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AN INVESTIGATION OF THE THERMODEGRADATION OF ABLATIVE
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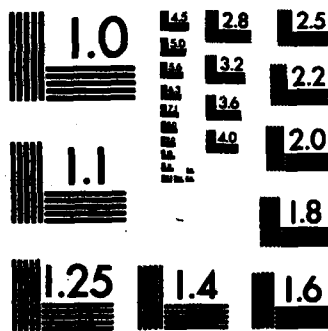
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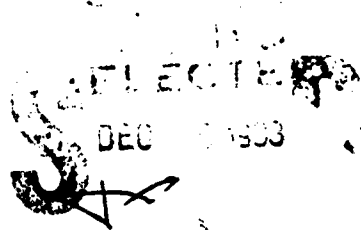
FOREIGN TECHNOLOGY DIVISION



AN INVESTIGATION OF THE THERMODEGRADATION
OF ABLATIVE ORGANIC SILICON RESIN

by

Sun-Wei Jun



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An Investigation of the Thermodegradation of Ablative Organic Silicon Resin*

Sun Wei Jun

[ABSTRACT] The GS-401 resin is a kind of high performance ablative material with an excellent thermal stability, a low weight loss under heat and with a high char yield ratio.

We have applied the TG, DTA and IR methods to examine the reaction of thermodegradation of the GS-401 ablative organic silicon resin. The results of our experiments show that the thermodegradation reaction of this kind of resin can be divided into several stages; the apparent activation energy as well as the order of reaction associated with each stage are different from those associated with other stages. Throughout the entire thermodegradation process, the methyl is always more stable than the benzol.

I. Introduction

In the past, we have already reported the results of our experiments concerning the high performance organic silicon ablative thermal insulation materials. The synthesized GS-401 ablative organic silicon resin has many characteristics, such as a high char yield ratio, a smooth and hard char layer, a good resistance against high pressure, a good resistance against

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high speed gas flow scouring, a good ablative thermal insulation property, a relatively low solidification temperature, can be dissolved in alcohol, can be firmly attached to base materials and requires only simple installation technology. It has overcome many deficiencies associated with the common organic silicon resin, such as the apparent plasticity under high temperature, low char yield ratio, loose structure of the char layer and poor resistance against scouring. With its superior characteristics, we can now apply this resin for the purpose of ablative thermal insulation under the conditions of high heat flow and high velocity shear. This is clearly an advancement from the situation in the past when organic silicon resin was only applied as an ablative thermal insulation material under the conditions of low heat flow and low velocity shear.

In order to explore the relationship between the ablative property of the organic silicon resin and the reaction of thermodegradation under high temperature, we have examined the thermodegradation reaction associated with the GS-401 organic silicon resin. A substantial amount of work has been conducted in the past concerning the dynamics of the thermodegradation reaction of the organic silicon and numerous reports were made such as those involving the silicon rubber^[1~4], the ladder-shaped compounds^[5~6], the tri-functional organic silicon^[7] and the metallic organic silicon oxyalkane^[8]. K.A. Anprianov et al have examined the thermodegradation reaction of pure methyl silicon

resin with functional degrees of $2.5 \sim 3.5$ ^[9]. There are, however, relatively few reported investigations concerning the more complicated thermodegradation reaction involving the methylbenzol organic silicon resin. There has also been no report concerning the research of the thermodegradation reaction of the ablative organic silicon resin.

We have applied the method of interrupted procedural temperature increase to measure the thermal weight loss and hence obtained the TG curve. We then applied the improved Freeman-Carroll differential-difference method^[10] to obtain the dynamic parameters. We have also measured the char yield ratio and analyzed the process of the thermodegradation reaction by using the differential thermal analysis and the infra red spectrum. The results obtained from these three methods are consistent with each other. The experimental results indicate the following characteristics associated with the thermodegradation reaction of the GS-401 organic silicon resin: the thermal stability of methyl is higher than that of the benzol, the thermal stability of the main chain is high and the char yield ratio is high. These characteristics show that GS-401 resin has relatively good ablative properties.

II. Experiment Section

MATERIAL The material used here is the GS-401 ablative

organic silicon resin. Its general equation is:



It was obtained from organic chlorine silicon alkane through hydrolysis and aggregation. Its properties are listed in Table 1.

1	性 质	6	指 标
2	外 观	7	白色或淡黄色粘稠液体
3	粘度 (秒) (80%甲苯溶液, 20±2°C, 4号粘度计)		50~100
4	挥发物 (%)		< 8
5	凝固 (200±2°C) (秒)		180~300

Table 1. The properties of the GS-401 organic silicon resin.

1. property 2. exterior appearance 3. viscosity (s)
 (80% methylbenzene solution, 20±2°C, number 4 viscosity
 meter) 4. volatile substance 5. aggregation speed
 (200±2°C) (s) 6. index 7. white or light yellow viscous
 liquid

PREPARATION OF SPECIMEN After the resin was solidified, it was treated for 3 hours at 220°C and then pulverized into fine particles with size < 80 mesh.

