

# TG-DTA-MS and DSC studies on the thermal-treatment process of the 20% $\text{AlO}_{3/2}$ - $\text{SiO}_2$ -epoxy $\text{SiO}_{3/2}$ organic-inorganic hybrid system<sup>1</sup>

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## Abstract

TG-DTA-MS and DSC techniques were applied to study the thermal behaviors, such as volatilization, evaporation of the liquid solvent phase and the organic modifying radicals of 20%  $\text{AlO}_{3/2}$ - $\text{SiO}_2$ -epoxy $\text{SiO}_{3/2}$  organic-inorganic hybrid system prepared by the sol-gel method in the thermal treatment process. © 1999 Published by Elsevier Science B.V. All rights reserved.

*Keywords:* 20%  $\text{AlO}_{3/2}$ - $\text{SiO}_2$ -epoxy $\text{SiO}_{3/2}$ ; Organic modifying radicals; Thermal behavior; TG-DTA-MS; DSC

## 1. Introduction

In recent years, great attention has been paid by scientists to make materials with some organic and inorganic characteristics by introducing different organic function radicals into the inorganic network, so that the available function and the range of application of the material can be greatly increased [1]. Organic modified silicates (ORMOSILs) prepared by means of the sol-gel method proposed by Schmidt et al. [2,3] have been successfully used as optical protecting coat, medical soft grit and internal wall coat in immunity analysis. Thus, the sol-gel method is among the most noticeable new ways of preparing ceramic material with organic radicals. The material obtained by the sol-gel method has some advantages,

such as high purity, high homogeneity and low sintering temperature. However, studies on the connecting state, existing mode and decomposition mechanism, etc. are seldom seen in the literature. The changes in thermal-treatment process for the eight ORMOSIL materials, such as 70  $(\text{C}_2\text{H}_6)_2\text{SiO}\cdot 30\text{TiO}_2$  and 70  $(\text{C}_2\text{H}_6)_2\text{SiO}\cdot 30\text{ZrO}_2$  were studied by thermal analysis methods (TG, DTA, etc.) in literature. In this work, the alkoxides and KH560  $[\text{CH}_2\text{-CH-CH}_2\text{-O}(\text{CH}_2)_3\text{-}$

$\text{Si}(\text{OCH}_3)_3]$  were used as precursor to prepare the 20%  $\text{AlO}_{3/2}$ - $\text{SiO}_2$ -epoxy $\text{SiO}_{3/2}$  organic-inorganic hybrid system by the sol-gel method. Thermal analysis methods, such as TG, DTA and TG-DTA-MS techniques were applied to characterize the changes in the hybrid system and the inorganic system during the thermal process [4–8]. The DSC method was also used to make further study for both the systems. The TG-DTA-MS results for the 20%  $\text{AlO}_{3/2}$ - $\text{SiO}_2$ -epoxy $\text{SiO}_{3/2}$  organic-inorganic hybrid system show that the volatilization of the solvent for the hybrid

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system appears at ca. 100°C, when most of the organic modifying radicals split and decompose at 260–320°C. The DSC results measured under air show that the organic modifying radicals of the hybrid system evaporate at 260–360°C and exothermic oxidation starts to appear at 360–460°C.

## 2. Experimental

### 2.1. The sol and film preparation

The chelate agents KH560  $[\text{CH}_2\text{-CH}(\text{CH}_2\text{-O}(\text{CH}_2)_3\text{-Si}(\text{OCH}_3)_3)]$  and TEOS  $[\text{Si}(\text{OC}_2\text{H}_5)_4]$  were mixed according to a proper ratio. The mixture of water and alcohol dropped in it at room temperature. The mixture was catalyzed by using CQ-50 type super-sound wave device at room temperature and placed into the  $\text{Al}(\text{OC}_4\text{H}_9)_3$  to form a stable gel. The cleaning substrate soaked into the gel for 1 min and then drew out off the liquid surface of the substrate. The composition of the formed hybrid film was 20%  $\text{AlO}_{3/2}\text{-SiO}_2\text{-epoxySiO}_{3/2}$ . According to the procedure, mentioned above for the preparation of the pure inorganic film. The composition of the formed inorganic system was 20%  $\text{AlO}_{3/2}\text{-80% SiO}_2$ .

