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# DYNAMIC AND ISOTHERMAL THERMOGRAVIMETRIC DEGRADATION OF POLY(VINYL CHLORIDE)/ CHLORINATED POLY(ETHYLENE) BLENDS

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## Abstract

The thermal degradation of poly(vinyl chloride)/chlorinated poly(ethylene) (PVC/CPE) blends of different compositions was investigated by means of dynamic and isothermal thermogravimetric analysis in flowing atmosphere of nitrogen. Kinetic parameters (the apparent activation energy $E$, and pre-exponential factor $Z$) were calculated after Flynn–Wall–Ozawa method for the first stage of dynamic degradation of PVC/CPE blends, and after Flynn method for the isothermal degradation. In both cases, there is the compensation dependence between the values $E$ and log$Z$. The values of compensation ratios as well as the characteristics of TG and DTG curves, confirm the stabilizing effect of CPE on PVC dehydrochlorination.

**Keywords:** dynamic and isothermal thermogravimetric analysis, kinetic parameters, PVC/CPE blends, thermal degradation

## Introduction

Poly(vinyl chloride) (PVC) is one of the most important thermoplastics and is very often blended with other polymers. Blending one polymer with another is a method of modifying the physical properties of a polymer in a desired manner. For example, by addition of chlorinated poly(ethylene) (CPE), the impact strength and processibility of PVC are improved. However, it has been noticed that the thermal stability of each polymer in the blend can be significantly changed due to the possible interaction of the polymer blend components and/or their degradation products [1]. Despite the immiscibility of PVC and CPE, the interactions of these polymers were detected, dependent on their ratio in the blend [2]. The main reaction of the PVC thermal degradation at moderate temperatures is dehydrochlorination, which is also a dominant reaction in the CPE degradation. While the dehydrochlorination of PVC is fast, specific

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(zipper) reaction, the dehydrochlorination of CPE is a slow reaction of random HCl elimination [3].

The physico-mechanical properties of PVC/CPE blends have been investigated [4–6], but few data are to be found on thermal stability. The aim of this work is to investigate the thermal degradation of PVC/CPE blends and the influence of CPE on PVC dehydrochlorination by means of dynamic and isothermal thermogravimetry.

## Experimental

The materials used in this study were commercially available suspension grade PVC S-700G (K-value 70; chlorine content 55.9%) supplied by Inavinil, Croatia, and CPE DOW XZ (chlorine content 38.5%; melting temperature 107.15°C; heat of melting 9.17 J $g^{-1}$) supplied by Dow, Germany.

PVC/CPE blends of different mass fraction of polymers (100/0, 90/10, 80/20, 70/30, 50/50, 30/70, and 0/100) were prepared by dry mixing polymer powders in mixer and then melt blending on a laboratory roller mill at 160°C for 60 s. The thickness of the drawn-out foils was 0.25±0.05 mm.

The sample of the blend (2.0±0.2 mg) was degradated under a nitrogen flow (30 $cm^3$ $min^{-1}$) in the thermobalance (Perkin Elmer TGS-2 system coupled to a microprocessor programmer System 4) under dynamic conditions (at the heating rates of 2.5, 5, 10 and 20°C $min^{-1}$) and isothermally (at the temperatures 240, 250, 260 and 270°C). In the latter case the sample was initially heated at the heating rate of 80°C $min^{-1}$ from the start (50°C) to the selected degradation temperature and then held at this temperature for 120 min.

## Results and discussion

The dynamic thermogravimetric (TG) curves, obtained for PVC/CPE blends in the temperature range 50–600°C at various heating rates are shown in Figs 1–4, while the corresponding derivative thermogravimetric (DTG) curves, only for the heating rate 2.5°C $min^{-1}$, in Fig 1. It is evident that the thermal degradation of PVC and CPE occurs through two basic degradation steps: the first one presents the process of dehydrochlorination of PVC or CPE respectively, while the second one presents the total degradation of the dehydrochlorinated residues. The maximal rate of PVC dehydrochlorination (the peak temperature at 261.61°C) is about six times greater than the maximal rate of CPE dehydrochlorination (the peak temperature at 328.54°C) (Fig. 1, curves 1 and 7). PVC/CPE blends also degradate within two basic steps (Fig. 1, curves 2–6). In the first step two peaks are evident on the DTG curves. The first one (I) corresponds to the maximal mass loss rate of PVC dehydrochlorination and the second one (II) corresponds to the maximal mass loss rate of CPE dehydrochlorination. The maximal rate of PVC dehydrochlorination decreases by increasing the ratio of CPE in the PVC/CPE blends and in the 30/70 blend is smaller than the maximal rate of CPE dehydrochlorination. The maximal rate of PVC dehydrochlorination depends not only on

