

1.2 Thermo volumetric measurements

Thermo volume analysis was carried out in an apparatus as shown in Fig. 1. The tubular reactor ($\phi = 4$ cm) with a constant temperature zone of 10 cm in a furnace was connected with an Erlenmeyer flask and a vessel through flexible tubes. The Erlenmeyer flask was cooled with ice and the vessel was filled with saturated salt solution. The pressure in the tube was kept in balance with the atmosphere through the deflection of the salt solution, whose volume equals that of the permanent pyrolysis gas. During the experiment, 10 g neat EVA (Elvax 150 or 460) were placed in the crucible in the reactor, which was then purged with Argon for about 90 min at a flow rate of 30 l/h. After that, the reactor was heated at a certain heating rate. The solution volume and the temperature of the crucible were noticed every five minutes. During pyrolysis, the pyrolysis gas with a high boiling point condensed in the Erlenmeyer flask and the flexible tubes. The weight of condensate was obtained by weighting the Erlenmeyer flask and the flexible tubes before and after the experiment.

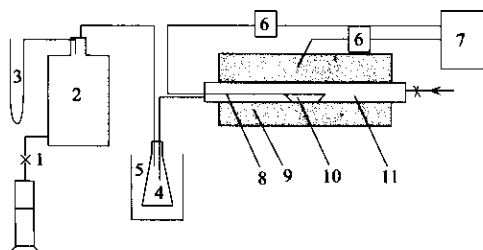


Fig.1 Schematic diagram of the experimental apparatus for thermovolumetry
1. valve; 2. vessel; 3. U form tube; 4. Erlenmeyer flask; 5. ice; 6. temperature transmitter; 7. temperature controller; 8. thermocouple; 9. furnace; 10. sample crucible; 11. reactor

2 Results and discussion

2.1 TGA and DTA

The combined TGA and DTA results of the neat EVA in nitrogen are shown in Fig. 2. The DTA showed three endothermic peaks. The first endothermic peak (63°C) corresponds to the melt points of the EVA. The second peak (334°C) reflects the endothermic degradation reaction (Equation 1) in the first pyrolysis stage. The second region of weight loss begins with predominantly endothermic reactions and ends with predominantly exothermic reactions. The results are consistent with the literature (Hrdina, 1998) but different from the other (Frison, 2000), where neither type nor the source of the EVA was stated. Note that the first melt peak (63°C) of the EVA used in this work is lower than that (88°C) reported by Hrdina (Hrdina, 1998), because of the different types of EVA (Table 1). The three endothermic peaks occurring during the EVA-pyrolysis should be favourable to the protection of the Si-wafer in the module from the damage of the thermal stress during the rapid heating stage of pyrolysis.

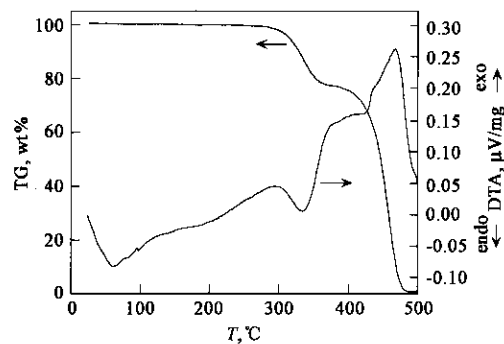


Fig.2 TGA/DTA of EVA copolymer in nitrogen at constant heating rate 5 K/min

Besides, the results of the EVA pyrolysis carried out under different oxidizing atmosphere (Fig. 3).

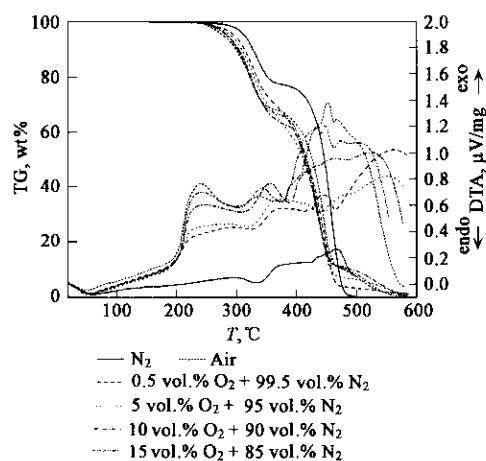


Fig.3 TGA/DTA of EVA copolymer at constant heating rate of 5 K/min under different oxidizing atmospheres