INSTRUMENTS AND METHODS The thermal analysis was conducted by using the model CFS-II differential thermal analysis meter (air atmosphere) and the model CDR-1 differential dynamic

thermal analysis meter (nitrogen atmosphere). The reference material is α - Al_2O_3 . The rate of increase of temperature during the differential thermal analysis was $10^\circ\text{C}/\text{minute}$; the recording speed was 300 mm/hour. The TG curve was constructed by using the above mentioned instruments with a rate of temperature increase equal to $10^\circ\text{C}/\text{minute}$; the weight loss at each point was measured by using the interruption method. The specimen used for the measurement all came from the same batch of very evenly mixed specimens. The weight of the specimen used by the CFS-II differential thermal analysis meter was 100 mg while that used by the CDR-1 differential dynamic thermal analysis meter was 10 mg. Corresponding to each weight loss data point and each point in the TG curve, we have also measured the infra-red spectrum for each of the specimens used in the thermodegradation experiments. The infra red measurements were conducted by using the IR-27 infra red spectrophotometer. After the specimen used in the thermodegradation experiments underwent weight loss, we then mixed the specimen with dry KBr. We subsequently pulverized this mixture, pressed it into a thin plate and then selected 7.9 micro meter and 6.9 micro meter for the computation of the ratio between the methyl and the benzol which linked with Si.

The general dynamical equation is usually the basis for examining the thermodegradation reaction of molecules with high molecular weight through the TG method. This is to say that we will be using the reaction speed equation

$$-\frac{dw}{dt} = Kw^n \quad (1)$$

and the Arrhenius equation $K = Ae^{-E/RT}$ (2)

Or we can express them as: $-dw/dt = Ae^{-E/RT}w^n$ (3)

in order to obtain the parameters n (the order of reaction), E (the apparent activation energy) and A (factor before the exponential expression). There has been a series of publications concerning the computation of these dynamical parameters since 1958. The most important ones are the Freeman-Carroll differential-difference method [10-11], the Reich turning point maximum speed method [12], the double TG curve method [13], the Doyle TG differential equation method (series expansion method) [14] and the improved Doyle equation proposed by Papkov-Slonimskiy [15]. All these methods have their strong points and their weak points. For relatively complicated thermodegradation reaction, the thermodegradation process can proceed within a relatively wide range of temperatures and there will exist conditions associated with different stages (corresponding to different thermodegradation process). Under these circumstances the application of the Freeman-Carroll differential-difference method is more appropriate than the other methods so this particular method was applied during the present study.

By taking the logarithm of equation (3) and linearizing it we can obtain $\lg\left(-\frac{dw}{dt}\right) = n \lg w - \frac{E}{2.3RT} + \lg A$ (4)

Since we have applied the procedural temperature increase method, the $1/T$ in equation (4) is a variable. By differentiating with

respect to it, we can obtain

$$d \left[\lg \left(-\frac{dw}{dt} \right) \right] = n (d \lg w) - \frac{E}{2.3R} d \left(\frac{1}{T} \right) \quad (5)$$

After converting equation (5) into the form of a difference equation, we have

$$\Delta \lg \left(-\frac{dw}{dt} \right) = n \Delta \lg w - \frac{E}{2.3R} \Delta \left(\frac{1}{T} \right) \quad (6)$$

When $\Delta(1/T)$ is a constant, we can construct a figure based on equation (6) with $\Delta \lg(-dw/dt)$ corresponding to $\Delta \lg w$. From the slope of this curve we can obtain the order of the reaction n and from the intercept we can obtain the activation energy E .

It is obvious that the smaller $\Delta(1/T)$ is the more accurate the result is going to be. Here we set $\Delta(1/T) = 1 \times 10^{-5} (^{\circ}\text{K})^{-1}$.

The reaction speed $-dw/dt$ of the thermodegradation process can be obtained from the first derivative of the original weight loss curve. This is to say that the reaction speed is the tangential value at each point along the curve.

The concentration of the reactant should not be the total weight of the specimen. It should be w : $w = W - W_c / W_s - W_c$. In this equation W is the instantaneous weight of the specimen during the reaction, W_c is the weight of the specimen at the end of the thermodegradation reaction and W_s is the weight of the specimen at the beginning of the thermodegradation reaction.

III Results and Discussion

The thermal weight loss curves of the GS-401 organic silicon resin in the air as well as in the nitrogen are shown in Figure 1.

