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# The kinetic parameters for the evaporation of plasticizers from plasticized poly(vinyl chloride)

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## Abstract

The process of loss of plasticizers: dioctyl phthalate, diisononyl phthalate, benzylbutyl phthalate, dioctyl adipate, phosphate plasticizer Reofos, polymeric plasticizer Reoplex and epoxidized soybean oil from plasticized poly(vinyl chloride) folies was studied by the method of isothermal thermogravimetry in the temperature range 120–150 °C. The investigated samples contained ca. 10–40 wt.% of plasticizers. The rate constants of the process of loss of plasticizers were calculated and the dependence of the rate constant on temperature and on the initial concentration of plasticizer in plasticized PVC were mathematically defined. The concentration dependence of the rate constant is expressed by parameters $k_0$ and $q$. The linear dependence of the function $k = f(c_0)$ suggests that the process of evaporation from the polymer surface, being slower, governs the process of the loss of plasticizers. The activation energy of the process was calculated from the exponential dependence of the rate constant of evaporation on temperature. Compensation parameters were also calculated as a measure of reaction ability of the system. The role of various parameters (molecular weight, static and dynamic structure of polymer, polarity) on the kinetic parameters of evaporation of plasticizers were discussed.

*Keywords:* Kinetic parameters; Plasticizers; Poly(vinyl chloride)

## 1. Introduction

The loss of additives from polymer material is a complex process, involving three physical processes: (1) diffusion of additives up to the interface, (2) transport through the interface, and (3) loss of additives from the surface into the surrounding medium. The mechanism of the loss of additives from the matrix depends on which one of these processes governs its loss.

The loss of additives from the surface of polymer material into the surrounding medium can take place through three specific processes:

- *Evaporation*: At which the additive goes into the surrounding gas medium (most often the air).
- *Extraction*: During which the additive goes into the surrounding liquid medium.
- *Migration*: At which the additive, in direct contact with the surface of the other polymer material, migrates into that material.

According to the literature data [1–3], in most polymer/additive systems two processes are crucial for additives' loss: evaporation from the surface of polymer article and diffusion through the polymer matrix up to the surface of the material. According to Calvert and Bilingham [1], first of all the additive has to be removed from the polymer surface into the

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surrounding medium (comparable with the surface emission of heat), and then, in order to compensate the resulting loss, the additive diffuses from the polymer mass toward the interface (comparable with heat conductivity).

The rate of evaporation is defined as the function of temperature and current concentration of the additive in polymer material. If the process of volatility is slower than the diffusion of polymer through the polymer matrix, then the rate of volatility is a linear function of concentration. In case the process of volatility is controlled by the additive diffusion through the polymer matrix, this dependence becomes non-linear. The process of additives' diffusion to the surface from the bulk of polymer material is described by Fick's law of diffusion.

One of the essential additives needed for modifying the mechanical properties of PVC is plasticizer. Studying the physical process of the loss of plasticizer from plasticized articles is important for the optimization of PVC processing, the quality of finished articles and for foreseeing the durability of the article.

In the previous paper [4], isothermal thermogravimetry was applied to investigate kinetic parameters of the process of volatilization of dioctyl phthalate plasticizer from plasticized poly(vinyl chloride) folies. In this paper, the investigations have been extended to other phthalate plasticizers as well as to adipate, phosphate polymeric plasticizer and epoxidized soybean oil.

## 2. Experimental

### 2.1. Materials

The materials used for this study were commercially available mass-polymerized PVC (*K*-value 67.9) (Adriachem, Zadar, Croatia), dioctyl phthalate (DOP) BASF, diisononyl phthalate (DINP) BASF, benzylbutyl phthalate (BBP) BAYER, dioctyl adipate (DOA) HOECHST, phosphate plasticizer Reofos, FMC, polymeric plasticizer Reoplex, FMC and epoxidized soybean oil (ESO) CIBA GEIGY. PVC folies with the amount of approximately 10–40 wt.% of the plasticizers with the addition of 1 wt.% of thermal stabilizer, modified butyl stannic mercaptide (BTF-80), were prepared using a Plastograph Brabender at the temperature of 170 ± 5°C, time of drawing 5 min, and thickness of the foil 0.1 ± 0.03 mm.

The actual concentrations of additives in the plasticized PVC folies are determined by extraction in Soxhlet apparatus by the adequate solvent, depending on the type of plasticizer. For thermogravimetric investigations, the samples were cut off in the form of 5 mm diameter discs each weighing 3 ± 0.5 mg.

### 2.2. Thermogravimetric measurements

The evaporation of plasticizers from plasticized PVC folies was studied by the method of isothermal thermogravimetry (Perkin Elmer TGS-2 with TADS Microprocessor) at 120, 130, 140 and 150 °C for 120 min, under nitrogen flow of 30 cm$^3$/min. The mass loss of some of the investigated plasticizer (ESO) at temperature lower than 120 °C is small, approximately equal to the experimental error of the method concerned. The testing conditions and calculation of kinetic parameters were widely described in [4].