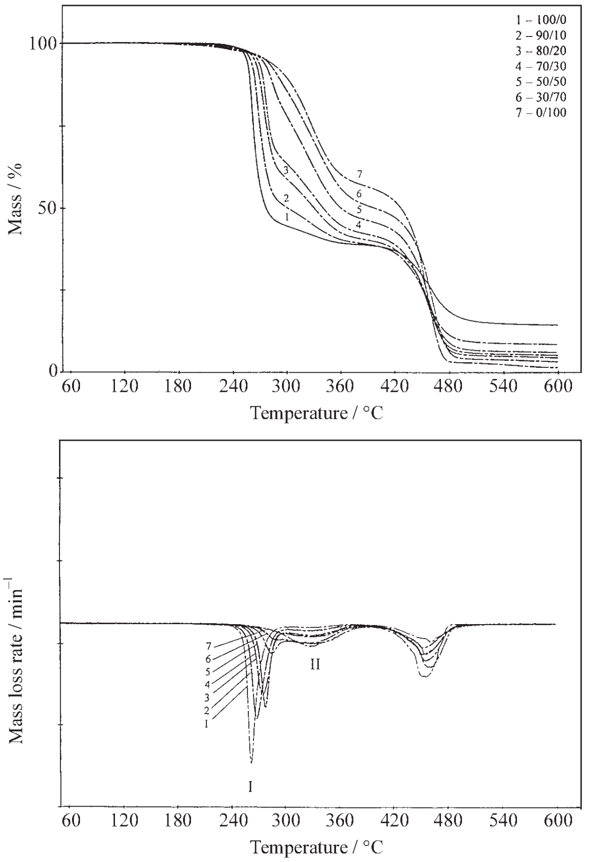

**Fig. 1** Dynamic TG and DTG curves for PVC/CPE blends of different compositions; heating rate 2.5°C min$^{-1}$ (the values of mass loss rate of the sample are not absolute)

the composition of the blend but also on the heating rate. It can be exemplified by the 50/50 blend in Fig. 5. In the blends of 100/0–50/50 composition, it decreases with the increasing of heating rate, but for the 30/70 blend it is the opposite. At the same time the maximal dehydrochlorination rate of 0/100 blend is independent on the heating rate.

The characteristics of TG and DTG curves, which also depend on the composition of the blend as well as on the applied heating rate, are: the onset temperatures of the first ($T_1^{\mathrm{o}}$) and second degradation step ($T_2^{\mathrm{o}}$) (the intersections of the extrapolated base lines with tangents drawn in the inflection points of the TG curve), the temperatures at the maximal rate of degradation in the first ($T_1^{\mathrm{m}}$) and second degradation step ($T_2^{\mathrm{m}}$), the degrees of conversion at the corresponding maximal rates ($\alpha_1^{\mathrm{m}}$ and $\alpha_2^{\mathrm{m}}$), and the mass losses at the end of the first ($\Delta m_1$) and second degradation step ($\Delta m_2$).

By increasing the ratio of CPE in the blends, the temperatures $T_1^{\mathrm{o}}$ and $T_1^{\mathrm{m}}$ are shifted toward higher values. This means that PVC in the first degradation step is sta-

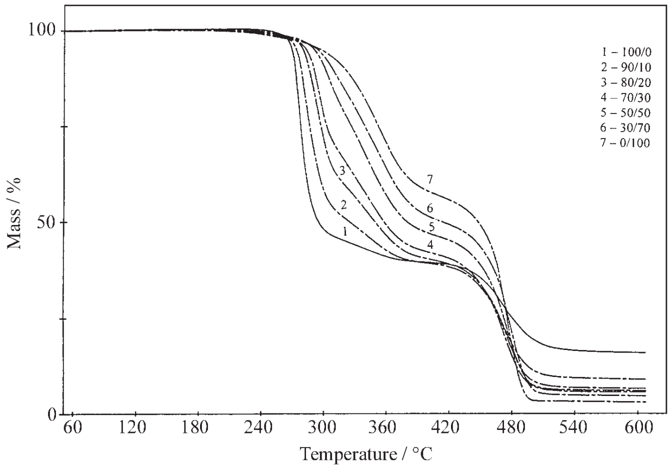

**Fig. 2** Dynamic TG curves for PVC/CPE blends of different compositions; heating rate 5°C min$^{-1}$

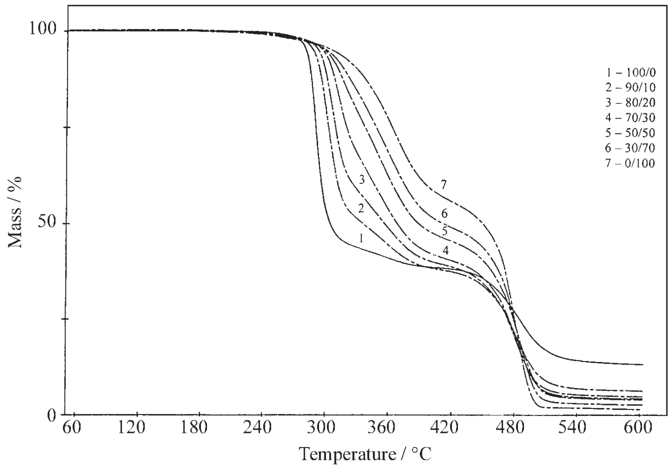

**Fig. 3** Dynamic TG curves for PVC/CPE blends of different compositions; heating rate 10°C min$^{-1}$

bilized by addition of CPE. At the same time, the shifts of $T_2^o$ and $T_2^m$ are considerably of a lesser degree, so it can be concluded that the interactions between PVC and CPE in the second degradation step are weaker.