Based on the original weight loss data set, we have obtained the first order differential quotient and then separately obtained the speed of the thermodegradation reaction in the air as well as in nitrogen. The degradation of the organic compound which was chain-linked to the silicon atom was the main reason for causing the weight loss since this kind of organic silicon resin will be converted into silicon dioxide, carbon and other volatile gases after the thermodegradation process. This is especially true for methyl. This is why the concentration of the reactant is the ultimate weight loss, not the total weight of the specimen. By using the ultimate weight loss as the initial concentration of the reactant and by treating the original weight loss curve based on the equation $w = W - W_c / W_s - W_c$, we can obtain the relationship between absolute temperature and the speed of the thermodegradation reaction and between the absolute temperature and the weight loss in the air as well as in nitrogen, as shown in Figure 2 and Figure 3. By setting $\Delta(1/T) = 1 \times 10^{-5}$, we can obtain the relationship between $\Delta \lg(-dw/dt)$ and $\Delta \lg w$ from Figure 2 and Figure 3 through equation (6). These curves are also called the dynamical curves and they are shown in Figure 5 and Figure 8. The speed of the thermodegradation reaction and $1/T$ has a linear relationship in the air for temperatures within $282 \sim 412^\circ\text{C}$ and $547 \sim 727^\circ\text{C}$. This linear relationship also exists in nitrogen for temperatures within $347 \sim 576^\circ\text{C}$ and $595 \sim 679^\circ\text{C}$. In other words, the order of reaction

$n=0$ under these conditions. The dynamical curves are shown separately in Figures 4,6,7 and 9.

Based on these dynamical curves we have computed the various orders of the reactions and the activation energies as well as their corresponding weight loss and speed of the thermodegradation reaction. These data sets are shown in Table 2. We can see from the data sets in Table 2 that during the entire thermodegradation process of the GS-401 resin, the activation energy and the order of reaction did not remain as just two constant values. Under different temperature ranges the corresponding activation energy and the order of the reaction were also different. This proves that the thermodegradation reaction of the GS-401 resin was extremely complicated and there existed several reaction processes as well as several values of the activation energies over a wide range of temperatures. We can not apply the method of just taking a simple average of the activation energies associated with various stages to describe such a complicated system and process. It is also inappropriate to apply the turning point maximum speed method.

From the results of the IR and DTA analyses (Table 3 and Table 4) we can see that even for the same activation energy, the corresponding thermodegradation reaction was not a simple basic reaction. It actually represented a mixture of several reactions. Corresponding to a certain specific activation energy, the reaction could include the beginning of a certain

degradation reaction, the end of another degradation reaction, the peak of yet another reaction and so on. This is why the activation energy obtained was superficial and stochastic. The determination of the activation energy is still meaningful, however, since we can still use its magnitude to judge and evaluate

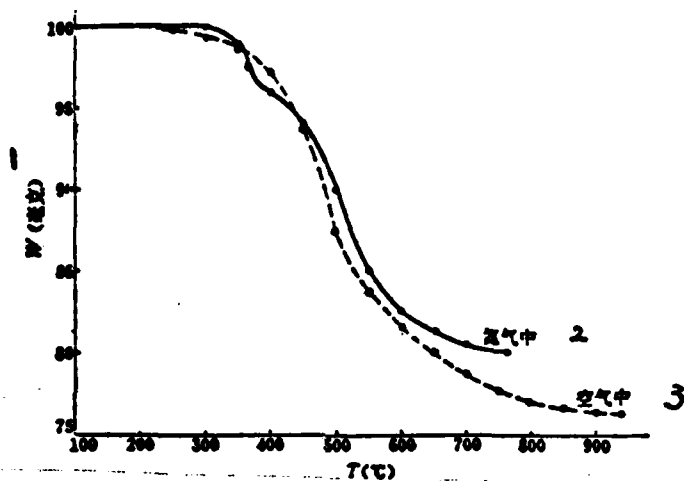


Figure 1. The weight loss curve of the GS-401 resin in the air and in nitrogen.

1. W (mg) 2. in nitrogen 3. in the air

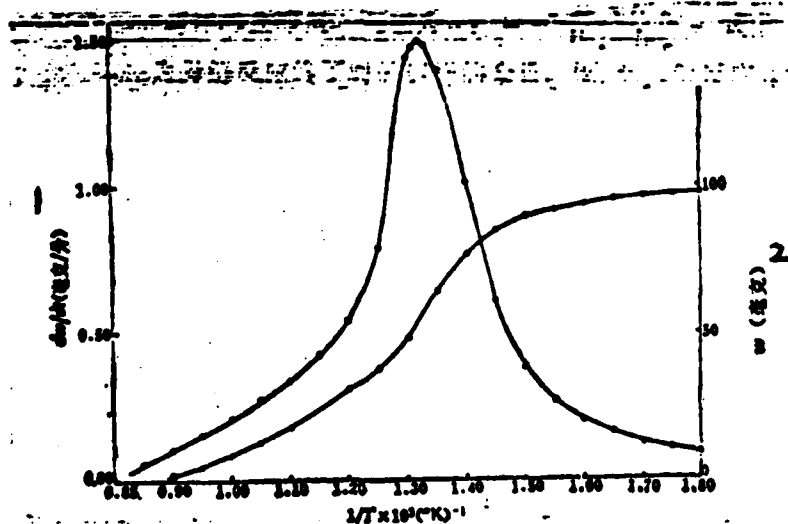


Figure 2. The relationship between temperature and the speed

of the thermodegradation reaction of the GS-401 resin in the air.

