Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 1065-1070

THERMAL DEGRADATION OF POLYVINYL CHLORIDE

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Abstract

The thermal degradation of a sort of polyvinyl chloride was investigated. Complex processes for polyvinyl chloride degradation were evidenced. The kinetic analysis of dehydrochlorination and of subsequent processes was carried out. A change of mechanism was detected when dehydrochlorination goes to completion. The values of non-isothermal kinetic parameters determined by various methods are in a satisfactory agreement. The obtained results allowed some clarifications concerning the thermal degradation steps.

Keywords: non-isothermal kinetic parameters, polyvinyl chloride, thermal degradation

Introduction

The polyvinyl chloride (PVC), one of the most used synthetic polymers, is a thermoplastic material with good elastic properties. The main disadvantage of its use consists in its relatively high thermal, photochemical and radiochemical instability.

Although the thermal degradation of polyvinyl chloride has been extensively investigated, there are still controversial aspects which need to be clarified. Different mechanisms of the degradation (radicalic, ionic, molecular) were proposed based on various experimental proofs [1]. A 'zipper' mechanism of polyvinyl chloride degradation proposed by Šimon [2] is usually mentioned.

It is generally accepted that a first degradation process which occurs at lower temperature, consists mainly of dehydrochlorination either with initiation at the defects of the polymeric chain (double bonds, tertiary and allylic chlorine, branching, etc.) [3, 4], or by random initiation in any point of the chain. Millan *et al.* [5] associated the instability of polyvinyl chloride with the presence of isotactic sequences as well as of some local conformations with a high number of degrees of freedom. Chirinos *et al.* [6] assigned the thermal instabilities of PVC to the presence of additives used during polymerization.

The number of thermal degradation steps and the values of kinetic parameters can be considered other controversial aspects [5, 7, 8].

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

In a previous paper [9], the results concerning the thermooxidative degradation of polyvinyl chloride in air have been presented. A value of the activation energy of 107(±3) kJ mol^{-1} was reported.

This work is dedicated to the thermal stability of a particular PVC type as well as to the non-isothermal kinetics of its thermal degradation.

Experimental

Powdered samples of a polyvinyl chloride have been subjected to thermogravimetric analysis. A sort of PVC obtained through emulsion in the CCMP laboratory from the ICECHIM Institute Bucharest has been used.

This type, called PVC–miniemulsion II is characterized by M_w=172000 and M_n=64000.

The curves TG and DTG have been recorded with a DuPont 1090 equipment by using aluminium open crucibles. The mass of the used samples was within the 12.7 12.85 mg range. The samples have been heated in flowing argon in the temperature range 293–773 K and heating rates 3, 4, 5, 8 and 10 K min^{-1}. A flow rate of 1 l h^{-1} and a purge time of 30 min were used. The gas was purified by using molecular sieves, silica gel and Deoxo units.

Results and discussions

Figure 1 shows the TG and DTG curves for a heating rate a=5 K min^{-1}. Similar curves have been obtained for other values of the heating rate.

The thermal degradation of polyvinyl chloride in the temperature range 293–773 K occurs through successive processes accompanied by mass loss. Finally a graphitic black coloured residue is obtained.

The first process observed in the temperature range 473–633 K, characterized by a mass loss of ~63%, is a complex one. The first step of this process can be assigned to the progressive dehydrochlorination of the polymer. The following one leads to release of HCl, aromatic hydrocarbons (mostly benzene and very small amounts of

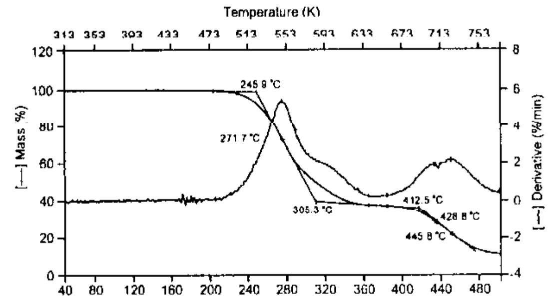

Fig. 1 The TG and DTG curves for the thermal degradation of polyvinyl chloride at a heating rate of a=5 K min^{-1}

toluene, styrene, etylbenzene, xylene isomers, naphthalene, indane, indene, etc) as well as to a conjugated polyene structure [10].

