Studies on The Thermal Decomposition Kinetics of Auto-Photosensitive Polyimide

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ABSTRACT

In this paper, the thermal behaviour of an inherent-photosensitive polyimide was studied by means of thermalgravimetry. This photosensitive polyimide was synthesized by the reaction of 3,3',4,4'-benzophenonetetracarboxylic dianhydride(BTDA) with four methyl-substituted aromatic diamines, e.g.,. 3,3',5,5'-tetramethyl-4,4'-diaminodiphenyl-methane(TMDDM) in refluxing m-cresol. The differentiation method has been used to deal with the experimental data. It only requires one thermogram. By choosing the cubic spline function to interpolate and differentiate the thermal gravity data, then by binary regression, we got the thermal decomposition kinetics parameters, such as activation energy, the reaction order as well as the frequency factor of the thermal decomposition. The investigation results show that the photosensitive polymer made by authors has excellent heat resistance.

INTRODUCTION

Photosensitive polyimides have widely been used in the micro-electronics industry as interlayer dielectrics, passivation layer, ion implantation mask etc. because they retain their excellent properties (dielectric, mechanical and thermal properties) at high temperature up to 450 ~ 500℃.[1-3] Recently a preimidized soluble photosensitive polyimide, Proimide 400 series,has been introduced by Pfeifer and Rohd [4]. This type of polymers is a fully imidized nonshrinking photoimageable polyimides system. These polyimides possess the following two properties in structure: (1) benzophenone moiety are included in the polymer backbone, and (2) the polymer backbone contains aliphatic pendant groups. Lin et al. [5] later studied the crosslinking mechanism of a benzophenone-containing ethyl-pendant polyimides system and concluded that photocrosslinking proceeds through hydrogen abstraction from the aliphatic group, ie.hydrogen donor, by an excited benzophenone molecule, and subsequently coupling of the radicals so formed.

In this article, we will report on the synthesis of an inherent-photosensitive polyimide and emphasis on the thermal decomposition kinetics of this type of polyimides.

EXPERIMENTAL

Preparation of polymer from TMDDM and BTDA

BTDA(1.9334g, 0.006mol) was added to a mechanically stirred solution of TMDDM(1.5262g, 0.006mol) in m-cresol(30ml) and toluene(30ml). Isoquinoline(8 drops) was added and the temperature of the solution was gradually increased. Water was removed by azeotropic distillation with the toluene under an atmosphere of flowing nitrogen. Excess toluene was removed and the reaction mixture was maintained at 175-180℃ for 3hr. The solution was slowly added to ethanol to precipitate a yellow solid, which was washed with ethanol and dried at room temperature in vacuum for 48hr. The inherent viscosity at a concentration of 0.5% at 30℃ in N-methyl-2-pyrrolidone is 1.07dl/g.

Thermal Stability Test

Thermogravimetric analysis of the fully dried polyimide was performed at a 5℃/min heating rate in air over the temperature 25-650℃,using a Rugaku TG-DTA.The thermogram is shown in Figure 1.

RESULTS and DISCUSSIONS

Determination of the Thermal Decomposition Parameters

The differentiation method has been used to deal with the experimental data. It only requires one thermogram to obtain the thermal decomposition activation energy(E), the reaction order(n) as well as the frequency factor of the thermal decomposition(A). Suppose the thermal decomposition reaction as follows:

A(solid) → B(solid)+C(gas)

with the kinetics rate equation based on above mechanism,we obtained:

$$-\frac{dc}{dt}=k\times f(c) \qquad (1)$$

$$-\frac{dc}{dT}=\frac{1}{b}(-\frac{dc}{dt}) \qquad (2)$$

where c is the weight percent of undecomposed sample, k is the rate constant, b is the heating rate, t is the reaction time and T is the decomposition temperature.

On substituting Eq.(1) into Eq.(2), then following the Arrennius relatonship,we obtained:

$$-\frac{dc}{dT}=\frac{A}{b}e^{-E/RT}f(c) \qquad (3)$$

$$Ln(-\frac{dc}{dT})=Ln(\frac{A}{b})+n\times Lnc-E/RT \qquad (4)$$

where $f(c)=c^n$.