1. dw/dt (mg/minute) 2. w (mg)

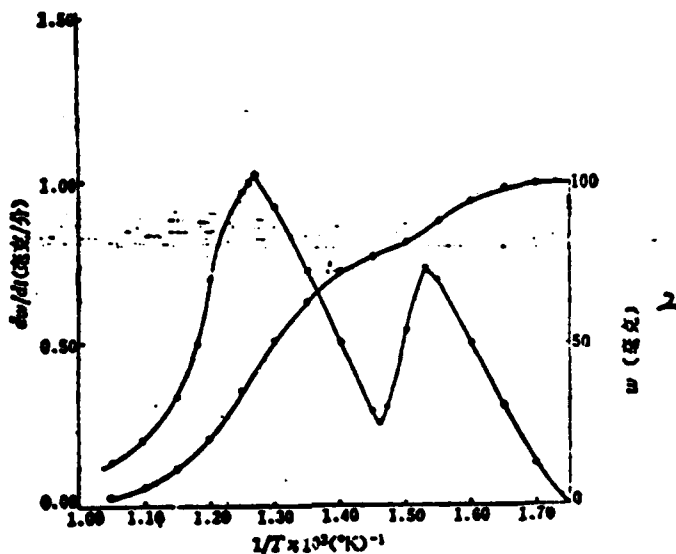


Figure 3. The relationship between temperature and the speed of the thermodegradation reaction of the GS-401 resin in nitrogen.

1. dw/dt (mg/minute) 2. w (mg)

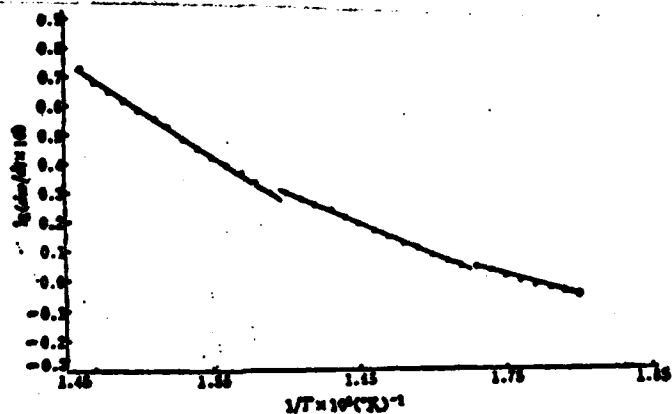


Figure 4. The dynamical curve representing the degradation

of the GS-401 resin in the air with a temperature range of 282~412°C.

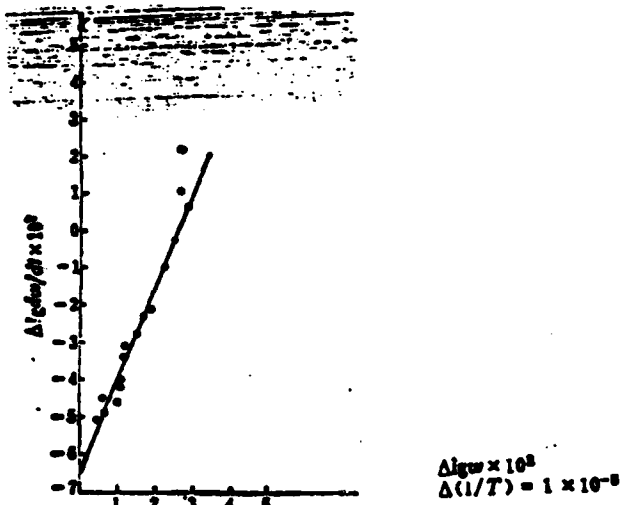


Figure 5. The dynamical curve representing the degradation of the GS-401 resin in the air with a temperature range of 412~496°C.

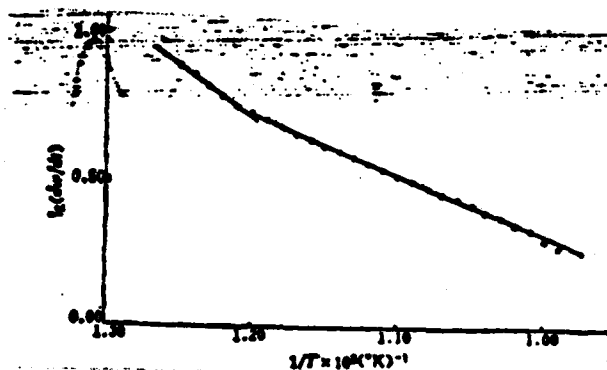


Figure 6. The dynamical curve representing the degradation of the GS-401 resin in the air with a temperature range of 547~727°C.

