information About the Maximum Rates of the Thermal Degradation of Samples

Sample no.	Temperature (°C)	$-dw/dT$ (min^{-1})	w_t (%)
1	524.87	0.99968	36.163
2	538.11	0.76223	46.124
3	528.22	0.71067	55.327
4	529.84	0.70083	56.066
5	520.56	0.62556	57.342

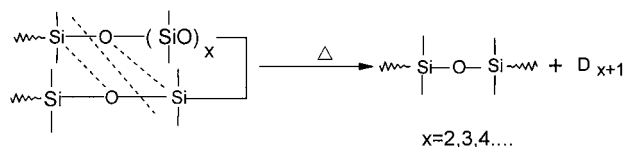Δ 1 g w. In this article, $\Delta(1/T)$ was taken at equal intervals of 10^{-6} k^{-1}.

As for unvulcanized silicone rubber, degradation of siloxane chains will occur in nitrogen at high temperature in two of the following ways[21–23]:

a. Degradation of siloxane chains initiated by the terminal group:
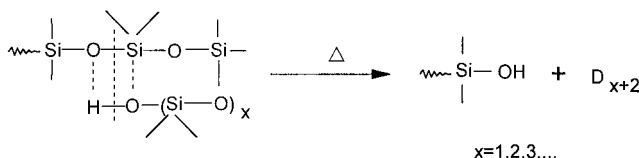
b. Degradation of the main chains of siloxane:

Here, D_3, D_4, and D_5 stand for hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and decamethylcyclopentasiloxane, respectively. For conductive silicone rubber, crosslinking can prevent the siloxane chains of silicone rubber from degradation at high temperature to a certain extent, and the addition of conductive fillers can also have influence on the degradation of the siloxane chains. In addition, the thermal weight loss of conductive silicone rubber also includes the thermal volatilization of low boiling point compounds remaining in the silicone gums during their preparation. Therefore, the thermal degradation

TABLE III
Temperatures (°C) at Different Weight Loss of Samples

| Sample no.	Temperature at 5% weight loss	Temperature at 10% weight loss	Temperature at 50% weight loss
1	416.64	441.33	510.33
2	432.69	458.51	532.69
3	418.79	453.18	535.59
4	425.84	457.21	539.38
5	419.11	447.97	533.03
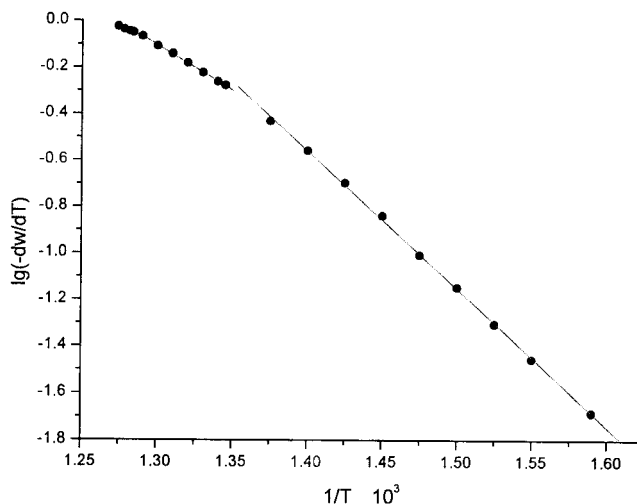
Figure 3 Kinetics of the thermal degradation of sample 1.

mechanisms of conductive silicone rubber are very complicated.

The thermogravimetric curves for the thermal degradation of samples are shown in Figure 1. It can be found from Figure 1 that an apparent weight loss appears after 350°C. For sample 1, the weight loss is relatively rapid between 380 and 600°C and most weight loss of the sample occurs in this temperature range. For samples with fillers, rapid weight loss moves to higher temperatures and occurs over the temperature interval of 400–600°C. The final residual weight of the samples depends on their loadings of fillers. Besides, the thermogravimetric curve of sample 5 is below that of sample 4. This means the weight loss of silicone rubber filled with silica is more than that of silicone rubber filled with the same amount of conductive carbon black at the same temperature.