## 3. Results and discussion

### 3.1. Thermograms

The thermograms of PVC, plasticized with various amounts of plasticizers, are shown in Figs. 1–4 on the example of the processes of evaporation of all the investigated plasticizers at 140 °C, and also in Fig. 5 on the example of PVC plasticized with 29.2 wt.% DOA at four different temperatures. The curves indicate that the residual weight decreases as the initial concentration of plasticizers in the plasticized PVC and temperature increase.

The mass loss of the plasticized PVC samples can be compared mainly with the volatility of pure plasticizers (Table 1) which grows up in the sequence ESO < DINP < Reoplex < Reofos < DOP < BBP < DOA. The exceptions are PVC plasticized with Reoplex polymer plasticizer and the thermally unstable folies with Reofos. Very little mass losses of PVC folies plasticized with ESO (of only 0.01 wt.% at 120 °C to maximum 0.25 wt.% at 150 °C) are comparable with the weight losses of pure PVC, which

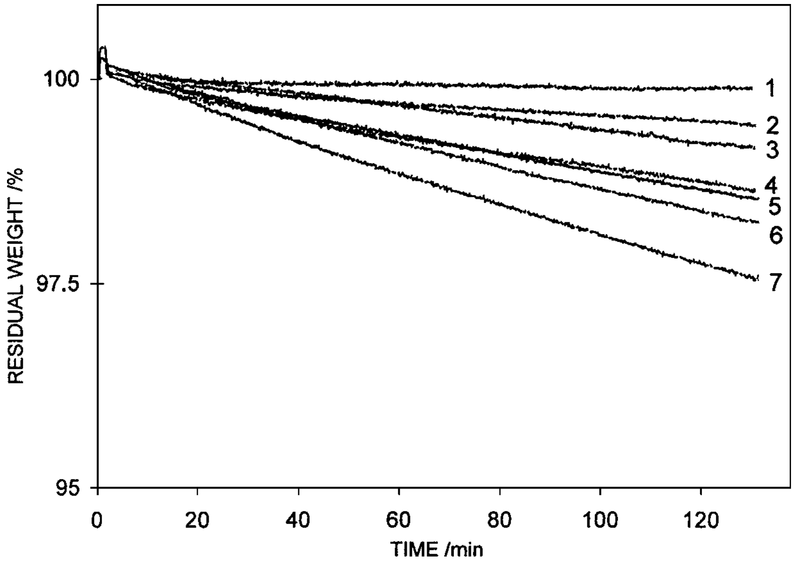

Fig. 1. Thermograms of evaporation of plasticizers from plasticized PVC with ≈10 wt.% of plasticizers at 140 °C—1: PVC/ESO, 2: PVC/Reofos, 3: PVC/Reoplex, 4: PVC/DINP, 5: PVC/DOP, 6: PVC/BBP, 7: PVC/DOA.

verges on sensitivity of the method of isothermal thermogravimetry. These values as well as the subsequent rate constants of volatility of PVC plasticized with ESO are certainly effected by the well-known stabilizing effect of epoxidizing soybean oil on PVC thermal degradation.

Comparing the weight loss of pure plasticizers with their viscosity (at 25 °C), a similar pattern can be observed; the most volatile plasticizer (DOA) is of the least viscosity, with the exception of Reoplex polymer plasticizer, which is of the highest viscosity, but is not of the lowest volatility.

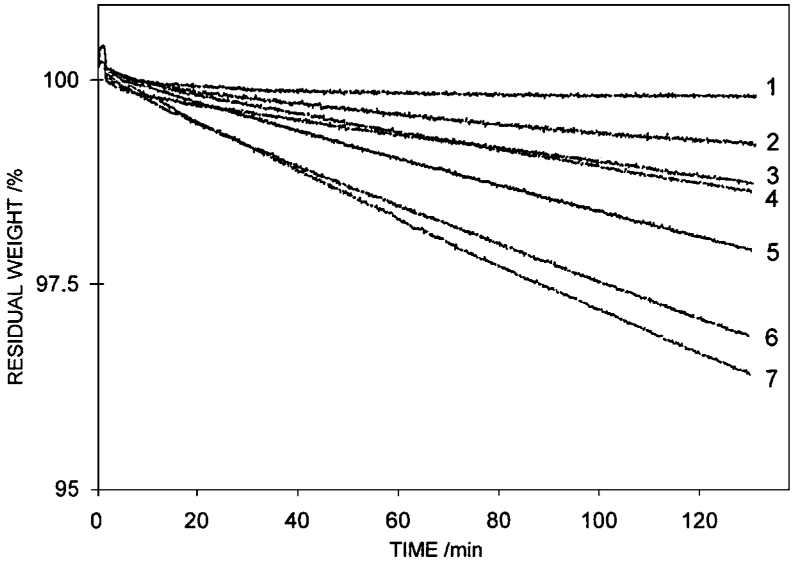

Fig. 2. Thermograms of evaporation of plasticizers from plasticized PVC with ≈20 wt.% of plasticizers at 140 °C—1: PVC/ESO, 2: PVC/Reofos, 3: PVC/Reoplex, 4: PVC/DINP, 5: PVC/DOP, 6: PVC/BBP, 7: PVC/DOA.