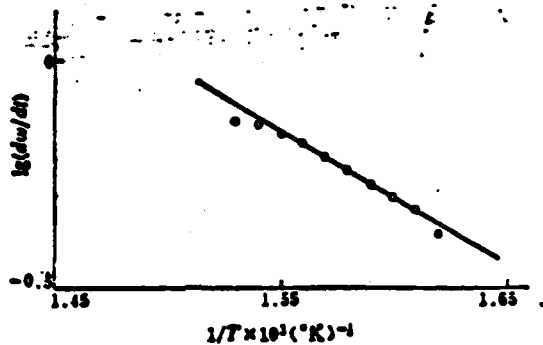


Figure 7. The dynamical curve representing the degradation of the GS-401 resin in nitrogen with a temperature range of 347~376°C.

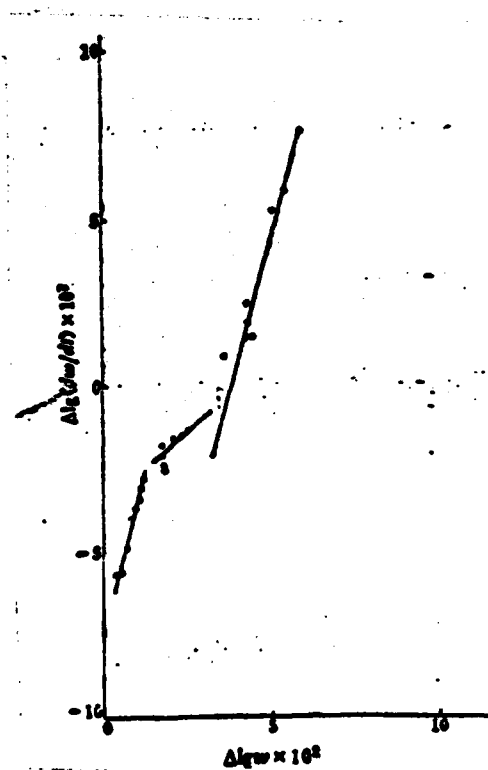


Figure 8. The dynamical curve representing the degradation of the GS-401 resin in nitrogen with a temperature range of 412~588°C.

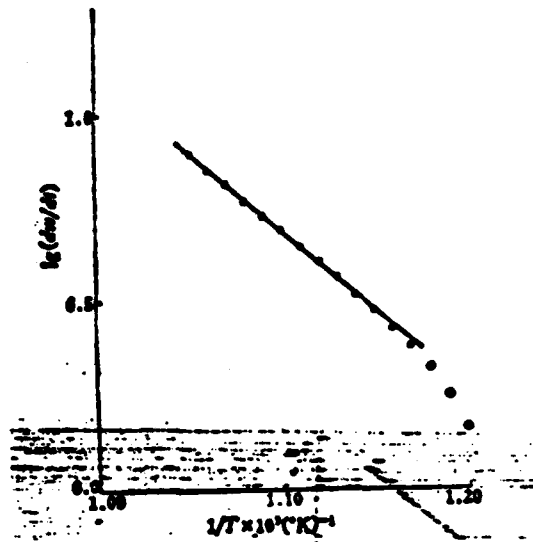


Figure 9. The dynamical curve representing the degradation of the GS-401 resin in nitrogen with a temperature range of 595 ~ 679°C.

I. 空气介质

温度(°C)	302~304	307~351	356~407	407~491	527~560	567~727	>727
反应级数 ⁿ	0	0	0	2.5	0	0	—
表观活化能E ^a (千卡/克分子)	0.48	0.61	14.73	30.28	16.47	9.15	—
失重(%)	0.48~0.80	0.80~1.40	1.50~2.20	2.20~11.40	14.90~16.60	16.80~20.90	20.90~23.70 (940°C)
降解速度(毫克/分)	0.09~0.106	0.11~0.20	0.21~0.54	0.54~1.47 max1.49	0.79~0.94	0.51~0.20	<0.20

II. 氮气介质

温度(°C)	<347	347~376	412~456	462~502	508~598	595~679	>679
反应级数 ⁿ	—	0	3.5	0.8	3.5	0	—
表观活化能E ^a (千卡/克分子)	—	12.20	25.17	15.74	64.06	19.16	—
失重(%)	<1.00	1.00~3.20	4.40~6.80	6.80~10.30	11.20~17.20	17.40~19.60	19.60~20.00 (775°C)
降解速度(毫克/分)	<0.42	0.45~0.72	0.25~0.64	0.68~0.95	0.98~0.38 max1.62	0.34~0.13	<0.13

Table 2. The dynamical parameters associated with the various stages during the thermodegradation process of the GS-401 resin.