Assuming $n_0=\ln(A/b), n_1=n, n_2=-E/R$, Eq.(4) can be simplified as:

$$Ln(-\frac{dc}{dT})=n_o+n_1 Lnc+n_2/T \qquad (5)$$

The author used binary regression method to obtain the constants n_0, n_1, n_2 in Eq.(5). Before regression, the cubic spline function method was used to interpolate and differentiate the thermogravimetric data.

First, assuming the cubic spline function to be C(T), from the TG curve, we know that the two limits of the curve's first order differentiation is zero, respectively,$C'(T_0)=0, C'(T_n)=0$, where n=28, which lead to the following equation group that only have n-1 equations.(In which m_1, m_2, m_3, ... is the first order differentiation,(dC/dT),in the temperature point of T_1, T_2, T_3,......respectively.) The equation group can be written as matrix form:

$$\begin{bmatrix} 2 & \mu_1 & & & & \\ \lambda_2 & 2 & \mu_2 & & & \\ & \lambda_3 & 2 & \mu_3 & & \\ & & \cdot & \cdot & \cdot & \\ & & & \cdot & \cdot & \cdot \\ & 0 & & & 2 & \mu_{n-2} \\ & & & & \lambda_{n-1} & 2 \end{bmatrix} \begin{bmatrix} m_1 \\ m2 \\ m_3 \\ \cdot \\ \cdot \\ m_{n-2} \\ m_{n-1} \end{bmatrix} = \begin{bmatrix} g_1 - \lambda_1 f_0 \\ g_2 \\ g_3 \\ \cdot \\ \cdot \\ g_{n-2} \\ g_{n-1} \end{bmatrix}$$

where

$$f_0' = c'(T_0) = 0$$

$$f_n' = c'(Tn) = 0$$

$$\mu_j = \frac{h_{j-1}}{h_j + h_{j-1}}$$

$$\lambda_j = \frac{h_j}{h_{j-1} + h_j}$$

$$h_j = T_{j+1} - T_j$$

$$g_j = 3[\lambda_j f(T_{j-1}, T_j) + \mu_j f(T_j, T_{j+1})]$$

$$f(T_j, T_{j=1}) = \frac{c_{j+1} - c_j}{h_j}$$

$$f(T_j, T_{j+1}) = \frac{c_j - c_{j-1}}{h_{j-1}} (j = 1,2,3,\cdots,n-1)$$

We obtained the function data C_0, C_1, C_2, ... at the temperature point T_0, T_1, T_2, ... through dealing with the data of Figure 1.

Thus

$$h_j = T_{j+1} - T_j = 10$$

$$\mu_j = \lambda_j = \frac{1}{2}$$

$$g_j = \frac{3}{2 \times 10}(c_{j+1} - c_j)$$

To obtain the differentiation at m_1, m_2, m_3, ······· , we made use of the Zhuigan-method to solve the equation.

Secondly, the binary regression method has been used to obtain the constants n_0, n_1, n_2. The results are shown in Table I.

Table I. The Results of the Binary Regression

n_0	n_1	n_2
12.84798	0.831317	-14334.46

Then we obtain the thermal decomposition kinetics parameters, which are shown in Table II.

Table II. The Thermal Decomposition Kinetics Parameters of Inherent-photosensitive Polyimide

$A(min^{-1})/10^6$	n	E(KJ/mol)
1.900101	0.83131793	119.1767

Based on the value of the kinetics parameters A,n,E, we can also determine the relationship between the thermal decomposition rate (dC'/dt,C' is the weight loss %) and temperature, which are shown in Fig.2. The peak of the curve is at 560 ℃. It shows this photosensitive resin has excellent heat resistance.