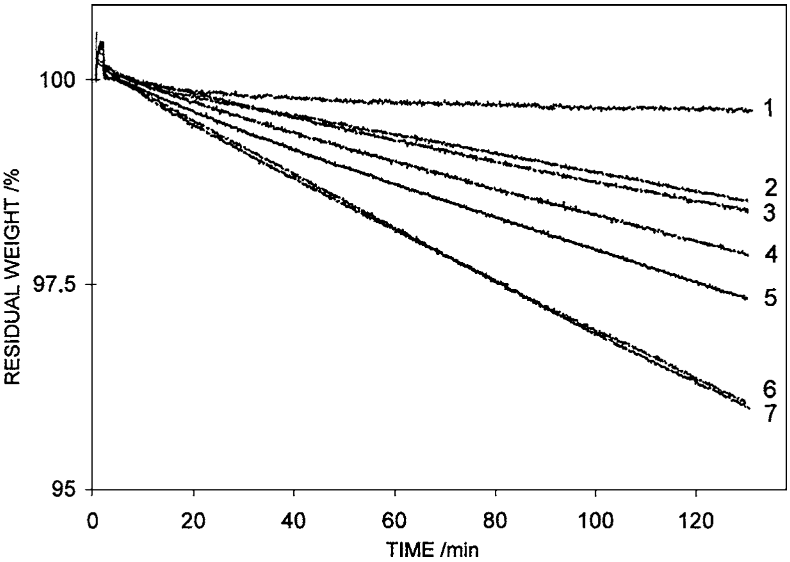

Fig. 3. Thermograms of evaporation of plasticizers from plasticized PVC with ≈30 wt.% of plasticizers at 140 °C—1: PVC/ESO, 2: PVC/Reofos, 3: PVC/Reoplex, 4: PVC/DINP, 5: PVC/DOP, 6: PVC/BBP, 7: PVC/DOA.

### 3.2. Determining the rate constant of evaporation of plasticizers

The shape of the plots $(c_0 - c)$ vs. $t$, where $c_0$ is the initial amount of plasticizer in polymer, and $c$ the amount of plasticizer evaporated from plasticized PVC in time $t$, shown in Fig. 6 on the example of sample plasticized with 10.89 wt.% of DOA, makes it possible to conclude the exponential dependence of the investigated variables for all plasticized folies, as it was found for PVC plasticized with DOP [4]. Pure plasticizers, as the example of BBP in Fig. 7, also

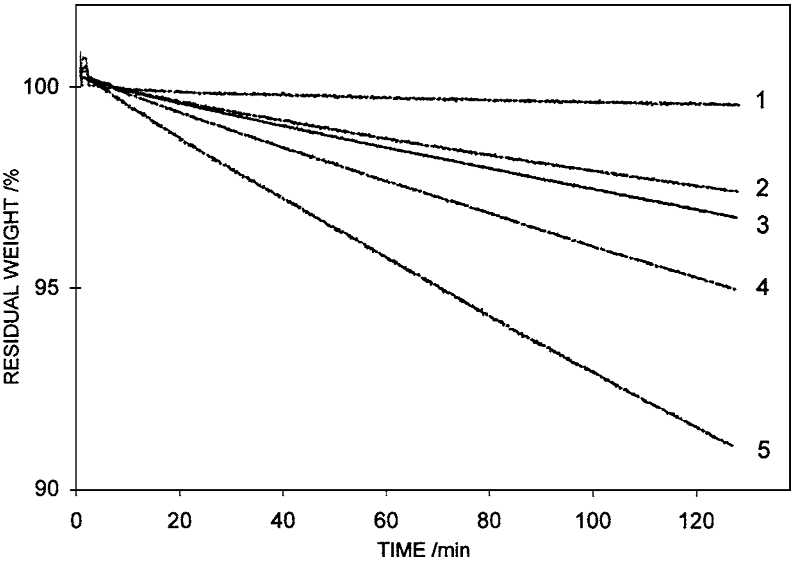

Fig. 4. Thermograms of evaporation of plasticizers from plasticized PVC with ≈40 wt.% of plasticizers at 140 °C—1: PVC/ESO, 2: PVC/DINP, 3: PVC/DOP, 4: PVC/BBP, 5: PVC/DOA.