- I. air medium 1. parameter 2. temperature 3. order of the reaction
 4. apparent activation energy (Kcal/g molecule)
 5. weight loss 6. speed of the degradation reaction (mg/minute)
- II. nitrogen medium 7. parameter 8. temperature 9. order of the reaction
 10. apparent activation energy (Kcal/g molecule)
 11. weight loss 12. speed of the degradation reaction (mg/minute)

1 热解温度 (°C)		正常值	400	500	600	700	750	800
2 甲基与苯基之比	空气	正常值°	3.20	~6.00	~	~	~	~
	氮气	正常值°	3.00 (420°C)	~6.00	~	~	~	~
3 甲基	空气	+	+	+	+	+	+	-
	氮气	+	+	+	+	+	(775°C)	=
4 苯基	空气	+	+	+	-	-	-	-
	氮气	+	+	+	-	-	(775°C)	=
5 样品外观颜色	空气	白	白	浅黄	黄	黑、光亮	黑、光亮	黑、光亮
	氮气	白	白	浅黄	黄	黑、光亮	黑、光亮	(775°C)
6 失重 (%)	空气	0.00	2.50	19.00	18.40	21.40	22.30	23.10
	氮气	0.00	4.10	10.00	17.20	19.50	20.00 (775°C)	=

33 • 正常值：指是技术条件规定的某一具体值。

34 • 表示无数据计算；=表示未进行测定；+表示存在；-表示消失。

Table 3. Results obtained from conducting the IR spectral analyses on the GS-401 organic silicon resin.

1. temperature of thermodegradation 2. ratio between methyl and benzol
 3. methyl 4. benzol 5. exterior color of the

specimen 6. weight loss 7. air 8. nitrogen 9. air
 10. nitrogen 11. air 12. nitrogen 13. air 14. nitrogen
 15. air 16. nitrogen 17. room temperature 18. normal value*
 19. normal value* 20. white 21. white 22. white 23. white
 24. light yellow 25. white 26. orange yellow 27. light yellow
 28. dark, with luster 29. orange yellow 30. dark, with luster
 31. dark, with luster 32. dark, with luster 33. * normal
 value: a certain specific value which satisfies the regulations
 of the technical conditions. 34. ~ represents unable to
 compute; = represents no measurement; + represents the existence
 of the substance; - represents the vanishing of the substance.

1 反应阶段	1	2	3	4	5	6	7	8	9	10		
2 峰的温度区间(°C)	3 空气	<295	295~	350~	400~	497~	530~	585~	610~	660~	700~	>750
		-ΔH	ΔH	ΔH	ΔH	ΔH	ΔH	ΔH	ΔH	-ΔH	ΔH	-ΔH
. 峰特征**	4 氮气	<345	345~	370~	474~	450~	510~	550~	590~	>750		
			ΔH	ΔH	ΔH	ΔH	ΔH	ΔH	ΔH	-ΔH	-ΔH	

5. 峰的温度区间给出了起始温度和终止温度值。

6. 峰的特征给出了吸热还是放热情况。ΔH表示放热，-ΔH表示吸热。

Table 4. Results obtain from the DTA analyses.

1. stage of reaction 2. temperature range*(°C) and its
 characteristics** 3. air 4. nitrogen 5. * the temperature
 range for the peak gives both the initial and the final temperature
 values 6.** the characteristics of the peak indicate whether

heat is being absorbed or being released. ΔH represents heat release and $-\Delta H$ represents heat absorption.

the thermal stability of the compound. We can see from both the curve and the data set that the stage which exerted the greatest influence on the entire thermodegradation process should be the stage with a relatively large variation in the speed of the thermodegradation reaction $-dw/dt$. In the air medium, the thermodegradation reaction occurring at a temperature range of $400\sim 500^{\circ}\text{C}$ has the greatest influence on the entire thermodegradation process. In nitrogen medium, the thermodegradation reaction occurring at a temperature range of $500\sim 600^{\circ}\text{C}$ has the greatest impact on the entire process. This is why it is relatively more appropriate to use the activation energy associated with this stage of the thermodegradation reaction (30.08 Kcal/ g molecule and 64.06 Kcal/g molecule, respectively) to represent the activation energy of the entire process. We can see from the data sets in Table 2 that the thermal stability of the GS-401 organic silicon resin was higher in nitrogen than in the air. This is due to the fact that the progression of the thermodegradation reaction was made more easily by the oxygen in the air. We should note, however, that the interior of a solid rocket propeller is basically an anoxic environment so the degradation condition in nitrogen is even closer to the working environment within the rocket propeller than that in the air. The measured activation energy

of the GS-401 organic silicon resin in nitrogen was 64.06 Kcal/g molecule. This value is higher than the values in the published literature concerning the activation energy of the heat resisting organic silicon resin during the thermodegradation process. V. A. Chubarov et al^[7] have used the Freeman-Carroll method to treat the TG data set obtained from the tri-functional benzol methyl organic silicon resin with a general equation of $[RSiO_{3/2}]_n$ and they have obtained activation energies of between 12~16 Kcal/g molecule.