Figure 2 gives the first derivatives of the primary thermogravimetric curves as a function of the temper-
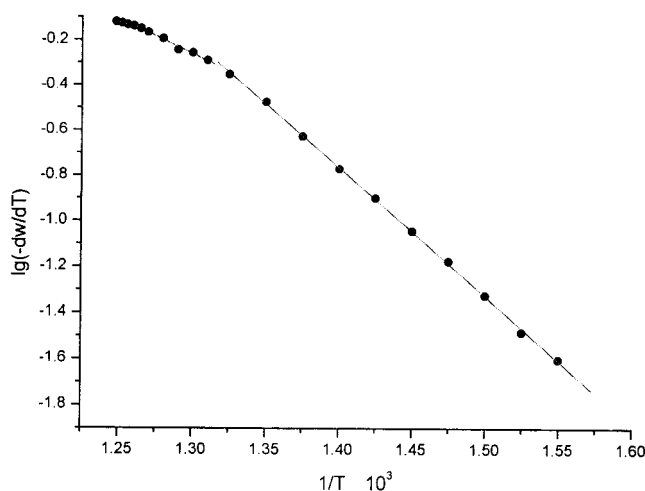
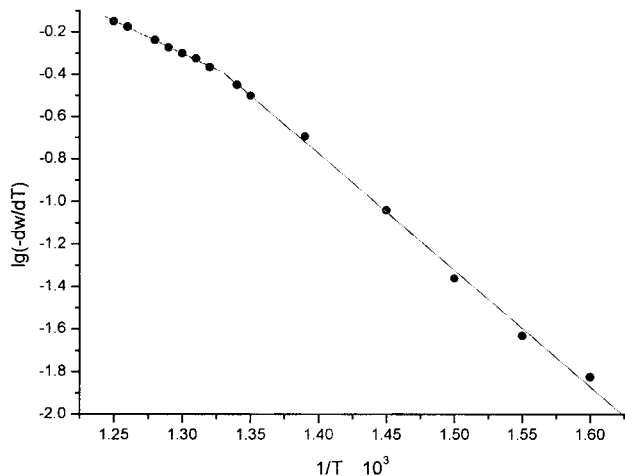**Figure 4** Kinetics of the thermal degradation of sample 2.

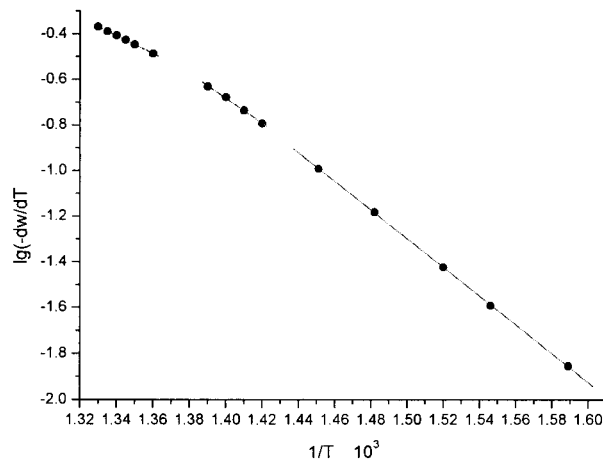**Figure 5** Kinetics of the thermal degradation of sample 3.