The maximal rate of PVC dehydrochlorination in 100/0, 90/10, and 80/20 blends is achieved at average degree of conversion $\bar{\alpha}_1^m$ (the value for all heating rates) about 21%, whereas $\bar{\alpha}_1^m$ for pure CPE is 26%. By increasing the ratio of CPE in the blend from 30 to 70%, $\bar{\alpha}_1^m$ lowers, and, for PVC/CPE 30/70 blend, it is 11%.

The average mass loss of PVC in the first degradation step is about 61% and is slightly higher than the stoichiometric quantity of HCl in the PVC. This difference

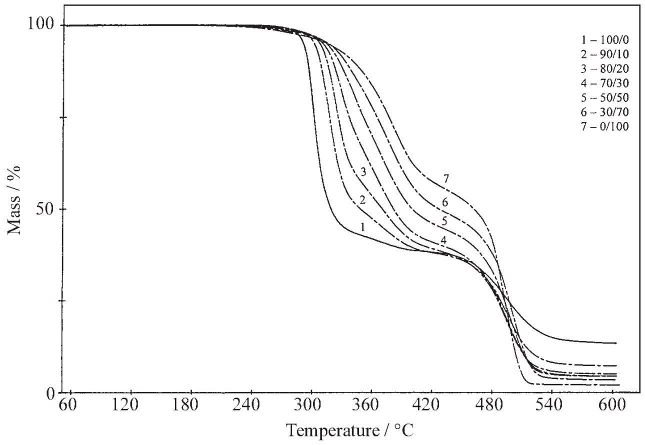

**Fig. 4** Dynamic TG curves for PVC/CPE blends of different compositions; heating rate 20°C min$^{-1}$

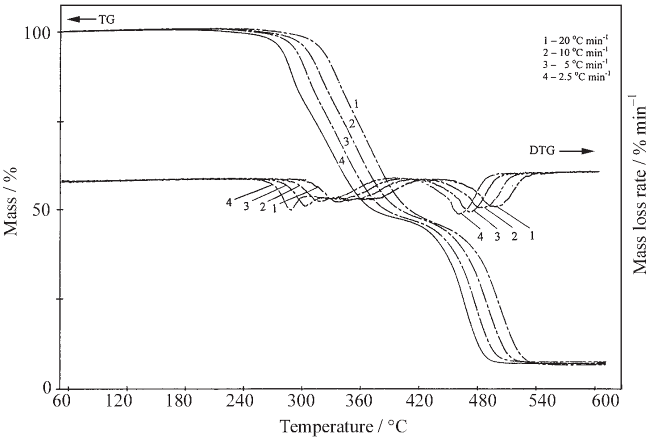

**Fig. 5** Dynamic TG and DTG curves for PVC/CPE blend of composition 50/50 obtained at different heating rates

corresponds to the formation of aromatic hydrocarbons, mainly benzene [7]. CPE dehydrochlorinates completely, as well as PVC, since its average mass loss, about 44%, is higher than the overall chlorine content in CPE. In the second degradation step the average mass losses of PVC and CPE are about 24 and 54%, respectively. By increasing the ratio of CPE in the PVC/CPE blends the mass loss linearly lowers in the first degradation step, while in the second one it linearly increases.

PVC/CPE blends were also degradated isothermaly at various temperatures in the range of 240–270°C. The example of isothermal TG curves of PVC/CPE blends of different compositions at 270°C is shown in Fig. 6. The shape of TG curves depends on the blend composition. The curves for the blends' compositions 100/0–50/50 are sigmoidal