We can see from the results of the infrared analysis (Table 3) that under low temperature ($< 400^{\circ}C$) the Me/ph value of the resin (the ratio between the methyl and the benzol) remained basically unchanged and the exterior appearance of the specimen also remained unchanged. The main reason for the occurrence of weight loss during this stage was the release of water from low molecular weight molecules due to the condensation reaction of the remaining residual hydroxyl in the resin after the resin has been solidified. The activation energy of the reaction associated with this stage was also relatively low (6.46 ~ 14.73 Kcal/g molecule in the air, 12.2 Kcal/g molecule in nitrogen). It is interesting to note that there were three stages in the air at temperatures below $400^{\circ}C$ and their corresponding activation energies were 6.46, 9.61 and 14.73 Kcal/g molecule so the rate of energy increase was 50%.

The weight loss of the GS-401 organic silicon resin was

very small under high pressure since it has a relatively high activation energy for its thermodegradation reaction. The extreme limiting weight loss in nitrogen was 20% and this weight loss was contributed almost entirely by the methyl which was chain-linked with the silicon atom. This result was far lower than the amount of thermal weight loss reported in the literature concerning the various kinds of heat resisting organic silicon resin. V. A. Markov et al^[8] have examined the tri-functional polybenzol metals (such as Mn, Co and Ni) and they found that the maximum weight loss of the organic silicon oxyalkane was 30~33%. V. A. Chubarov al^[7] have examined the tri-functional joint polymethyl, the polymethylbenzol and the polybenzol silicon oxyalkane and the weight loss they found was all higher than 50%.

The small weight loss of this kind of resin was linked to its relatively high char yield ratio. Its char yield ratio in the air was 81.18% of the ideal value (100% conversion from benzol to carbon) and this ratio in nitrogen was 93.33% of the ideal value. They are all higher than those of the common organic silicon resin. High char yield ratio is precisely what we desire for the ablative high molecular weight materials.

The temperature at which the main chain of the GS-401 resin will be broken is relatively high. By comparing the data sets from the TG, DTA and IR analyses we found that the main Si-O-Si chain of the GS-401 resin was broken when the temperature was above 750°C. In the air there was an obvious heat absorption peak when the temperature range was between 770 ~ 780°C.

Corresponding to this feature, a clear fracture of the main Si-O-Si chain can also be identified in the infra red spectrum (Figure 12).

It is obvious that the main chain of the GS-401 resin has relatively high thermal stability and this stability can be related to the thermal stability of the organic substitution derivative in the side chain. From the characteristic absorption of the infra red spectra associated with different degradation temperatures (Figure 10 and Figure 11) as well as the result of the analysis (Table 3), we found that throughout the entire thermodegradation process the thermal stability of the methyl was higher than that of the benzol for this kind of resin. The temperature ranges used in the analyses were $25 \sim 940^{\circ}\text{C}$ in the air and $25 \sim 775^{\circ}\text{C}$ in nitrogen. As clearly indicated by the data sets in Table 3 the ratio between methyl and benzol, measured quantitatively through the infrared spectrum, always increased with the increase in temperature regardless of whether the medium was the air or the nitrogen. In other words, the ratio between the degradation speed of the benzol and the degradation speed of the methyl increased with the increase in temperature. During the initial stage of the degradation process, the variation in the ratio between methyl and benzol was relatively slow. This variation became very rapid after temperatures approached 500°C . At 500°C , the speed of degradation of the benzol was more than one time faster than that of the methyl. We can

also clearly see from the infrared spectrum that benzol has completely disappeared at 600°C while methyl still existed for temperatures at 750°C (in the air) and 775°C (in nitrogen). The final total disappearance of the methyl occurred simultaneously with the fracture of the main Si-O-Si chain.