Figure 7 Kinetics of the thermal degradation of sample 5.

ature, which illustrates how the rate of thermal degradation changes as the temperature changes. From Figure 2, it can be found that below 380°C the rates of thermal degradation of the five samples are all small. After 380°C, the rates of thermal degradation increase rapidly as the temperature increases until the maximum rates are reached. The main thermal degradation of the samples occurs in this temperature range. After reaching the maximum rate of degradation, decomposition is slow again until it is finished above 600°C. It is obviously shown by Figure 2 that the rate of the thermal degradation of sample 1 is higher than those of other samples in the main course of thermal degradation. In addition, the rate of the thermal degradation of sample 5 is higher than that of sample 4 with the exception of the maximum rate. The maximum rates of the thermal degradation of the samples and the corresponding temperatures and the residual weights were found from the TGA data and are listed in Table II. From the data in Table II, it can be found that the maximum degradation rate of the samples decreases as the loading of conductive carbon black increases

and the temperatures corresponding to the maximum degradation rate of the conductive silicone rubber are higher than that of the silicone rubber without the loading of conductive carbon black. Sample 5, filled with 40 wt parts of silica, has the lowest temperature corresponding to the maximum degradation rate and the smallest maximum degradation rate as well.

Considering all the above-mentioned, it can be concluded that conductive silicone rubber has better thermal stability than that of general silicone rubber. This may be due to two reasons: First, the addition of conductive carbon black increases the rigidity of siloxane chains and thus hinders the degradation of siloxane chains caused by heat rearrangement to a certain extent. Second, in the course of mixing silicone gum and conductive carbon blacks, some of siloxane bonds may be opened by mechanical power and macromolecular free radicals may be formed.[24] Chain reactions of these macromolecular free radicals can be ended on
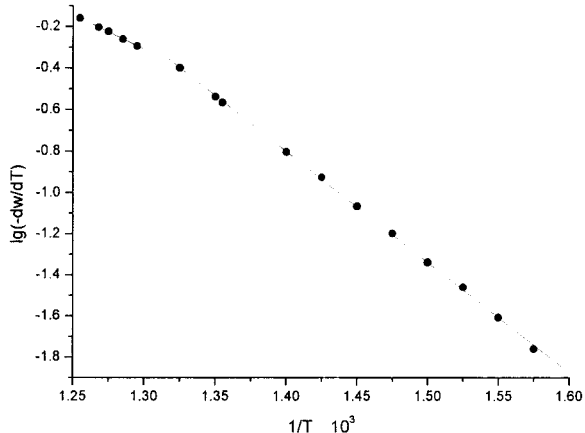

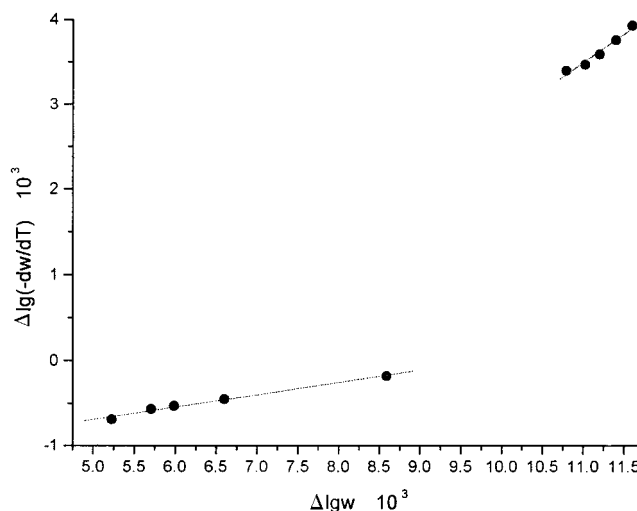**Figure 6** Kinetics of the thermal degradation of sample 4.

Figure 8 Kinetics of the thermal degradation of sample 1 in sectional temperature range.