It is very obvious that the oxidizing atmosphere can accelerate the degradation reaction and the optimal O_2 content is about 5 vol. %. But, in comparison with that in nitrogen, a shoulder occurs in all the TGA curve in the temperature range from 460°C to 570°C under all different oxidizing atmospheres. This should be caused by the carbonization of EVA under oxidizing atmosphere. To eliminate the coke, a higher end pyrolysis temperature is necessary, though it may bring damage to the Si-wafer. The influence of higher temperature on the quality of the Si-wafer should be investigated further. Another disadvantage of oxidizing atmosphere is that a strong exothermal peak occurs in the second pyrolysis stage under the air condition, which may indicate a burning reaction of the pyrolysis production and may damage the Si-wafer also. The exothermal peak gets observably weaker at O_2 content lower than 10 vol. %. Under 100 vol. % N_2 , the EVA shows a different pyrolysis behavior (solid line in Fig. 3). Although the pyrolysis temperature at the same degradation rate under nitrogen is in most cases higher than that in oxidizing atmosphere, its end pyrolysis temperature (approx. 480°C), however, is much lower than 570°C under oxidizing atmosphere. To decrease the

exothermal effect and the end pyrolysis temperature, pyrolysis under inner or weak oxidizing atmosphere is highly recommended.

2.2 Thermovolumetry and pyrolysis mass balance

2.2.1 Influence of heating rate and EVA-types on the pyrolysis gas volume and gas releasing rate

The results of thermovolumetry (Fig. 4) are consistent with that of TGA (Fig. 2). The pyrolysis gas begins to release obviously at about 275°C and its releasing rate shows two peaks also. The first rate peak moves from 310°C to 340°C depending on the heating rates and the second peak appears at about 460°C. The permanent gas volume increased slightly

with the increasing of the heating rate. In the second stage the releasing rate of the permanent pyrolysis gas is a little smaller than that in the first stage but both of them are comparable. Although the max weight loss (approx. 78 wt. %) occurs in the second stage (Fig. 2), the permanent pyrolysis gas amount in this stage is smaller than in the first stage.

The amount of the permanent pyrolysis gas depends strongly on the vinyl acetate content in EVA, as shown in Fig. 4. More permanent gas is produced from the pyrolysis of EVA with higher content of VA.

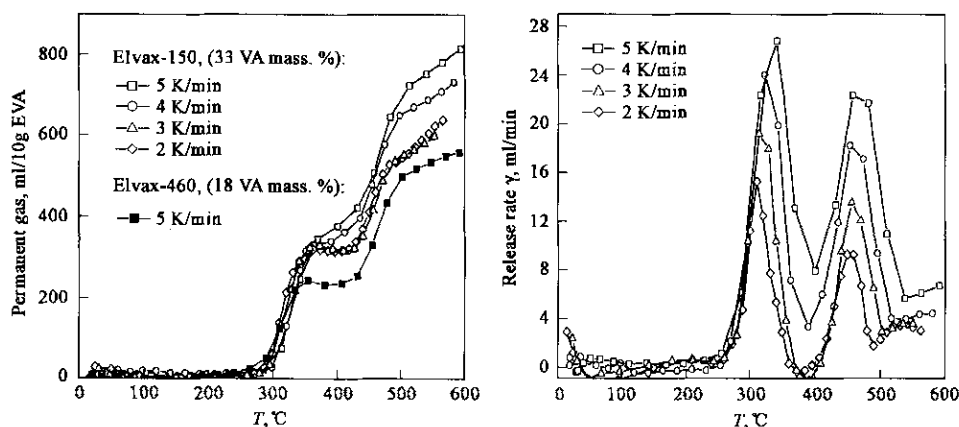


Fig.4 Influence of the heating rate on the volume and the releasing rate of permanent pyrolysis gas

2.2.2 Production compositions and mass balance of EVA pyrolysis

The mass balance of the EVA pyrolysis in nitrogen is shown in Fig. 5. The main product of the EVA pyrolysis is the low volatile condensate that accounts for about 90% of the EVA. This places a special requirement for the burner of the pyrolysis gas and condensate, which burns the pyrolysis organic productions to fulfil the heat requirement in the pyrolysis process in industry. The little residue coke (0.1 wt. %) is favourable for the surface chemical treatments of the Si-wafer after the pyrolysis.