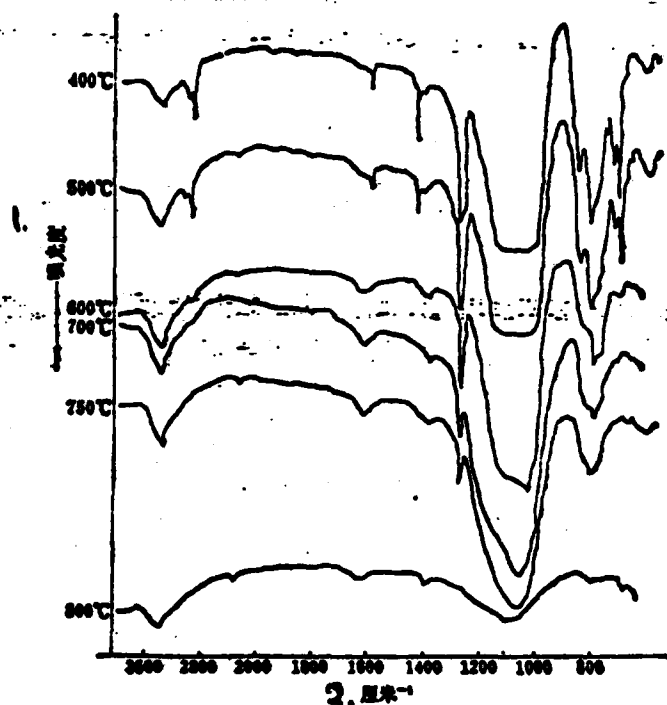


Figure 10. The infrared spectra of the GS-401 resin in the air under different degradation temperatures.

1. degree of light absorption 2. mm^{-1}

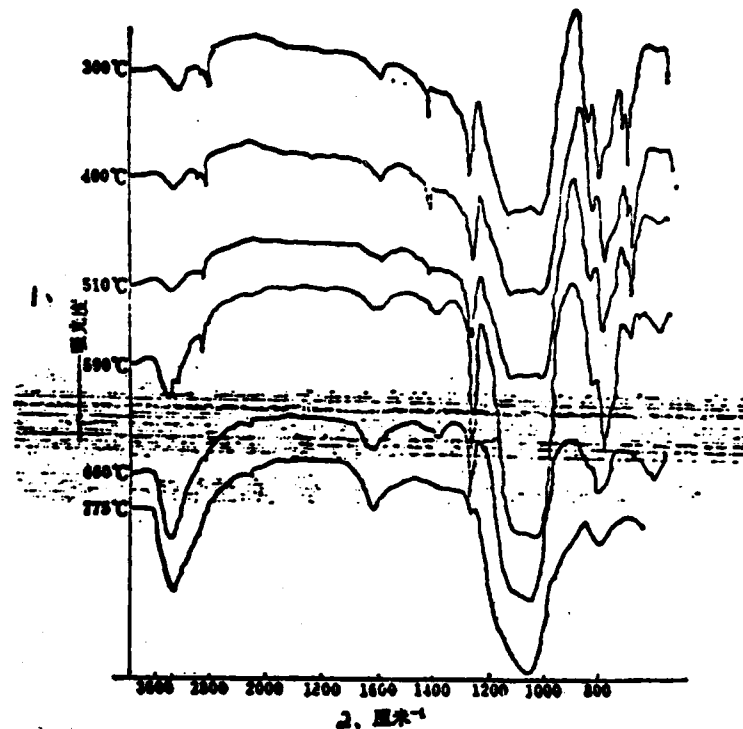


Figure 11. The infrared spectra of the GS-401 resin in nitrogen under different degradation temperatures.

1. degree of light absorption 2. mm^{-1}

During the entire thermodegradation process, the methyl in the silicon was more stable than the benzol. This characteristic is not exhibited by the common organic silicon resin.

This result shows that the concept which promotes the increase of the benzol content in the organic silicon resin for the purpose of improving or increasing the thermal stability of the resin is at least non-universal. Our work has shown that excessive increase in the benzol content will not help to improve

the thermal stability of the resin nor will it help to improve the ablative thermal insulation property of this resin.

What is meaningful here is that this kind of principle in the variation of the ratio between methyl and benzol is consistent with the char yield condition. The time when the specimen began to convert from an orange yellow color to a dark color was precisely when benzol vanished from the infra red spectrum and only a small amount of methyl remained in the air with a temperature range of $600 \sim 700^{\circ}\text{C}$. This is to say that the key for low thermal weight loss and high char yield ratio of this kind of resin lies with the existence of the methyl during the char formation process. During the thermodegradation process, the existence and the relative stability of the methyl makes it more difficult for the free benzol to form benzene gas and leak out and it is easier to form carbon by releasing the hydrogen atom.

IV. Conclusion

1. Throughout the entire thermodegradation process of the GS-401 organic silicon resin examined by this paper, the methyl on the silicon atom exhibited higher thermal stability than the benzol while the degradation speed of the benzol was faster than that of the methyl.

2. Considering the above mentioned characteristics, this resin has high thermal stability, low heat weight loss and high char yield ratio so it has good ablative property.

3. The thermodegradation reaction of the GS-401 resin is extremely complicated. Under wide temperature ranges the degradation reaction will occur in different stages. The corresponding apparent activation energy and order of the reaction will also be different associated with each different stage.

The comrades who contributed to this experimental work are as follows: Sun Long Cheng, Tan Wen Xiu, Liu Su Qing, Wong De Quan, Xie Guang Shun, Wong Li Yun and Lin Hua Wen.

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