TABLE IV
Kinetic Parameters for the Thermal Degradation of Samples

1	T	355–467	470–505	506–514	517–530	533–547
	N	0	0	0	0.145	0.648
	E	111.8	73.33	48.25	27.19	70.84
	W	98.7–80.3	78.8–54.7	54.0–46.6	43.6–31.1	27.9–16.6
	K	0.020–0.494	0.524–0.888	0.894–0.965	0.982–0.975	0.946–0.723
2	T	352–482	490–517	520–528		
	N	0	0	0		
	E	107.6	58.59	31.21		
	w_t	99.1–81.5	77.7–61.5	59.4–53.6		
	K	0.025–0.447	0.511–0.705	0.723–0.756		
3	T	352–473	478–527			
	n	0	0			
	E	103.9	59.36			
	w_t	97.8–84.4	82.6–56.0			
	K	0.015–0.355	0.393–0.709			
4	T	352–496	499–524			
	n	0	0			
	E	101.8	64.72			
	w_t	98.5–76.1	74.7–60.0			
	K	0.016–0.499	0.507–0.697			
5	T	351–421	426–451	457–484		
	N	0	0	0		
	E	120.4	104.1	75.25		
	w_t	98.1–94.7	94.1–89.2	87.5–77.4		
	K	0.014–0.125	0.138–0.259	0.305–0.462		

T, °C; E, kJ/mol; w_t, %; K, min^{-1}.

carbon blacks since carbon blacks are accepters of free radicals. Furthermore, more than one free radical can be ended on the same particle of carbon black. Thus, carbon gels with a structure of three-dimensional space are formed. This can also hinder the degradation of siloxane chains caused by heat rearrangement to a certain extent. So, conductive silicone rubber loaded with conductive carbon black has better thermal stability than that of general silicone rubber. More information on the weight loss of the samples is given in Table III. It can be found from Table III that prior to 400°C the total weight loss of the conductive silicone rubber was less than 5%, and a 10% weight loss appears between 440 and 450°C. When the temperature is above 520°C, the weight loss of conductive silicone rubber is over 50% and decomposition is severe. In comparison with sample 4, sample 5 has higher temperatures corresponding to the three weight losses. This is in agreement with the conclusion made above. The kinetics of the reaction were evaluated from the thermogravimetric and derivative thermogravimetric curves shown in Figures 1 and 2 by the method of Freeman–Carroll.

As shown by Figures 3–7, a series of linear relationships was obtained when $\lg(-dw/dT)$ was plotted against $1/T$. It is known from eq. (5) that, in this circumstance, the orders of the reaction are all zero and the activation energies in every temperature range were determined from the slopes and are listed in Table IV. In the temperature range near the maximum rates of the thermal degradation of the five samples, the orders of the reaction are not zero. As for blank silicone rubber, there is a linear relationship between $\Delta \lg(-dw/dT)$ and $\Delta \lg w$, which is shown by Figure 7. The order of the reaction and the activation energy were determined from the slope and the intercept, respectively. The results are also listed in Table IV. The reaction orders in the two temperature ranges are between zero and one. The maximum degradation rate is included in the temperature range of 517–530°C and the corresponding activation energy is the smallest one of the sample. As for conductive silicone rubber, in the temperature ranges near the maximum degradation rates, the thermal decomposition is too complicated to conform to either eq. (5) or eq. (7) and the kinetics could not be obtained by the method of Freeman–Carroll. However, it can be found from Table IV that these temperature intervals without kinetic parameters are all very narrow, and the temperature ranges of sample 2, sample 3, and sample 4 are 543–574°C, 533–564°C, and 533–553°C, respectively. This is also the case for sample 5.

Thermal degradation of a composite is very complicated. A certain activation energy does not mean a simple basic degradation reaction. In fact, it is a combination of several kinds of reactions. One reaction may be principal and others may be secondary. Thus,

the evaluated activation energy is apparent and statistical.

From Table IV and Figures 3–7, it can be found that the thermal degradation of the samples are all multistage, in which zero-order reactions are principal. This means that the kinetics of the thermal degradation of both blank and conductive silicone rubber has relevance to the temperatures, and in most temperature ranges, the rates of degradation are independent of w, the residual percentage of the weight loss of the samples. The initial thermal degradation of blank silicone rubber begins at 355°C and ends at 467°C, and the activation energy is 111.8 kJ/mol. As for conductive silicone rubber loaded with 20, 30, and 40 wt parts of conductive carbon black, the initial thermal degradation occurs over the temperature ranges of 352–482°C, 352–473°C, and 352–496°C, respectively. The activation energies for the initial thermal degradation of the three samples of conductive silicone rubber are 107.6, 103.9, and 101.8 kJ/mol, respectively. In the case of silicone rubber filled with 40 wt parts of silica, the initial thermal degradation occurs over the temperature range of 351–421°C and the activation energy is 120.4 kJ/mol, which is slightly higher than that of the other samples.