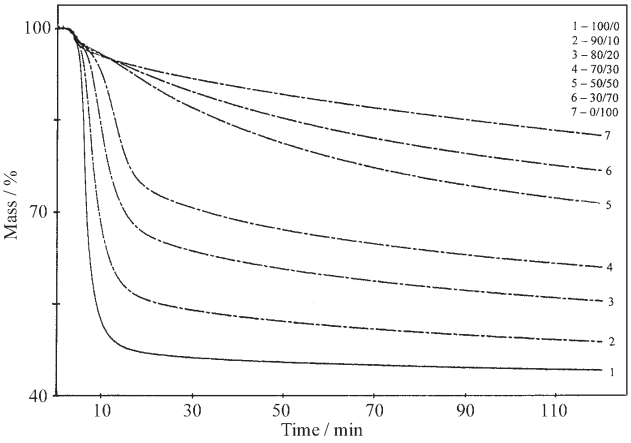

**Fig. 6** Isothermal TG curves for PVC/CPE blends of different compositions at 270°C

which is characteristic of autocatalytic reactions and reactions with zero initial rate [8]. On the other hand, TG curves of 30/70 and 0/100 blends are convex, which confirms that the addition of CPE diminishes the catalytic effect of HCl on polymer degradation. The shape of TG curves depends also on the degradation temperature, which is shown for the 50/50 blend in Fig. 7. By increasing temperature from 240 to 270°C the mass loss at the end of heating, for a certain composition of the blend, increases. On the other hand, by increasing the ratio of CPE in PVC/CPE blends, the selected degree of conversion during the degradation at a particular temperature is reached in a longer time (Table 1). The mass loss of PVC/CPE blends of various composition during the 120 min heating in the investigated temperature range of 240–270°C, does not exceed 60%, which corresponds to the first degradation step of dynamic degradation where dehydrochlorination of polymers is

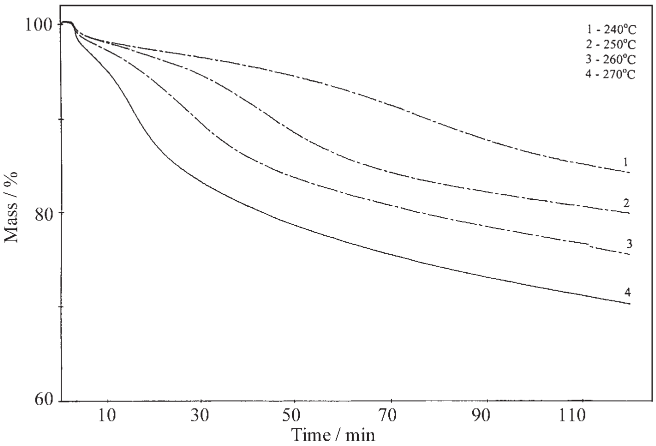

**Fig. 7** Isothermal TG curves for PVC/CPE blend of composition 50/50 obtained at different degradation temperatures

the main reaction. For example, the mass loss at the end of the isothermal heating of PVC and CPE at 270°C is 56 and 17.5%, respectively. It can be deduced that the dehydrochlorination of PVC is completed after 120 min of degradation at this temperature, while the dehydrochlorination of CPE is partial.

**Table 1** Isothermal degradation of PVC/CPE blends of different composition. Time required to reach certain conversion

| | $\alpha$/% | 3 | 4 | 5 | 7.5 | 10 | 12.5 | 15 | 20 | 25 | 30 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PVC/ CPE | $T$/K | Time, $t$/min | | | | | | | | | |
| 100/0 | 513 | – | – | 17.97 | 19.91 | 21.08 | 21.98 | 22.73 | 24.07 | 25.38 | 26.81 |
| | 523 | – | – | 10.17 | 11.33 | 12.12 | 12.76 | 13.35 | 14.44 | 15.56 | 16.86 |
| | 533 | – | – | 6.63 | 7.13 | 7.44 | 7.78 | 8.05 | 8.57 | 9.11 | 9.74 |
| | 543 | – | – | 4.95 | 5.28 | 5.51 | 5.69 | 5.85 | 6.15 | 6.43 | 6.79 |
| 90/10 | 513 | – | – | 20.38 | 23.00 | 25.12 | 26.40 | 28.07 | 30.79 | 33.97 | 38.09 |
| | 523 | – | – | 11.85 | 13.50 | 14.47 | 15.30 | 16.07 | 17.56 | 19.25 | 21.43 |
| | 533 | – | – | 7.59 | 8.50 | 9.05 | 9.70 | 10.06 | 11.05 | 12.19 | 13.60 |
| | 543 | – | – | 5.68 | 6.11 | 6.56 | 6.80 | 7.19 | 7.83 | 8.56 | 9.52 |
| 80/20 | 513 | – | – | 26.61 | 30.38 | 33.89 | 36.50 | 39.44 | 44.72 | 51.11 | 60.27 |
| | 523 | – | – | 13.50 | 15.60 | 17.50 | 19.17 | 20.83 | 24.44 | 28.61 | 34.17 |
| | 533 | – | – | 10.34 | 11.94 | 12.89 | 13.83 | 14.61 | 16.80 | 19.67 | 23.89 |
| | 543 | – | – | 6.86 | 7.50 | 8.33 | 8.89 | 9.47 | 10.76 | 12.46 | 15.22 |
| 70/30 | 513 | – | – | 37.58 | 45.69 | 51.20 | 55.68 | 59.78 | 68.89 | 82.50 | – |
| | 523 | – | – | 22.75 | 28.70 | 33.06 | 36.64 | 40.18 | 45.80 | 55.11 | 113.34 |
| | 533 | – | – | 11.97 | 15.08 | 17.24 | 19.03 | 20.73 | 25.00 | 34.61 | 67.78 |
| | 543 | – | – | 8.33 | 9.94 | 11.05 | 11.97 | 12.83 | 15.00 | 18.61 | 33.34 |
| 50/50 | 513 | – | – | 46.24 | 64.32 | 77.83 | 91.43 | 111.59 | – | – | – |
| | 523 | – | – | 28.81 | 38.16 | 45.74 | 53.74 | 65.67 | 118.08 | – | – |
| | 533 | – | – | 17.96 | 24.05 | 29.25 | 35.19 | 43.80 | 75.54 | – | – |
| | 543 | – | – | 10.56 | 13.89 | 16.94 | 20.56 | 25.34 | 44.56 | 76.67 | – |
| 30/70 | 513 | 27.56 | 47.22 | 65.00 | 94.00 | 107.50 | – | – | – | – | – |
| | 523 | 16.21 | 26.56 | 37.21 | 61.67 | 92.11 | – | – | – | – | – |
| | 533 | 10.18 | 15.78 | 21.76 | 37.78 | 56.67 | 75.56 | 102.22 | – | – | – |
| | 543 | 6.58 | 9.25 | 12.33 | 20.00 | 29.17 | 39.83 | 52.78 | – | – | – |
| 0/100 | 513 | 28.89 | 55.56 | 91.39 | – | – | – | – | – | – | – |
| | 523 | 12.71 | 26.79 | 43.46 | 110.00 | – | – | – | – | – | – |
| | 533 | 7.81 | 13.69 | 21.05 | 50.56 | 87.33 | – | – | – | – | – |
| | 543 | 5.47 | 8.52 | 12.39 | 26.67 | 45.00 | 71.11 | 92.50 | – | – | – |