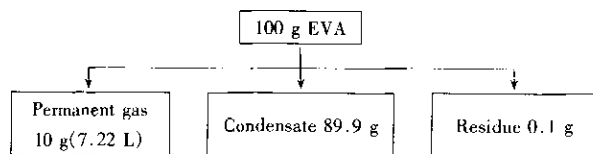


Fig. 5 Mass balance of EVA pyrolysis

The compositions of the permanent gas and condensate of the EVA pyrolysis, which are the average values of over 20 experiments at different heating rates, are given in Table 2 and Table 3, respectively. The compositions of CH₄, CO₂

and CO in the permanent gas should be the secondary degradation productions of the acetic acid, the weight of which, according to the literature (Haussler, 1998; Munteanu, 1977), equals the weight loss of EVA in the first stage (about 22 wt. % according to Fig. 2). From Fig. 5 and Table 2 it can be calculated that about 5.17 g acetic acid from 100 EVA is degraded to CH₄, CO₂ and CO. The rest 17 g acetic acid should stay in the condensate and accounts for 17/89.9 = 17 wt. %. The composition of the acetic acid in the condensate is determined experimentally to be about 12 wt. %, being lower than the theoretically calculated, because of the incomplete condensation of the acetic acid in the experimental process.

Different gas compositions are expected in the two degradation stages because of the different reaction mechanisms. Table 4 shows the experimental results of the compositions of permanent gas at different pyrolysis stages. In the first stage the main compositions are CH₄, CO₂ and CO resulting from the degradation of the acetic acid. Correspondingly, their heating value is much lower. Noteworthy is that there are still CO₂ in the second stage.

Table 2 Composition and heating value Hu of the permanent pyrolysis gas (vol. %)

Substance	H ₂	CH ₄	CO	CO ₂	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	I-C ₄ H ₁₀	N-C ₄ H ₁₀	Hu *
Average value	8.43	22.12	2.71	26.11	12.22	10.92	5.26	10.41	0.17	1.61	39.6

Note: * Hu in MJ/m³

Table 3 Composition of the condensate from EVA pyrolysis(wt. %)

Element	C	H	O	N	S
Composition	81.2	12.2	5.9	0.5	0.2

Notes: H₂O: < 2 wt. %, CH₃COOH: 12 wt. %, aliphatic hydrocarbon: 80 wt. %

That means that the acetic group was not removed completely from the main chain or the acetic acid generated in the first stage did not diffuse completely from the molten polymer.

Table 4 Gas compositions(vol. %) and heating value Hu(MJ/m³) at different EVA pyrolysis stage *

Substance	H ₂	CH ₄	CO ₂	CO	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	I-Butan	N-Butan	Hu
Stage I	3.0	15.2	68.7	9.2	0.8	0.5	0.7	0.4	1.2	0.3	10
Stage II	3.4	18.3	14.9	2.4	15.2	15.9	15.5	10.0	0.2	4.2	53

Note: * The heating rate is 5 K/min

For the kinetic analysis using TGA weight loss data several methods are available. One of them is the constant heating rate method(Nam, 1992; Moddeman, 1986). In the case of EVA degradation, the following kinetic equation is applied:

$$d\alpha/dt = Ag(\alpha)\exp(-E/kT), \tag{2}$$

where α is the mass fraction remaining, t is the time, A is the pre-exponent, E is the activation energy, $g(\alpha) = (1 - \alpha)^n$, n is the reaction order, k is the gas constant.

Taking the logarithm of Eq.(2) we have

$$\ln(d\alpha/dt) = \ln(A) + \ln[g(\alpha)] - E/kT. \tag{3}$$

A plot of $\ln(d\alpha/dt)$ versus $1/T$ for various constant levels of conversion α should then yield a straight line with slope of $-E/k$. The treatment of the experimental data in Fig.6 with the Eq.(3) yields the reaction activation energies at different conversion rate α shown in Fig.7. The average activation energies in the first pyrolysis stage is 216 kJ/mol and obviously higher than those(163–186 kJ/mol) from the literatures(Hrdina, 1998; Salin, 1993).

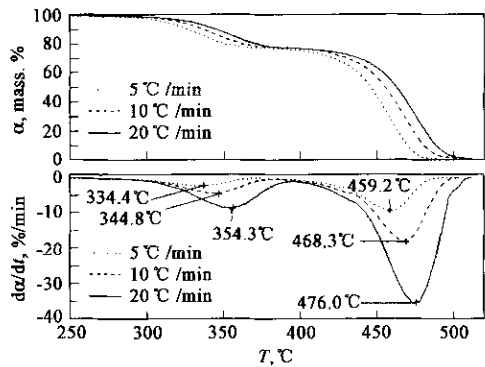


Fig. 6 TGA of EVA in nitrogen at different constant heating rates

To examine the correctness of the above results, another method, which was derived by Kissinger(Kissinger, 1957), is applied to calculate the reaction activity energy. Kissinger applied the maximum decomposition rate conditions to Eq.(2), i.e. $d(d\alpha/dt)/dt = 0$, and after differentiation found

2.3 Reaction kinetic

Because that the kinetic parameters vary with the change of amount of vinyl acetate in EVA (Hrdina, 1998), the determination of the pyrolysis kinetic parameters of the EVA used in solar modules, is necessary, although some kinetic parameters of the EVA pyrolysis were published for other goals(Hrdina, 1999; Salin, 1993).