The second complex process occurring in the temperature range 653–773 K, is accompanied by a mass loss of ~27%, and corresponds to the pyrolysis of the polyene. According to the literature data, this process is characterized either by a single step [8], or by two competitive reactions [11]. The shapes of the DTG curves suggest two competitive reactions.

Figure 2 shows the mass losses associated to the first process in the temperature range 473–673 K and for the heating rates of 3, 4, 5, 8 and 10 K $\min^{-1}$.

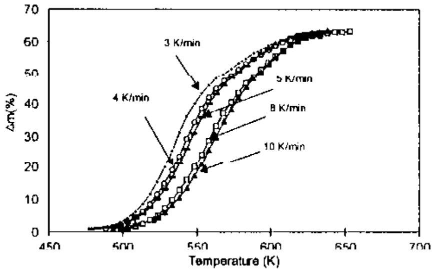

Fig. 2 The curves Δm *vs.* T

In order to evaluate the nonisothermal kinetic parameters, some differential and integral methods have been used.

Isoconversional Flynn-Wall-Ozawa method [12,13]

For $2.5\% \leq \Delta m \leq 50\%$ the isoconversional diagrams for heating rates in the range 3–10 K $\min^{-1}$ have been recorded (Fig. 3).

As the slope keeps a quasiconstant value for $2.5\% \leq \Delta m \leq 45\%$ (Δm is the mass loss) one can conclude on a single decomposition mechanism based on the irreversible dehydrochlorination reaction.

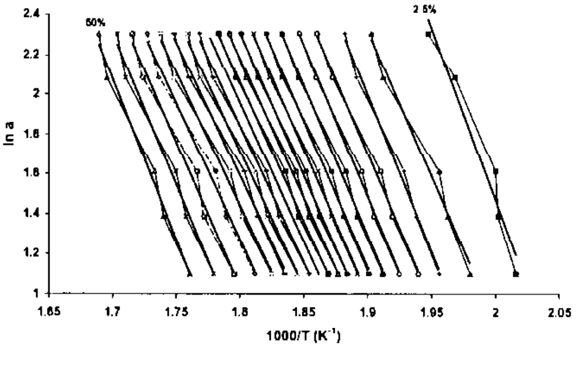

Fig. 3 The Flynn-Wall-Ozawa isoconversional diagrams

By using the Flynn-Wall-Ozawa diagram, the values of the activation energy at various values of mass loss Δm were estimated for this reaction (Table 1).

Table 1 Values of the activation energy obtained by the Flynn-Wall-Ozawa isoconversional method for various value of Δm and 3 K min^{-1} $\leq a \leq$10 K min^{-1}

Δm /%	2.5	5	7.5	10	12.5	15
E/kJ mol^{-1}	117.4±17.3	115.2±9.2	119.3±6.9	117.6±9.4	119.1±4.7	118.2±4.6
r*	0.9692	0.9904	0.9958	0.9972	0.9977	0.9977
Δm /%	17.5	20	22.5	25	27.5	30
E/kJ mol^{-1}	115.8±4.4	113.7±4.5	113.1±4.3	110.6±4.2	109.9±4.0	109.4±4.7
r	0.9977	0.9978	0.9981	0.9978	0.9979	0.9976
Δm /%	32.5	35	37.5	40	42.5	45
E/kJ mol^{-1}	106.7±5.1	105.6±5.3	105.0±5.3	105.5±5.5	107.5±6.2	110.9±7.1
r	0.9966	0.9963	0.9961	0.9956	0.9947	0.9938
Δm /%	47.5	50	52.5	55	57.5	60
E/kJ mol^{-1}	120.0±8.2	127.6±8.7	147.8±9.9	161.6±18.1	185.0±26.4	224.7±55.4
r	0.9930	0.9828	0.9933	0.9815	0.9706	0.9200

* r is the correlation coefficient of the corresponding linear regression

As shown in the table for 2.5%$\leq \Delta m \leq$45% the activation energy values fluctuates around the average value of 113(±5) kJ mol^{-1}. For Δm>45% a dependence of the activation energy on the degree of conversion has been noticed. This is probably due to the change of the reaction mechanism in the non-isothermal conditions used.