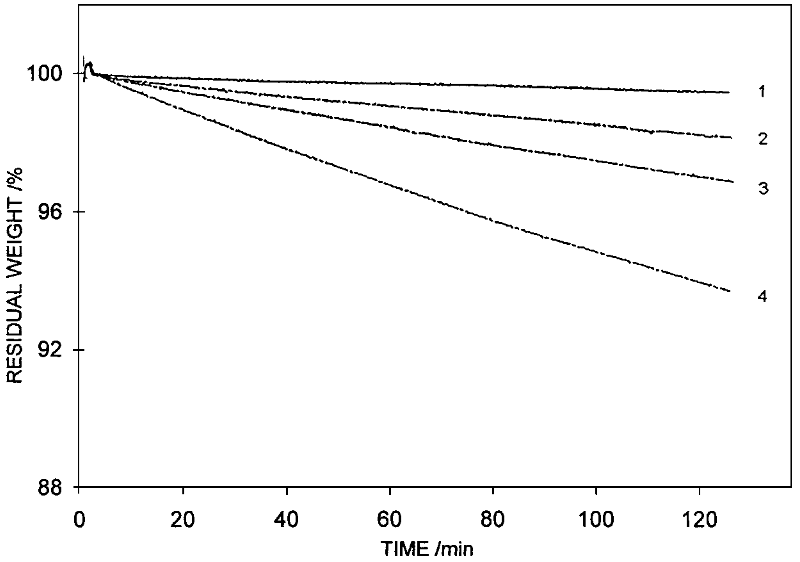

Fig. 5. Thermograms of evaporation of DOA from plasticized PVC with 29.2 wt.% DOA—1: 120 °C, 2: 130 °C, 3: 140 °C, 4: 150 °C.

indicate the exponential type of function $c_0 - c = f(t)$ in the form of $c_0 - c = c_0 \exp(-kt)$. This function represents the solution of linear differential first-order equation $-(\mathrm{d}c/\mathrm{d}t) = kc$, and can be recommended as a kinetic model which describes the process of loss of plasticizers from plasticized PVC folies for the chosen initial concentrations of plasticizers, temperatures and thickness of the folies. At the same time the detected mathematical dependence indicates that evaporation from the polymer surface, being the slower process, governs the kinetics of the plasticizers' loss.

The conditions under which the diffusion of plasticizers inside the polymer would become a controlling step, when the dependence $\mathrm{d}c/\mathrm{d}t = kc$ is not linear, could be achieved at low temperatures in vacuum. The linear dependence of the rate of plasticizers' weight loss on $\sqrt{t}$ is usually taken as an indicator which shows that diffusion is the process governing the additives' loss from the solid phase.

The rate constant of evaporation of plasticizers, $k$, were calculated from the diagram $-\ln[(c_0 - c)/c_0]$ vs. $t$ (Fig. 8) by the method of linear regression analysis. The results are shown in Table 2. The rate constants' values of the evaporation process of plasticizers increase with the increase of temperature in the range 120–150 °C approximately two times for each 10 °C, which is in agreement with the known kinetic laws. The rate constants of evaporation of pure plasticizers are higher than those for the corresponding plasticized PVC folies at the same temperature. Thus, as expected, this relation is the smallest with the plasticized articles with the greatest share of plasticizer (≈40 wt.%) and amounts mainly 2–3 times.

The influence of the initial concentration in plasticized PVC folies on the rate constant of evaporation is also evident; as a rule, $k$ increases with the increase of $c_0$. But the influence of temperature is much more pronounced than the influence of the initial concentration of the plasticizer. The values of $k$ are in the range $0.06 \times 10^{-4}\,\mathrm{min}^{-1}$ for PVC/ESO to $9.59 \times 10^{-4}\,\mathrm{min}^{-1}$ for PVC/DOA.

The values of the rate constants of the plasticizers' evaporation process from plasticized PVC folies decrease as follows: PVC/DOA > PVC/BBP > PVC/DOP ⩾ PVC/DINP > PVC/Reoplex > PVC/Reofos > PVC/ESO, which corresponds to the sequence of weight loss of pure plasticizers.