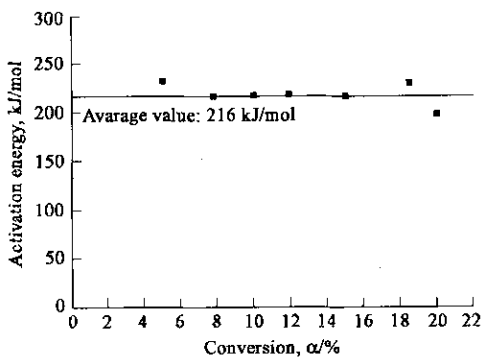


Fig. 7 Activity energy as function of conversion at the first pyrolysis stage of EVA

$$\beta/T_m^2 = (A_m R)/E_m \exp(-E_m/RT_m), \tag{4}$$

where $\beta = dT/dt$ is the heating rate, and the subscript m denotes values at the maximum decomposition rate.

The natural log of Eq.(4) is taken such that

$$\log(\beta/T_m^2) = K - E_m/RT_m. \tag{5}$$

Substituting the experimental data(Fig. 6) in Eq.(5) yields the linear relation between the two terms $\log(\beta/T_m^2)$ and $1/T_m$ as shown in Fig. 8. It can be seen that the activation energies for the first stage calculated with different methods are identical. The difference from the other literature (Hrdina, 1998; Nam, 1992) can be attributed to the acetic acid content in EVA, which is 22 wt.% for our system matching 30 wt.% and 12 wt.% in the EVA used by Nam (Nam, 1993) and Hrdina(Hrdina, 1998), respectively.

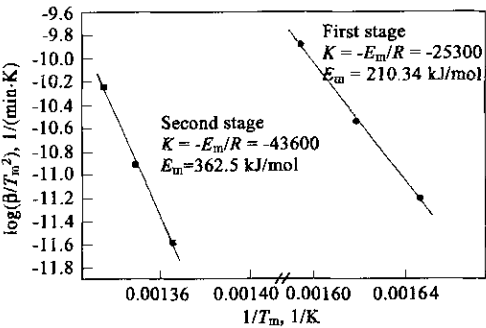


Fig. 8 TGA data plotted according to Kissinger's method

The influence of the temperature on the reaction rate can be known from the activation energy. The influence is larger in the second stage than in the first, for example, when the temperature is 20 K higher, the reaction rate increase 4 times and 6 times in the first and second stage, respectively. So, in the industrial practice the solar modules should be heated as evenly as possible, because the slowest reaction district always decides the reaction time needed for the whole module.

3 Conclusions

The basic pyrolysis behavior of neat ethylene-vinylacetate(EVA) copolymer was investigated by TGA and DTA at different heating rate under different oxidizing atmosphere. The DTA of EVA gave three endothermic peaks, which will protect the Si-wafer in the solar modules from be damaged by the thermal stress during the rapid heating stage of the pyrolysis of solar modules. The partial oxidizing atmosphere can accelerate the pyrolysis reactions but results in the formation of an abundant amount of coke. To eliminate the residual coke thoroughly, a higher end pyrolysis temperature (570°C) is necessary. Besides, a strong exothermal peak was observed in the EVA pyrolysis under air condition. This peak may indicate a combustion reaction. The strong exothermal peak disappears when the O₂ content is lower than 10 vol.%. The mass balance of EVA pyrolysis has been made according to the thermovolumetry, which gave the output of 10 wt.% permanent gas, 89.9 wt.% condensate and 0.1 wt.% residual coke. The different compositions of the permanent gas in different pyrolysis stages result in different heating values of the gas, corresponding to the known pyrolysis mechanism. Furthermore, the gas composition in the second stage indicated that the acetic acid was not completely released from the matrix plastic in the first pyrolysis stage. The kinetic parameter of the EVA (Elvax-150) pyrolysis was derived from the TG data. In short, the pyrolysis behaviours of EVA, such as the thermal effects, melting point, pyrolysis gas amount, kinetic parameter etc., are strongly influenced by the content of vinyl acetate in it.

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