### 2.2. TG, DTA and TG-DTA-MS analysis

Simultaneous thermal analyzer (Netzsch-STA429) coupled with quadrupole mass spectrometer (Balzers QMG511) was used for TG, DTA and MS analyses. The weight of the sample was 100 mg. The region in which temperature increased was 20–600°C. The full scale of DTA was 0.2 mV and the full scale of TG was 25 mg. The heating rate was 10°C/min.

TG experiments for the comparison of the weight losses for the inorganic system and the hybrid system

were carried out at 120°C in air and held at that temperature for 20 min.

DTA experiments for the comparison of the inorganic system and the hybrid system were carried out in air.

*TG-DTA-MS experiments for the hybrid system.* The scanning speed of mass was 1 a.m.u/s. The time for mass filtering was 0.03 s. The vacuum of the MS system was under  $3 \times 10^{-5}$  mPa. Static Ar was used as the carrier gas. The proposed mass number, the ion-current intensity and the amplifying rate are listed in Table 1.

## 3. Results and discussion

Table 2 shows the comparison of weight loss for the inorganic system gel and the hybrid system gel heated at 120°C and held at that temperature for 20 min. The results show that the weight loss for inorganic system was 18.8% and the weight loss for hybrid system was 10.2%.

It is obvious that, due to the introduction of organic radical, the porosity of the hybrid material was less than that of the inorganic system. Thus, the amount of adsorbed liquid phase of the hybrid system was much less than that of the inorganic system. Fig. 1 shows two TG curves of the two systems after thermal treatment at 120°C. The TG results indicate that the weight loss of the inorganic system appears with a constant speed in the whole temperature region. There

Table 2

The comparison of weight loss for the inorganic and hybrid systems during thermal process

System	Temperature (°C)	Keeping time (min)	Rate of weight loss %
Hybrid	120	20	10.2
Inorganic	120	20	18.8

Table 1  
Parameters for MS analysis

Proposed positive ion	$\text{CH}_3^+$	$\text{C}_2\text{H}_5^+$	$\text{CH}_3\text{O}^+$	$\text{CH}_2\text{CH}^+$ $\diagdown$ $\text{O}$	$\text{C}_2\text{H}_5\text{O}^+$	$\text{CH}_2\text{CHCCH}_2^+$ $\diagdown$ $\text{O}$	$\text{CH}_2\text{CHCH}_2\text{O}^+$ $\diagdown$ $\text{O}$
<i>m/z</i>	15	29	31	43	45	57	73
Intensity (A)	$10^{-9}$	$10^{-9}$	$10^{-11}$	$10^{-9}$	$10^{-9}$	$10^{-9}$	$10^{-11}$
Amplifying rate	$\times 10$	$\times 10$	$\times 1$	$\times 10$	$\times 10$	$\times 1$	$\times 1$

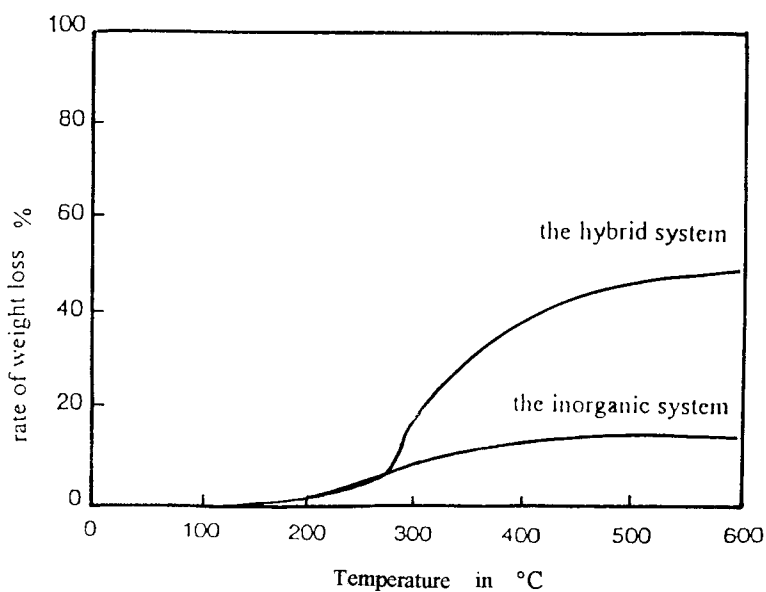


Fig. 1. TG curves under air for the inorganic and hybrid systems after treatment at 120°C.