### *3.3. Dependence of rate constant of plasticizers' evaporation process on initial concentration*

The graphic descriptions of function $k = f(c_0)$ shown on the example of plasticized PVC at 130 °C, in Fig. 9, indicate for all the investigated

Table 1
Weight loss of plasticized folies and pure plasticizers at 120 and 150 °C and viscosity of plasticizers[a]

| Plasticizer and initial concentration of plasticizer in plasticized PVC, $c_0$ (wt.%) | Weight loss of pure plasticizer and plasticized PVC in 60 min at 150 °C, $c$ (wt.%) | Plasticizers' viscosity at 25 °C (mPa s) |
|---|---|---|
| *ESO* | | |
| Pure plasticizer[b] | – | 600 |
| 9.8 | 0.17 | |
| 19.4 | 0.19 | |
| 28.6 | 0.23 | |
| 39.3 | 0.25 | |
| *DINP* | | |
| Pure plasticizer | 1.32 | 110 |
| 10.0 | 0.74 | |
| 23.2 | 1.08 | |
| 29.9 | 1.49 | |
| 39.9 | 1.49 | |
| *Reoplex*[c] | | |
| Pure plasticizer | 2.32 | 1500 |
| 10.0 | 0.55 | |
| 20.0 | 1.03 | |
| 30.0 | 1.59 | |
| *Reofos*[c] | | |
| Pure plasticizer | 3.32 | 93 |
| 10.0 | 0.94[d] | |
| 20.0 | 0.67[d] | |
| 30.0 | 1.33[d] | |
| *DOP* | | |
| Pure plasticizer | 5.94 | 75 |
| 10.1 | 1.48 | |
| 20.2 | 2.06 | |
| 30.6 | 2.04 | |
| 37.1 | 2.05 | |
| *BBP* | | |
| Pure plasticizer | 9.43 | 63 |
| 9.9 | 1.38 | |
| 19.7 | 2.56 | |
| 30.4 | 3.69 | |
| 36.1 | 3.91 | |
| *DOA* | | |
| Pure plasticizer | 11.8 | 15 |
| 10.9 | 2.21 | |
| 19.6 | 3.25 | |
| 29.2 | 3.31 | |
| 38.0 | 6.01 | |

[a] The order of presentation of plasticized PVC matches approximately the sequence of weight loss increase of pure plasticizers.
[b] The weight loss of pure ESO plasticizer is not determined.
[c] Folies of plasticized PVC with ≈40 wt.% of plasticizer were not possible to be manufactured in laboratory conditions.
[d] The change of the color of the sample indicates the thermal degradation.

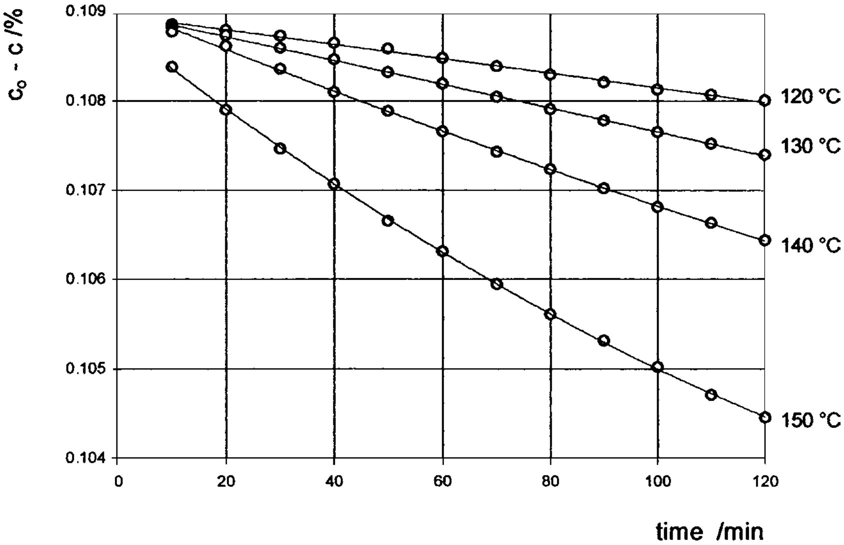

Fig. 6. Residual concentration of DOA $(c_0 - c)$ from PVC plasticized with 10.89 wt.% of DOA.

samples, identically as previously for PVC/DOP, the linear dependence of plasticizer loss rate constant on the initial concentration of plasticizer in the plasticized PVC at the investigated temperatures range in the form of

$$k = k_0c_0 + q \qquad (1)$$

The linear dependence of $k$ vs. $c_0$ indicates that the rate-controlling step in the process of the plasticizers' loss from the polymer/plasticizer system is the evaporation of plasticizer from the surface of plasticized article into the surrounding medium. The constants $k_0$ and $q$ are determined by linear regression analysis (Table 3). The values $k_0$ are within limits from $0.11 \times 10^{-6}\,\text{min}^{-1}$ (for PVC/ESO) to $20.3 \times 10^{-6}\,\text{min}^{-1}$ (for PVC/DOA). The values of parameter $q$ are higher than the values of constant $k_0$ and they are within the limits from $0.78 \times 10^{-5}\,\text{min}^{-1}$ (PVC/ESO) to $19.5 \times 10^{-5}\,\text{min}^{-1}$ (PVC/DOP). The effect of temperature on these parameters is evident. Thus, the least