Although PVC and CPE are chemically similar, they have different degradation mechanism and thermal stability, which can be explained by differences in the microregularity of the corresponding polymer chains. The mutual location of the monomer segments in PVC corresponds to 'head to tail' pattern. PVC releases HCl more readily on dehydrochlorination, since the chloroallylic fragments of relatively weak C–Cl bond are formed. CPE has non-regular location of chlorine atoms along the polymer chain associated with certain 'blockwise' structures involving 'head to head', 'tail to tail' and other patterns of mutual connection of the chain segments. The dehydrochlorination results in the formation of 'vinyl' structure of much stronger C–Cl bonds [3]. As a consequence of that CPE with the same chlorine content as in PVC has superior thermal stability than PVC. Dehydrochlorination of CPE is a slow random reaction, in contrast to fast autocatalytic dehydrochlorination of PVC.

Both, the dynamic and isothermal TG curves of PVC/CPE blends were used for the calculation of kinetic parameters of dehydrochlorination processes. Flynn–Wall–Ozawa (FWO) isoconversion method [9] uses dynamic TG curves, according to the Eq. (1):

$$\log\beta = -0.457\frac{E}{R}\frac{1}{T} - 2.315 + \log\frac{ZE}{R} - g(\alpha) \qquad (1)$$

$$(\alpha=\text{const.})$$

where $\beta$ is the heating rate, $E$ is the apparent activation energy, $Z$ is the pre-exponential factor, $R$ is the gas constant, $g(\alpha)$ is the kinetic model and $T$ is temperature read off from TG curve for certain conversion $\alpha$, where $\alpha=(m_0-m_t)/m_0$ ($m_0$ and $m_t$ are the sample masses at times zero and $t$). By plotting $\log\beta$ *vs.* $1/T$ a set of straight lines can be obtained. The values $E$ and $Z$ were calculated from the slopes and intercept of the straight lines for every selected conversion. The example of FWO plots is shown