In comparing the kinetic parameters for the initial thermal degradation of the four samples, it can be found that the initial thermal degradation of conductive silicone rubber begins at a lower temperature and the corresponding activation energy is also smaller than that of blank silicone rubber. This may be due to the acidic groups on the surface of carbon black, such as carboxyl and phenol groups, which can promote the degradation of siloxane chains. So, as the loading of conductive carbon black increases, the activation energy for the initial thermal degradation of conductive silicone rubber decreases. Because the amount of these acidic groups is very small, therefore, the influence is also very slight. Since the silica filled in sample 5 was treated with octamethylcyclotetrasilazane, the influence of Si—OH on the thermal stability of silicone rubber was diminished to a certain extent. However, the activation energies for the initial thermal degradation of the five samples are much less than is the bond energy of the siloxane bond of 422.5 kJ/mol.[25] This suggests that thermal degradation is governed mainly by the molecular structure and not by bond energies. It is possible that the silicon atom in the polymer utilizes its vacant $3d$ orbitals to form energetically favorable transition states. A way is then opened for a low-energy reaction path of decomposition.[22]

The initial thermal degradation of the samples has the widest temperature range and the highest activation energy among the overall decomposition process. Meanwhile, the degradation rate and the weight loss are all small in this temperature range. As temperature increases, the thermal degradation is more and more

rapid until the maximum rate is reached (see Table II). At that time, the temperatures are near 530°C (as for sample 2, it is even as high as 538°C) and the total weight loss of the five samples corresponds to 64, 54, 45, 44, and 43% of the initial weight of the samples, respectively, which decreases as the weight percent of the filler increases. All in all, up to these points, most decomposition has occurred. In the meantime, the orders of the reaction are not zero. Afterward, the orders of the reaction become zero again and the reactions slow. The evaluated activation energies become negative numbers and are meaningless. In fact, at that time, a very high temperature is reached. For sample 1, the corresponding temperature is 550°C, and for the three samples of conductive silicone rubber, the corresponding temperatures are 543, 533, and 533°C, respectively. The silicone rubber almost decomposes completely at such high temperature.

In the overall decomposition process, the activation energies are not constant and are temperature-sensitive. Generally, they change from big to small. This means the difference in energy between activated and general molecules becomes small as temperature increases, namely, the thermal degradation of conductive silicone rubber proceeds easily as temperature increases. In addition, according to the differential form of the Arrhenius equation,[26]

$$d \ln k/dT = E/RT^2 \qquad (7)$$

a smaller activation energy means a smaller change of the rate constant with temperature. In other words, as temperature increases, the rate constant for the thermal degradation of conductive silicone rubber changes little as the temperature changes.

CONCLUSIONS

The thermal degradation of conductive silicone rubber began at 352°C and ended at about 600°C. The activation energies for the initial thermal degradation of conductive silicone rubbers loaded with 20, 30, and 40 weight parts of conductive carbon black were 107.6, 103.9, and 101.8 kJ/mol, respectively, which were all smaller than that of the general silicone rubber. The thermal degradation of conductive silicone rubber is multistage, in which zero-order reactions are principal. The activation energies are temperature-sensitive and their sensitivity to temperature becomes weak as temperature increases. The activation energy changes from large to small and, in the meantime, the rate of the thermal degradation changes from slow to rapid until the maximum ones are reached. Then, the evaluated activation energies become negative numbers and the rates become small again until the decomposition is finished. Compared with general silicone rub-

ber, conductive silicone rubber has better thermal stability.

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