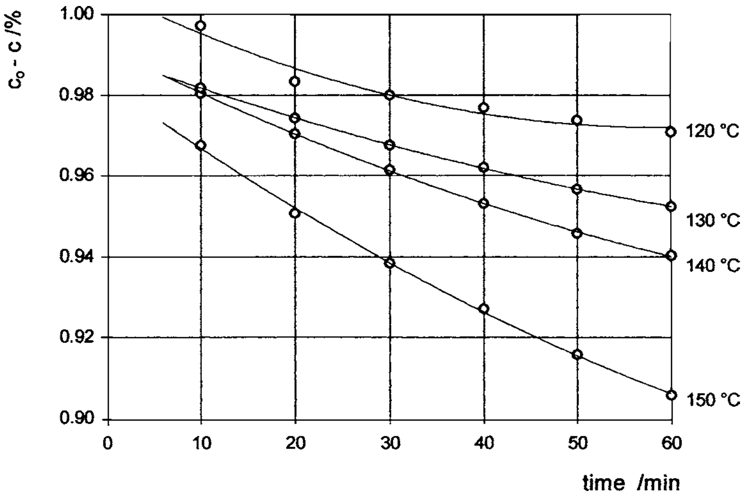

Fig. 7. Residual concentration for evaporation of pure plasticizer BBP.

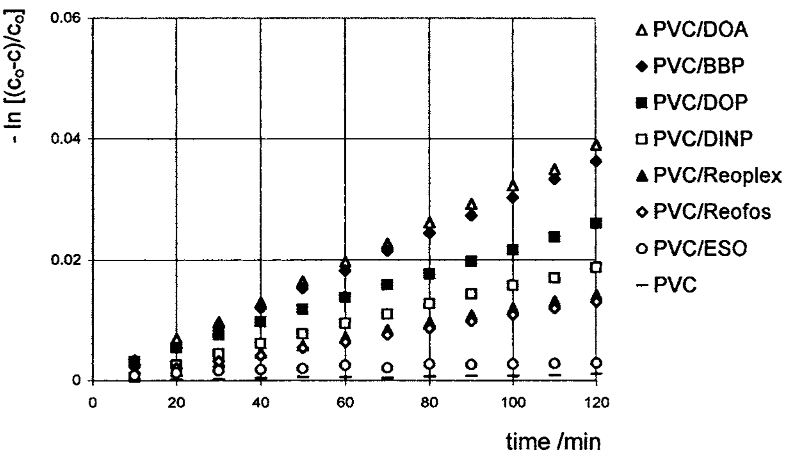

Fig. 8. Graphical determination of the rate constant of evaporation for PVC plasticized with 40 wt.% of plasticizers at 140 °C.

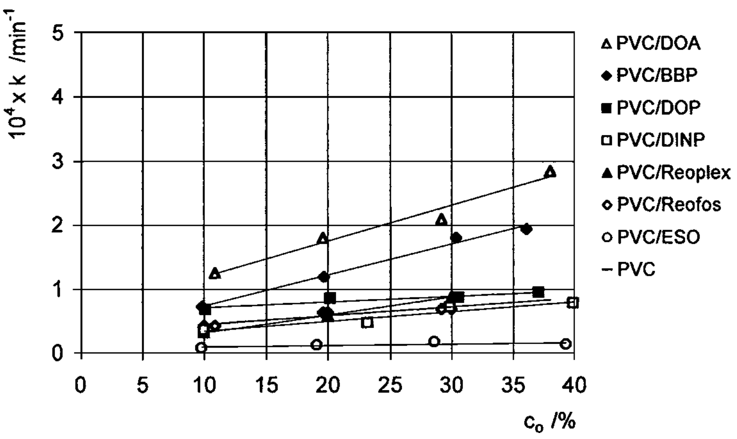

Fig. 9. Dependence of the rate constant of evaporation of plasticizers at 130 °C on the initial concentration of plasticizers in plasticized PVC.

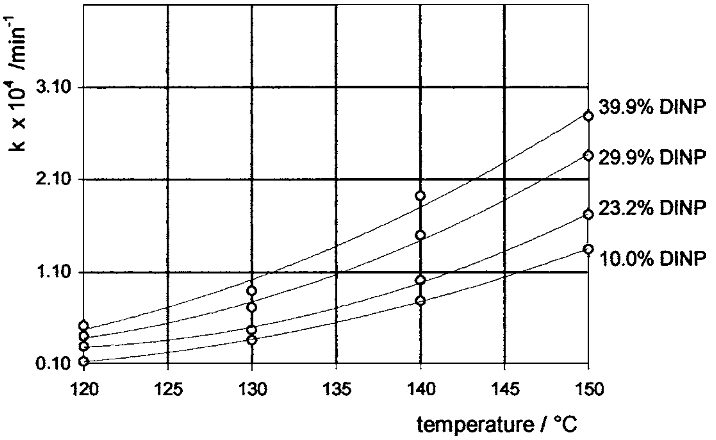

Fig. 10. Dependence of the rate constant of evaporation of DINP on temperature.