is no sudden change of the weight loss in the TG curve. However, the weight loss of the hybrid system began to increase rapidly at 260°C and continued to do so till 510°C. The weight loss of the hybrid system can be

explained as being due to the increase in temperature, and the appearance of breaking and evaporation of the organic modifying radicals. Fig. 2 shows the DTA curves for the inorganic and hybrid systems. Both

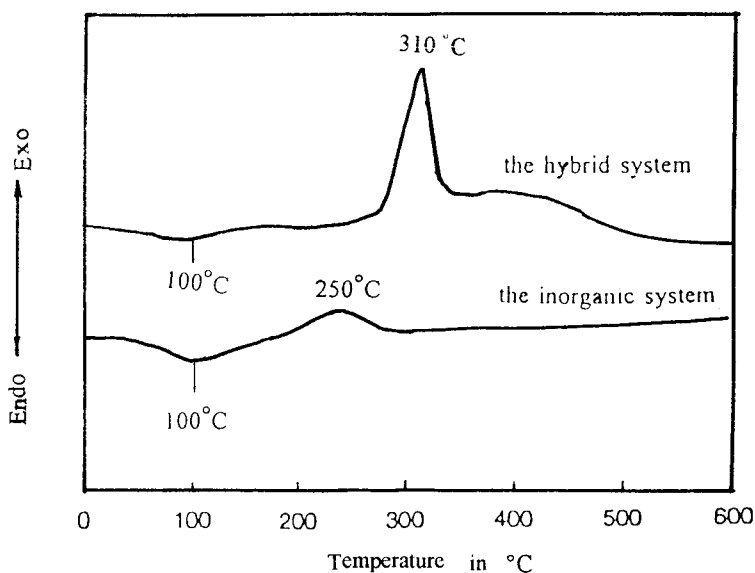


Fig. 2. DTA curves under air for the inorganic and hybrid systems.