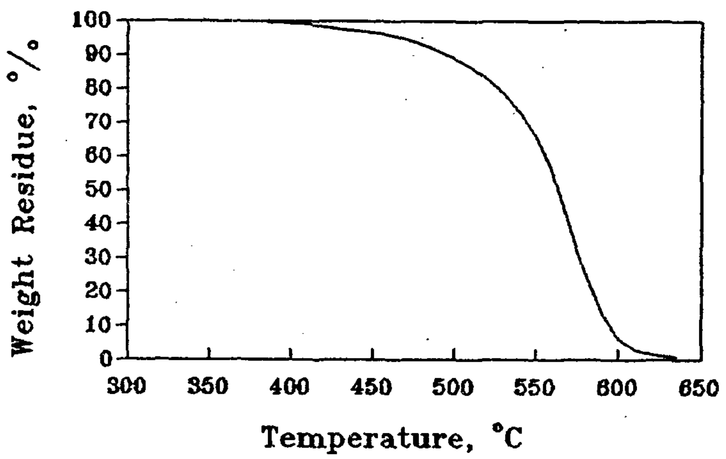

Fig. 1 Thermolgravimetric curve of polyimide

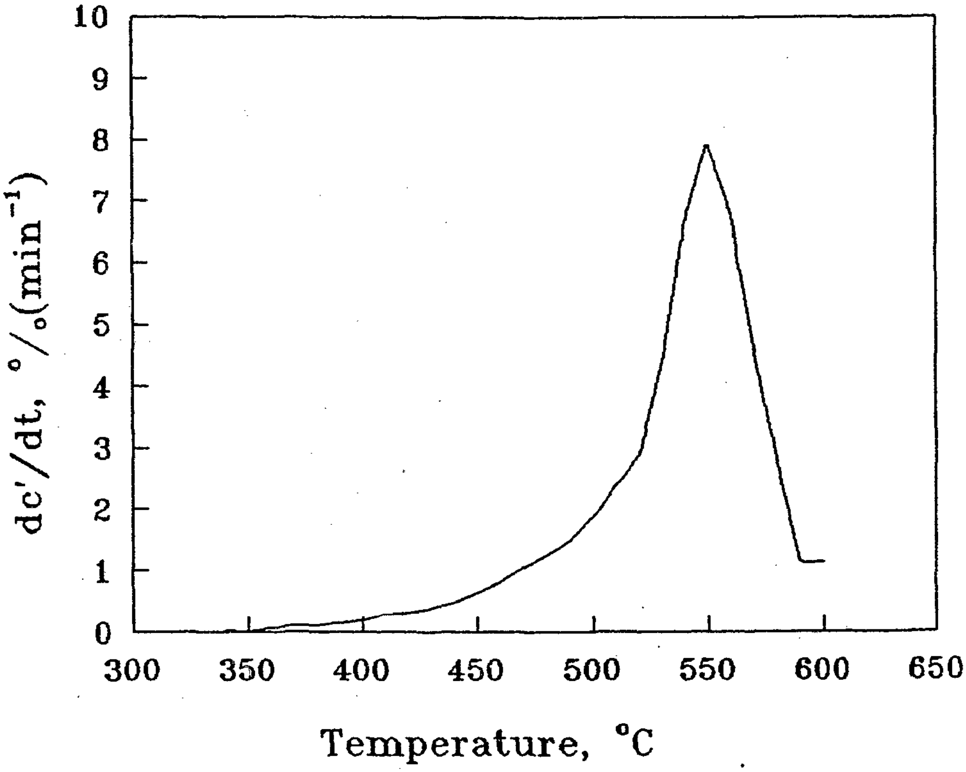

Fig. 2 The relationship between thermal decomposition rate and temperature

CONCLUSIONS

1. In this article, we synthesized an inherent-photosensitive polyimide. By dealing with the thermal gravity data with the differentiation method, choosing the cubic spline function to interpolate and differentiate the data, then by binary regression, we got the thermal decomposition kinetics parameters.

2.The thermal decomposition parameters A, n and E can characterize the heat-stability of the photosensitive polyimide resin. We can also determine the relationship between the thermal decomposition rate and temperature from the kinetics parameters A, n and E. The investigation results show that the maximum rate of thermal decomposition is at 560℃,and the weight loss of the polymer is very low below 400℃. It showed that the polymer has excellent heat resistant.

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