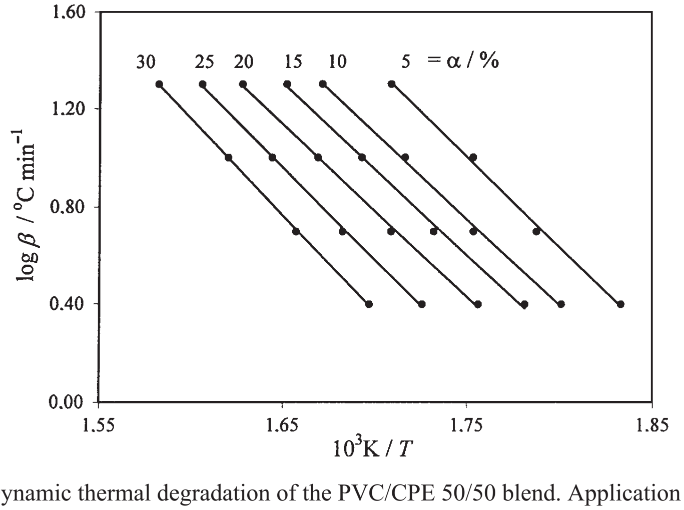

**Fig. 8** Dynamic thermal degradation of the PVC/CPE 50/50 blend. Application of the Flynn–Wall–Ozawa equation

**Table 2** Dynamic thermal degradation of PVC/CPE blends. Kinetic parameters determined by Flynn–Wall–Ozawa equation

| PVC/ CPE | α/% | 5 | 10 | 15 | 20 | 25 | 30 | (5–30) |
|---|---|---|---|---|---|---|---|---|
| 100/0 | $E$/kJ mol$^{-1}$ | 144.3 | 141.2 | 138.9 | 137.2 | 136.0 | 135.3 | 139.5 |
| | $Z$/min$^{-1}$ | $1.51\cdot10^{12}$ | $1.26\cdot10^{12}$ | $1.02\cdot10^{12}$ | $8.73\cdot10^{11}$ | $8.04\cdot10^{11}$ | $7.68\cdot10^{11}$ | $1.04\cdot10^{12}$ |
| | $E$/log$Z$ | 11.84 | 11.67 | 11.56 | 11.49 | 11.43 | 11.38 | 11.56 |
| 90/10 | $E$/kJ mol$^{-1}$ | 122.6 | 119.4 | 118.3 | 116.8 | 115.4 | 115.7 | 118.5 |
| | $Z$/min$^{-1}$ | $8.37\cdot10^{9}$ | $6.55\cdot10^{9}$ | $6.91\cdot10^{9}$ | $6.12\cdot10^{9}$ | $5.22\cdot10^{9}$ | $5.98\cdot10^{9}$ | $6.52\cdot10^{9}$ |
| | $E$/log$Z$ | 12.35 | 12.17 | 12.02 | 11.94 | 11.88 | 11.83 | 12.03 |
| 80/20 | $E$/kJ mol$^{-1}$ | 124.5 | 122.6 | 120.6 | 120.3 | 120.4 | 120.7 | 121.7 |
| | $Z$/min$^{-1}$ | $9.78\cdot10^{9}$ | $9.76\cdot10^{9}$ | $8.06\cdot10^{9}$ | $9.03\cdot10^{9}$ | $1.03\cdot10^{10}$ | $1.16\cdot10^{10}$ | $9.76\cdot10^{9}$ |
| | $E$/log$Z$ | 12.47 | 12.28 | 12.17 | 12.08 | 12.02 | 11.99 | 12.17 |
| 70/30 | $E$/kJ mol$^{-1}$ | 125.6 | 117.5 | 112.4 | 107.8 | 103.0 | 98.6 | 113.2 |
| | $Z$/min$^{-1}$ | $1.02\cdot10^{10}$ | $2.54\cdot10^{9}$ | $1.08\cdot10^{9}$ | $4.83\cdot10^{8}$ | $1.94\cdot10^{8}$ | $7.63\cdot10^{7}$ | $2.43\cdot10^{9}$ |
| | $E$/log$Z$ | 12.54 | 12.49 | 12.44 | 12.41 | 12.43 | 12.51 | 12.47 |
| 50/50 | $E$/kJ mol$^{-1}$ | 134.5 | 128.5 | 128.5 | 128.7 | 137.3 | 143.3 | 134.5 |
| | $Z$/min$^{-1}$ | $5.66\cdot10^{10}$ | $1.79\cdot10^{10}$ | $1.86\cdot10^{10}$ | $1.91\cdot10^{10}$ | $9.15\cdot10^{10}$ | $2.44\cdot10^{11}$ | $7.46\cdot10^{10}$ |
| | $E$/log$Z$ | 12.51 | 12.53 | 12.52 | 12.52 | 12.52 | 12.58 | 12.53 |
| 30/70 | $E$/kJ mol$^{-1}$ | 144.9 | 140.9 | 145.2 | 146.1 | 156.1 | 163.4 | 146.6 |
| | $Z$/min$^{-1}$ | $4.64\cdot10^{11}$ | $1.75\cdot10^{11}$ | $3.76\cdot10^{11}$ | $3.68\cdot10^{11}$ | $2.11\cdot10^{12}$ | $6.90\cdot10^{12}$ | $1.73\cdot10^{12}$ |
| | $E$/log$Z$ | 12.42 | 12.53 | 12.55 | 12.64 | 12.66 | 12.72 | 12.59 |
| 0/100 | $E$/kJ mol$^{-1}$ | 145.4 | 142.9 | 142.4 | 141.4 | 140.1 | 132.8 | 142.4 |
| | $Z$/min$^{-1}$ | $4.51\cdot10^{11}$ | $1.57\cdot10^{11}$ | $1.10\cdot10^{11}$ | $7.70\cdot10^{10}$ | $5.21\cdot10^{10}$ | $1.02\cdot10^{10}$ | $1.43\cdot10^{11}$ |
| | $E$/log$Z$ | 12.47 | 12.76 | 12.89 | 12.99 | 13.07 | 13.27 | 12.91 |