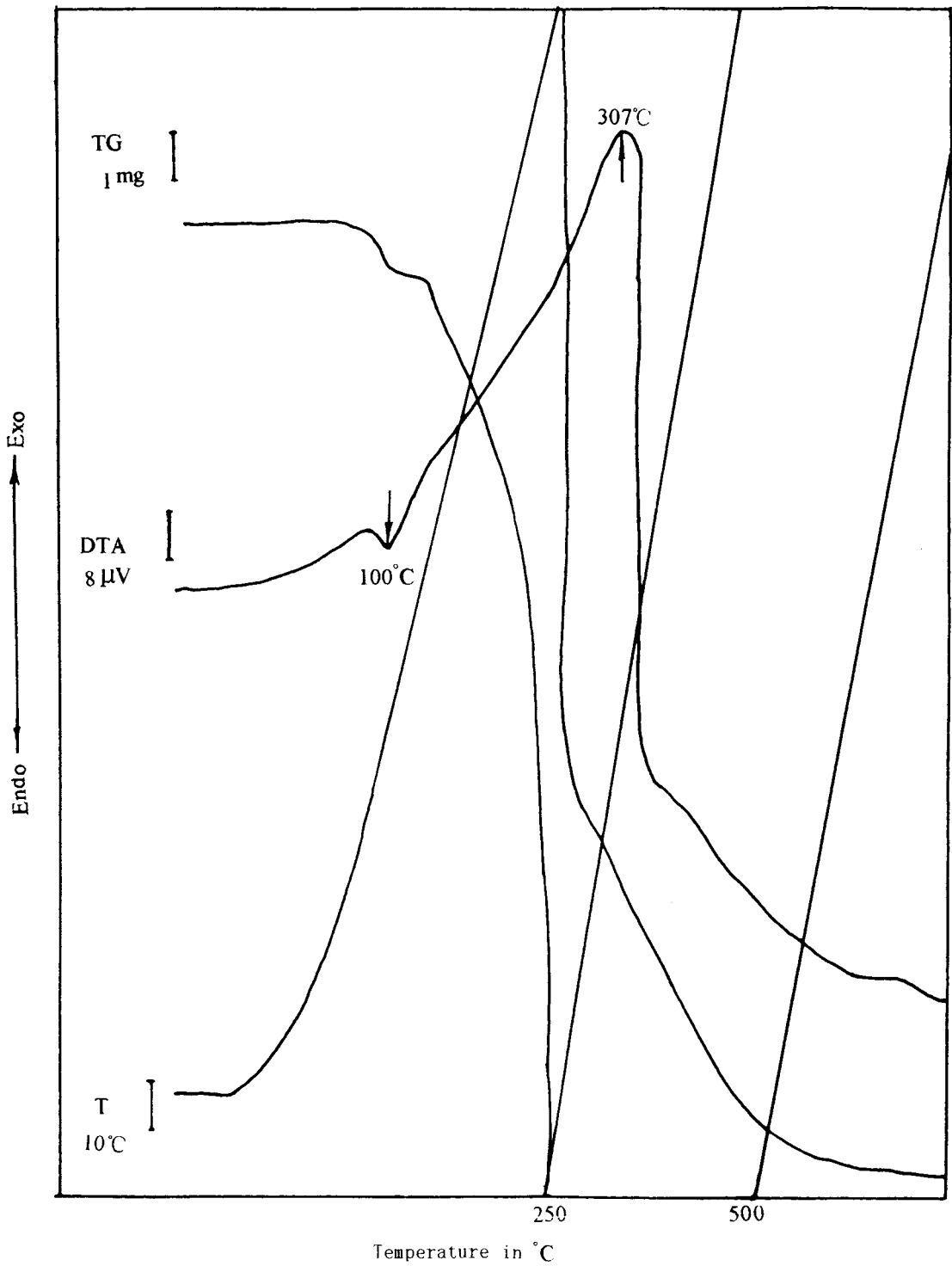


Fig. 3. (a) TG-DTA curves under Ar for the hybrid system; and (b) MS spectra under Ar for the hybrid system.