Table 2
The rate constants of evaporation of plasticizers from plasticized PVC folies

| Plasticizer and initial concentration of plasticizer in plasticized PVC, $c_0$ (wt.%) | Rate constant, $k$ ($\times 10^4$ min$^{-1}$) | | | |
|---|---|---|---|---|
| | 120 °C | 130 °C | 140 °C | 150 °C |
| *DOP* | | | | |
| Pure plasticizer | 1.23 | 3.05 | 5.87 | 8.79 |
| 10.1 | 0.42 | 0.68 | 1.28 | 2.13 |
| 20.2 | 0.51 | 0.86 | 1.66 | 3.09 |
| 30.6 | 0.51 | 0.87 | 2.05 | 3.22 |
| 37.1 | 0.46 | 0.95 | 2.43 | 3.25 |
| *DINP* | | | | |
| Pure plasticizer | 0.39 | 0.69 | 1.14 | 2.25 |
| 10.0 | 0.13 | 0.36 | 0.78 | 1.35 |
| 23.2 | 0.29 | 0.47 | 1.01 | 1.72 |
| 29.9 | 0.40 | 0.72 | 1.64 | 2.47 |
| 39.9 | 0.52 | 0.79 | 1.92 | 2.36 |
| *BBP* | | | | |
| Pure plasticizer | 4.74 | 6.08 | 8.44 | 13.0 |
| 9.9 | 0.38 | 0.73 | 1.48 | 2.19 |
| 19.7 | 0.61 | 1.19 | 2.19 | 4.05 |
| 30.4 | 1.01 | 1.81 | 3.08 | 6.12 |
| 36.1 | 1.04 | 1.94 | 3.69 | 6.38 |
| *DOA* | | | | |
| Pure plasticizer | 2.30 | 4.96 | 10.10 | 19.20 |
| 10.9 | 0.76 | 1.25 | 2.02 | 3.41 |
| 19.6 | 0.79 | 1.80 | 2.9 | 5.56 |
| 29.2 | 1.09 | 1.90 | 3.19 | 5.77 |
| 38.0 | 1.31 | 2.85 | 7.04 | 9.59 |
| *ESO* | | | | |
| Pure plasticizer[a] | – | – | – | – |
| 9.8 | 0.06 | 0.08 | 0.14 | 0.14 |
| 19.1 | 0.15 | 0.13 | 0.15 | 0.18 |
| 28.6 | 0.09 | 0.18 | 0.15 | 0.18 |
| 39.3 | 0.12 | 0.14 | 0.196 | 0.23 |
| *Reofos*[b] | | | | |
| Pure plasticizer | 0.64 | 1.69 | 2.53 | 5.15 |
| 10.0 | 0.03 | 0.43 | 1.06 | 1.44[c] |
| 20.0 | 0.18 | 0.64 | 0.96[c] | c |
| 30.0 | 0.36 | 0.69 | 1.10 | 2.18[c] |
| *Reoplex*[b] | | | | |
| Pure plasticizer | 0.64 | 1.23 | 2.33 | 3.64 |
| 10.0 | 0.25 | 0.32 | 0.48 | 0.61 |
| 20.0 | 0.19 | 0.58 | 0.67 | 1.28 |
| 30.0 | 0.35 | 0.88 | 1.25 | 2.22 |

[a] Not determined.

[b] Folies of plasticized PVC with ≈40 wt.% of plasticizer were not possible to be manufactured in laboratory conditions.

[c] The change of the color of the sample indicates thermal degradation.