**Table 3** Isothermal degradation of PVC/CPE blends. Kinetic parameters determined by Flynn equation

| PVC/ CPE | α/% | 5 | 7.5 | 10 | 12.5 | 15 | 20 | 25 | 30 |
|---|---|---|---|---|---|---|---|---|---|
| 100/0 | $E$/kJ mol$^{-1}$ | 103.0 | 107.2 | 109.5 | 110.8 | 112.0 | 114.0 | 116.3 | 118. 5 |
| | $Z$/min$^{-1}$ | $1.7\cdot10^{9}$ | $4.2\cdot10^{9}$ | $6.6\cdot10^{9}$ | $8.6\cdot10^{9}$ | $1.1\cdot10^{10}$ | $1.6\cdot10^{10}$ | $2.5\cdot10^{10}$ | $3.9\cdot10^{10}$ |
| | $E$/log$Z$ | 11.14 | 11.14 | 11.14 | 11.15 | 11.16 | 11.17 | 11.18 | 11.19 |
| 90/10 | $E$/kJ mol$^{-1}$ | 99.3 | 103.0 | 104.3 | 104.9 | 104.4 | 106.0 | 106.5 | 107.0 |
| | $Z$/min$^{-1}$ | $6.7\cdot10^{8}$ | $1.4\cdot10^{9}$ | $1.8\cdot10^{9}$ | $1.9\cdot10^{9}$ | $1.6\cdot10^{9}$ | $2.1\cdot10^{9}$ | $2.2\cdot10^{9}$ | $2.2\cdot10^{9}$ |
| | $E$/log$Z$ | 11.25 | 11.27 | 11.29 | 11.31 | 11.35 | 11.37 | 11.41 | 11.46 |
| 80/20 | $E$/kJ mol$^{-1}$ | 100.6 | 104.6 | 104.8 | 105.9 | 107.5 | 107.8 | 106.8 | 104.0 |
| | $Z$/min$^{-1}$ | $7.1\cdot10^{8}$ | $1.6\cdot10^{9}$ | $1.5\cdot10^{9}$ | $1.7\cdot10^{9}$ | $2.4\cdot10^{9}$ | $2.2\cdot10^{9}$ | $1.5\cdot10^{9}$ | $6.7\cdot10^{8}$ |
| | $E$/log$Z$ | 11.36 | 11.38 | 11.43 | 11.45 | 11.47 | 11.53 | 11.63 | 11.78 |
| 70/30 | $E$/kJ mol$^{-1}$ | 119.6 | 121.0 | 121.6 | 121.9 | 122.1 | 119.8 | 114.0 | |
| | $Z$/min$^{-1}$ | $4.1\cdot10^{10}$ | $4.4\cdot10^{10}$ | $4.5\cdot10^{10}$ | $4.5\cdot10^{10}$ | $4.3\cdot10^{10}$ | $2.2\cdot10^{10}$ | $4.7\cdot10^{9}$ | |
| | $E$/log$Z$ | 11.28 | 11.36 | 11.41 | 11.45 | 11.48 | 11.59 | 11.79 | |
| 50/50 | $E$/kJ mol$^{-1}$ | 114.5 | 117.4 | 116.5 | 113.6 | 112.7 | | | |
| | $Z$/min$^{-1}$ | $8.9\cdot10^{9}$ | $1.4\cdot10^{10}$ | $9.4\cdot10^{9}$ | $4.0\cdot10^{9}$ | $2.7\cdot10^{9}$ | | | |
| | $E$/log$Z$ | 11.47 | 11.58 | 11.68 | 11.83 | 11.95 | | | |
| | α/% | 3 | 4 | 5 | 7.5 | | | | |
| 30/70 | $E$/kJ mol$^{-1}$ | 110.4 | 125.3 | 128.4 | 128.2 | | | | |
| | $Z$/min$^{-1}$ | $6.4\cdot10^{9}$ | $1.2\cdot10^{11}$ | $1.8\cdot10^{11}$ | $1.0\cdot10^{11}$ | | | | |
| | $E$/log$Z$ | 11.26 | 11.30 | 11.41 | 11.64 | | | | |
| 0/100 | $E$/kJ mol$^{-1}$ | 127.3 | 146.2 | 155.8 | 167.4 | | | | |
| | $Z$/min$^{-1}$ | $3.5\cdot10^{11}$ | $1.4\cdot10^{13}$ | $8.2\cdot10^{13}$ | $4.8\cdot10^{14}$ | | | | |
| | $E$/log$Z$ | 11.20 | 11.11 | 11.20 | 11.40 | | | | |

in Fig. 8 for the 50/50 blend. The straight lines parameters for all investigated PVC/CPE blend compositions, as well as the average values of $E$ and $Z$ for the selected conversion range are shown in Table 2.

Flynn equation [10] was used to calculate $E$ and $Z$:

$$\ln t = \ln g(\alpha) - \ln Z + \frac{E}{R}\frac{1}{T} \tag{2}$$

The time $t$ needed to achieve a certain degree of conversion $\alpha$ at different temperatures was read off from the isothermal TG curves (Table 1). If the kinetic model $g(\alpha)$ is constant, the straight lines $\ln t$ *vs.* $1/T$ for a given conversion are obtained. In Fig. 9 the example of isoconversional straight lines, obtained for 50/50 blend in range of conversions 5–15%, is shown. The value $E$ and $Z$, calculated from the parameters of the straight lines, are shown in Table 3. By increasing the ratio of CPE in the blends, the range of Flynn equation application becomes narrower, shifting toward lower conversions, which indicates differences in degradation mechanism of PVC and CPE.