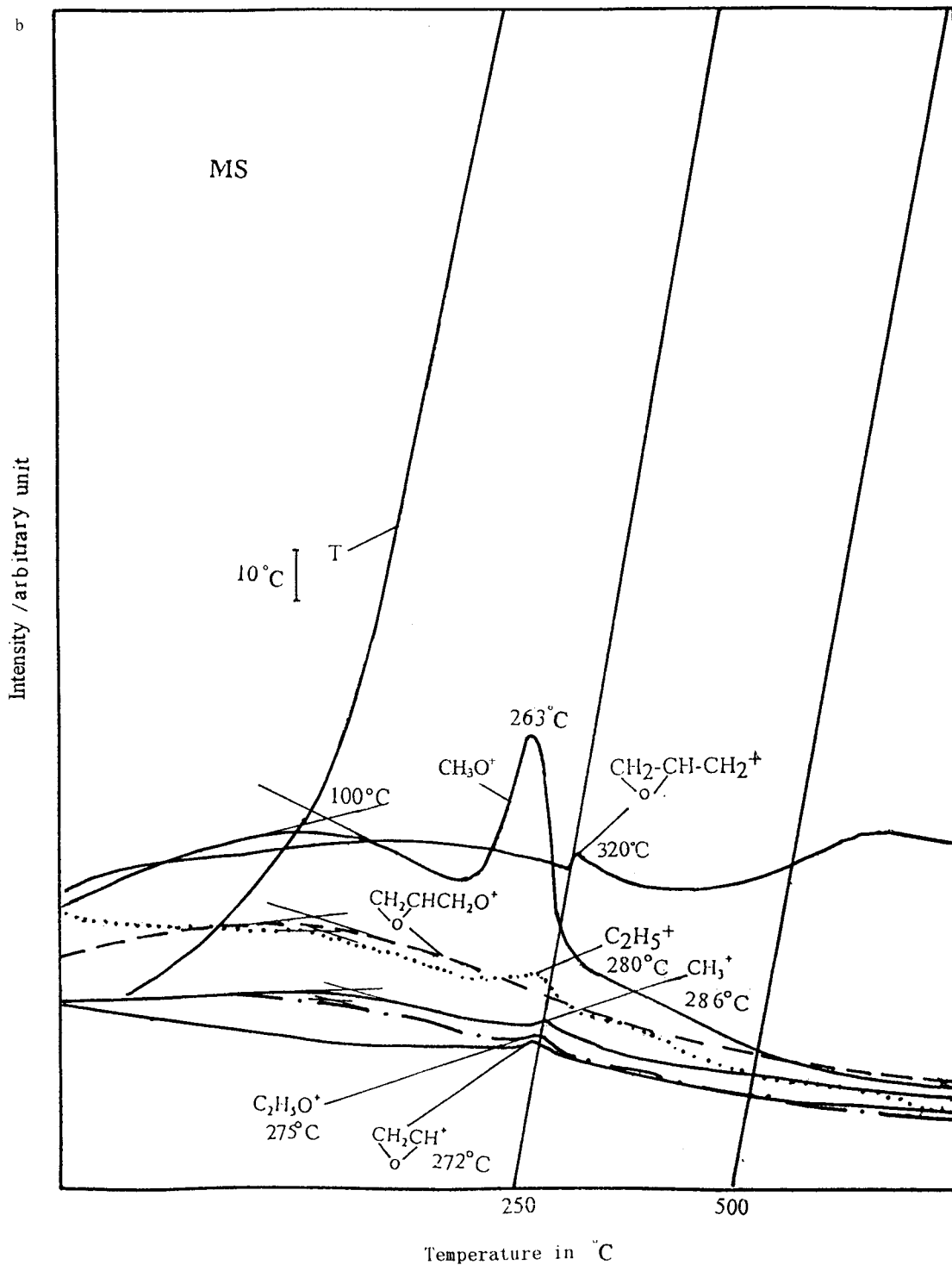


Fig. 3. (Continued)

the DTA curves show endothermic peaks at 100°C. This kind of endothermic effect is related to the volatilization of the liquid solvent in the inorganic and the hybrid systems. The DTA curve of the inorganic system shows a smaller exothermic peak at 250°C. It corresponds to the evaporation of the binding solvent in the inorganic film. The DTA curve of the hybrid system shows a bigger exothermic peak at 310°C. It indicates that the exothermic process of the hybrid system is related not only to the evaporation of the binding solvent but also to the breaking and the evaporation of the organic modifying radicals.

The TG-DTA-MS curves of the hybrid system are shown in Fig. 3(a and b). The TG curve in Fig. 3(a) shows a smaller step at ca. 100°C. The DTA curve in Fig. 3(a) also shows a smaller endothermic peak at 100°C. Meanwhile, the MS curves in Fig. 3(b) show  $\text{CH}_3^+$  ( $m/z = 15$ ),  $\text{C}_2\text{H}_5^+$  ( $m/z = 29$ ),  $\text{CH}_3\text{O}^+$  ( $m/z = 31$ ),  $\text{C}_2\text{H}_5\text{O}^+$  ( $m/z = 45$ ) and  $\text{CH}_2\text{-CH-CH}_2\text{O}^+$  ( $m/z = 73$ ) flat peaks at ca. 100°C. These peaks are probably associated with the volatilization of the solvent and the producing alcohol in the hybrid system.

The TG curve in Fig. 3(a) shows a bigger step at 130–360°C. The DTA curve in Fig. 3(a) shows a bigger exothermic peak at 307°C. In the correspond-

ing region of temperature, the MS curves in Fig. 3(b) show some peaks:  $\text{CH}_3\text{O}^+$  (263°C),  $\text{CH}_2\text{-CH}^+$  (272°C),  $\text{C}_2\text{H}_5\text{O}^+$  (275°C),  $\text{C}_2\text{H}_5^+$  (280°C),  $\text{CH}_3^+$  (286°C) and  $\text{CH}_2\text{-CHCH}_2^+$  (320°C). Among them, the  $\text{CH}_3\text{O}^+$  peak intensity is the highest. These peaks are probably related to the split decomposition and the evaporation of the binding solvent and the organic modifying radicals of the hybrid system. Because of the complexity of the splitting decomposition process of the organic modifying material, it is difficult to propose all the possible splitting fragment ions during the thermal treatment process. Therefore, it is necessary to further investigate the pyrolysis behavior of the hybrid system.

The DSC curves under  $\text{N}_2$  and air for the inorganic system and the hybrid system are shown in Figs. 4 and 5. For the inorganic system, DSC curves under  $\text{N}_2$  and air in Fig. 4 show exothermic peaks at 240°C, which correspond to the evaporation of the binding solvent of the inorganic film. For the hybrid system, the DSC curves under  $\text{N}_2$  and air in Fig. 5 show bigger exothermic peaks at 322°C. The area of this exothermic peak is bigger than that of the inorganic system. It can be proposed that this process for the hybrid system included the evaporation of the binding solvent and the