Isoconversional Friedman method [14]

In order to evaluate the activation energy more precisely, the term ln(dΔm/dT) was obtained by numerical derivation of the curve Δm *vs*. T with respect to T and

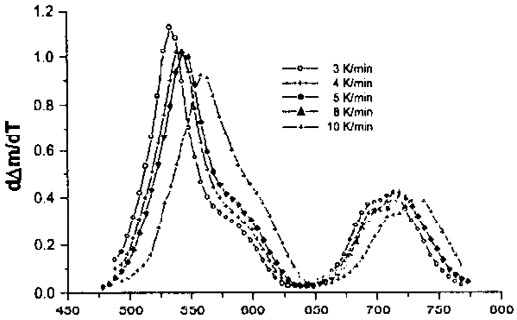

Fig. 4 The curves dΔm /dT *vs*. T for the used heating rates

subsequent taking logarithms. The curves dΔm/dT *vs.* T for the applied heating rates are given in Fig. 4.

These curves confirm the existence of a complex processes of thermal degradation with successive reactions for the first process and competitive for the second one. For the first degradation process (dehydrochlorination) the values of the activation energy as obtained from the slopes of the straight lines ln(dΔm/dT) *vs.* (1/T) are listed in Table 2.

Table 2 Values of the activation energy obtained by using the Friedman isoconversional method

Δm /%	2.5	5	7.5	10	12.5	15
E/kJ mol^{-1}	137.2±38.4	127.8±7.7	116.3±3.5	116.3±3.1	111.8±2.8	104.4±1.9
r*	0.8996	0.9947	0.9985	0.9989	0.9990	0.9967
Δm /%	17.5	20	22.5	25	27.5	30
E/kJ mol^{-1}	98.5±5.4	97.6±6.2	97.3±6.5	96.0±6.4	94.4±6.6	93.2±7.2
r	0.9953	0.9941	0.9933	0.9933	0.9929	0.9915
Δm /%	32.5	35	37.5	40	42.5	45
E/kJ mol^{-1}	93.3±7.8	95.3±7.8	99.7±7.8	108.2±8.9	119.5±10.4	133.1±11.4
r	0.9897	0.9902	0.9909	0.9899	0.9886	0.9890
Δm /%	47.5	50	52.5	55	57.5	60
E/kJ mol^{-1}	150.4±13.0	170.9±15.2	194.1±20.3	217.8± 30.4	252.8±48.2	324.8±116.7
r	0.9891	0.9883	0.9839	0.9721	0.9498	0.8485

* r is the correlation coefficient of the corresponding linear regression

As shown from the table for 2.5%≤Δm≤45% the values of the activation energy are close to the average of 111(±7) kJ mol^{-1}, in fair good agreement with the one obtained by applying Flynn-Wall-Ozawa method. Above Δm>45% again a dependence of the activation energy on the degree of conversion due to the change of the reaction mechanism should be noticed.

Kissinger's method [15]

Figure 5 shows the straight line ln(a/T_M^2) *vs.* (1/T_M), where T_M is the temperature corresponding to the maximum reaction peak (peak of the DTG curve), the slope of which allowed to estimate the activation energy.

The obtained value of the activation energy is E=(103.4±3.3) kJ mol^{-1}, in a satisfactory agreement with the values obtained using other methods.

For the two competitive pyrolysis reactions of the second thermal degradation process using Kissinger's method we obtained:

E=(300.8±21.7) kJ mol^{-1}, r=0.9925 for the first reaction;
E=(213.1±10.7) kJ mol^{-1}, r=0.9962 for the second reaction.

These values are close with those reported by Wu *et al.* [11].

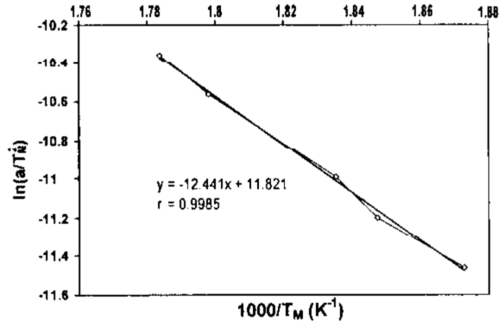

Fig. 5 Kissinger's plot for dehydrochlorination step

Conclusions

The investigation concerning the thermal degradation of polyvinyl chloride allowed:

- to put in evidence two complex degradation processes;
- to calculate the activation energy value for the dehydrochlorination, which is in fair good agreement with the value obtained for the thermooxidative degradation in air;
- to evidence the change of mechanism for Δm>45% (first degradation process); to discriminate two competitive reactions of the second process;
- to estimate the activation energies values for the two competitive pyrolysis reactions.

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