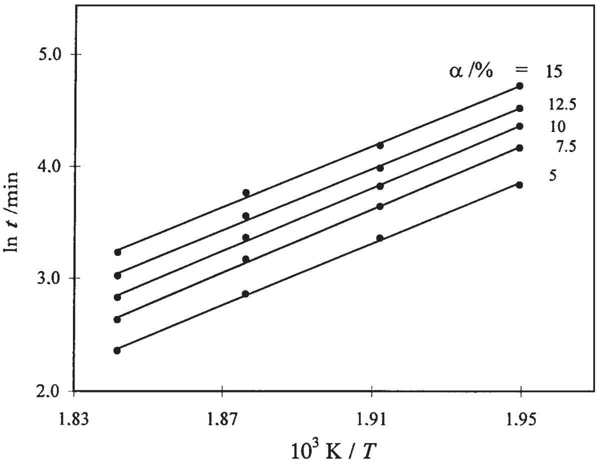

**Fig. 9** Isothermal degradation of PVC/CPE 50/50 blend. Application of the Flynn equation

Both activation energies, the one of isothermal degradation of PVC/CPE blends as well as the one of dynamic thermal degradation, change depending on the composition of the blend. The variation of this energy with the composition of the blend does not necessarily mean the change of the reaction ability of the system because the thermal degradation of polymer blends belongs to the heterogeneous chemical reactions and the calculated activation energy of the overall transformation is the apparent activation energy. Therefore, activation energy can be used only together with the corresponding pre-exponential factors as the criterion of the blend's thermal stability [11]. Between the apparent activation energy and the logarithm of preexponential factor, the linear dependence i.e. kinetic compensation effect [12, 13] has been found. The values of ratio $E/\log Z$ confirm that by addition of CPE, thermal stability of

PVC/CPE blends increase. But, it must be noticed that Flynn equation satisfies in a very narrow range of conversions (3–7.5%) for 30/70 and 0/100 blends.

## Conclusions

The dynamic thermal degradation of PVC/CPE blends in temperature range of 50–600°C occurs through two basic degradation steps where the first basic step consists of two substeps, with dehydrochlorination of PVC and CPE as the main degradation reactions. PVC dehydrochlorination is several times faster than CPE dehydrochlorination. By increasing the ratio of CPE in the blends the maximal rate of PVC dehydrochlorination in blends lowers.

The shape of isothermal TG curves depends on the composition of PVC/CPE blends and on degradation temperatures. The sigmoidal TG curves obtained for PVC/CPE 100/0–50/50 blends indicate an autocatalytic effect of HCl on degradation of PVC. While the 30/70 and 0/100 blends are being degradated, statistical dehydrochlorination of CPE prevails, so that TG curves of these blends are convex. Different thermal degradation mechanisms of PVC and CPE are the consequence of differences in microregularity of corresponding polymer chains. In the investigated temperature range of 240–270°C, after 120 min, PVC dehydrochlorinates completely and CPE partially. By increasing the ratio of CPE in the PVC/CPE blends the time necessary to reach the particular conversion increases, too.

The kinetic parameters of dynamic thermal degradation of PVC/CPE blends were calculated after Flynn–Wall–Ozawa equation in a conversion range 5–30%. The range of applicability of Flynn equation on isothermal TG curves reduces by increasing the ratio of CPE in the blend. The apparent activation energies and pre-exponential factors for dehydrochlorination of PVC in the PVC/CPE blends change by increasing the ratio of CPE in the blend, but these kinetic parameters are related to the kinetic compensation dependence. The increase of compensation ratio values confirms the stabilizing influence of CPE on PVC dehydrochlorination.

## References

1 I. C. McNeill and J. Gorman, Polym. Degrad. Stabil., 33 (1991) 263.
2 I. Klarić, N. Stipanelov Vrandečić and U. Roje, J. Appl. Polym. Sci., 78 (2000) 166.
3 S. Stoeva, K. Gjurova and M. Zagorcheva, Polym. Degrad. Stab., 67 (2000) 117.
4 M. T. Berard and S. M. Williams, J. Vinyl Additive Tech., 2 (1996) 117.
5 C. H. Chen and J. R. Collier, J. Appl. Polym. Sci., 58 (1995) 1087.
6 M. Rusu, F. Petraru and L. Gramescu, Angew. Macromol. Chem., 144 (1986) 193.
7 A. Marcilla and M. Beltran, Polym. Degrad. Stabil., 48 (1995) 219.
8 M. E. Brown, Thermochim. Acta, 300 (1997) 93.
9 H. Sharp, Thermochim. Acta, 104 (1986) 395.
10 S. Basan and O. Guven, Thermochim. Acta, 106 (1986) 169.
11 M. Macijevski, J. Thermal Anal., 33 (1988) 243.
12 R. Budrugeac and E. Segal, Thermochim. Acta, 260 (1995) 75.
13 R. Budrugaec, Polym. Degrad. Stabil., 38 (1992) 229.