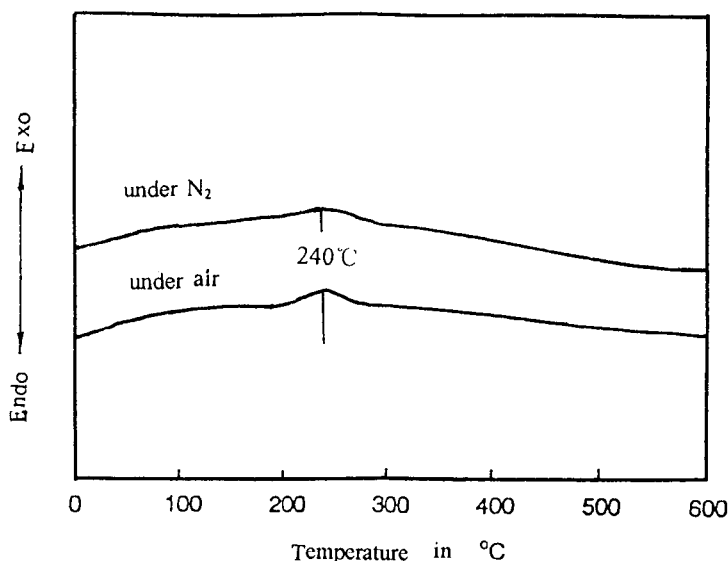


Fig. 4. DSC curves under  $\text{N}_2$  and air for the inorganic system.

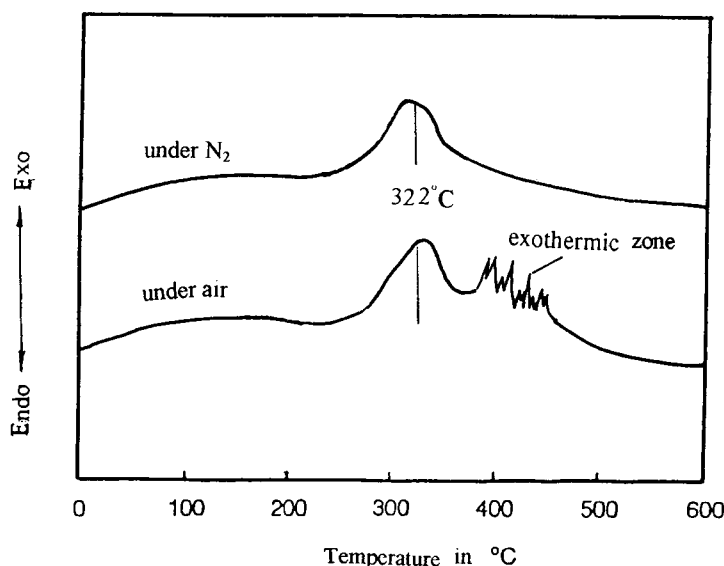


Fig. 5. DSC curves under  $N_2$  and air for the hybrid system.

organic modifying radicals. In addition, the DSC curve under air for the hybrid system shows a bigger exothermic zone at 360–460°C. This phenomenon is not found in the DSC curve under  $N_2$  for the hybrid system and in the DSC curves under  $N_2$  and air for the inorganic system, which can be proposed as being the result of further exothermic oxidation of the organic radicals and oxygen in air.

#### 4. Conclusion

The TG-DTA-MS and DSC results show that the thermal pyrolysis process of the 20%  $AlO_{3/2}$ - $SiO_2$ -epoxy  $SiO_{3/2}$  organic-inorganic hybrid system basically proceeds in three steps: the first step is at ca. 100°C, the TG curve reveals a small weight loss and the DTA curve shows an endothermic effect, the corresponding MS curve show  $CH_3^+$  ( $m/z = 15$ ),  $C_2H_5^+$  ( $m/z = 29$ ),  $CH_3O^+$  ( $m/z = 31$ ),  $C_2H_5O^+$  ( $m/z = 45$ ) and  $CH_2-CHCH_2O^+$  ( $m/z = 73$ ) flat peaks

at ca. 100°C, which are probably related to the volatilization of the solvent in the hybrid film. The second step is at ca. 130–360°C. The TG curve reveals big weight loss at 130–360°C, the DTA curve shows a strong exothermic peak at 307°C and the corresponding MS curves show some peaks:  $CH_3O^+$

(263°C),  $CH_2-CH^+$  (272°C),  $C_2H_5O^+$  (275°C),  $C_2H_5^+$  (280°C),  $CH_3^+$  (286°C) and  $CH_2-CHCH_2^+$  (320°C);

among them the  $CH_3O^+$  peak is the highest. These peaks are probably associated with the evaporation of the binding solvent and the organic modifying radicals of the hybrid system. The third step is at ca. 360–460°C. The DSC curve measured under air shows a bigger exothermic zone at 360–460°C, which can be proposed as the result of further exothermic oxidation of the organic radicals and the oxygen in air.

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