Table 3
The values of concentration dependence parameters $k_0$ and $q$

| Sample temperature (°C) | $k_0$ ($\times 10^6$% min$^{-1}$) | $q$ ($\times 10^5$ min$^{-1}$) |
|---|---|---|
| *PVC/DOP* | | |
| 120 | 0.17 | 4.32 |
| 130 | 0.89 | 6.22 |
| 140 | 4.21 | 8.28 |
| 150 | 3.97 | 19.50 |
| *PVC/DINP* | | |
| 120 | 1.31 | 8.21 |
| 130 | 1.56 | 1.87 |
| 140 | 4.03 | 3.00 |
| 150 | 3.81 | 9.93 |
| *PVC/BBP* | | |
| 120 | 2.72 | 1.06 |
| 130 | 4.83 | 2.55 |
| 140 | 8.95 | 5.09 |
| 150 | 16.70 | 6.97 |
| *PVC/DOA* | | |
| 120 | 2.15 | 4.66 |
| 130 | 5.31 | 6.61 |
| 140 | 16.70 | 2.66 |
| 150 | 20.30 | 11.5 |
| *PVC/ESO* | | |
| 120 | 0.11 | 0.80 |
| 130 | 0.23 | 0.78 |
| 140 | 0.19 | 1.12 |
| 150 | 0.27 | 1.17 |
| *PVC/Reofos* | | |
| 120 | 1.66 | 1.42 |
| 130 | 1.29 | 2.70 |
| 140 | 0.20 | 9.99 |
| 150 | 3.70 | 10.7 |
| *PVC/Reoplex* | | |
| 120 | 0.49 | 1.70 |
| 130 | 2.78 | 3.87 |
| 140 | 3.86 | 2.63 |
| 150 | 8.05 | 2.39 |

temperature susceptibility of the kinetic rate constant of evaporation is in the case of PVC/ESO.

### 3.4. Dependence of the rate constant of evaporation of plasticizers on temperature

The dependence of the rate constant of evaporation of plasticizers on temperature, shown in Fig. 10 on the example of PVC/DINP, for all plasticized folies is of exponential form and can be described by Arrhenius equation. From the linearized Arrhenius plots (ln $k$ vs. $1/T$) the values of apparent activation energy $E$ and pre-exponential factor $z$ were calculated. The results are shown in Table 4.

The values of activation energies for the folies plasticized by phthalate plasticizers (PVC/DOP, PVC/BBP and PVC/DINP) as well as for the plasticized folies PVC/DOA and PVC/Reoplex are within the range 70–108 kJ/mol (exception is PVC/Reoplex with the amount of 10 wt.% of plasticizers). Activation energy for PVC/ESO is from 20 to 40 kJ/mol, and for PVC/Reofos it is substantially higher.

In the study of Luston et al. [5], the activation energies for evaporation of UV-absorbers from isotactic polypropylene in the temperature range 130–160 °C amounted from 15.4 to 86.7 kJ/mol, which is approximately equal to activation energies of evaporation of plasticizers from plasticized PVC in this paper. The high values of activation energies of the evaporation process of phosphate plasticizer from PVC/Reofos can be attributed to thermal degradation of this sample. This is supported by the results of investigation of thermal degradation of PVC plasticized by phosphate plasticizer 2-ethylhexyldiphenyl-phosphate where the activation energy of thermal degradation process amounted 141.9 kJ/mol [6]. The decrease of activation energy with the increase of share of Reofos can be attributed to the greater effect of plasticizer on the change of physical state of the plasticized article. That is the reason why the foil with 40 wt.% of Reofos was not possible to be made by Plastograph in laboratory conditions.

Comparing the activation energies of evaporation of plasticizers from investigated plasticized samples, the effect of static and dynamic aspect of molecular structure of plasticizer is noticeable. Activation energy is higher as the molecule of plasticizer (penetrant) is larger and branching of the molecule greater. Therefore, with the penetrants of approximately equal molecular weight, $E$ increases with branching of their molecules. The motion of branched molecules goes on in cooperative segmental motion, similar to macromolecular coil, and the adjacent branches put up resistance to the segment motion [7]. However, $E$ does not depend on the size of molecules for remarkably big penetrants, but their motion is controlled by the motion of polymeric chains. As to polymer matrix, the greatest influence on the motion of penetrants has

Table 4
Activation energy, pre-exponential factor and compensation parameter of the process of evaporation

| Initial concentration of plasticizer in plasticized PVC, $c_0$ (wt.%) | Activation energy, $E$ (kJ/mol) | Pre-exponential factor, $z$ (min$^{-1}$) | Compensation parameter, Sp$^*$ | Average value of compensation parameter, $\overline{\mathrm{Sp}^*}$ |
|---|---|---|---|---|
| *PVC/DOP* | | | | |
| 10.1 | 76.38 | $5.5 \times 10^5$ | 5.77 | |
| 20.2 | 84.29 | $7.5 \times 10^6$ | 5.32 | |
| 30.6 | 88.49 | $2.8 \times 10^7$ | 5.16 | |
| 37.1 | 94.07 | $1.5 \times 10^8$ | 5.10 | 5.34 |
| *PVC/BBP* | | | | |
| 9.9 | 82.67 | $3.6 \times 10^6$ | 5.46 | |
| 19.7 | 87.33 | $2.3 \times 10^7$ | 5.14 | |
| 30.4 | 82.26 | $8.1 \times 10^6$ | 5.16 | |
| 36.1 | 85.04 | $2.0 \times 10^7$ | 5.06 | 5.20 |
| *PVC/DINP* | | | | |
| 10.0 | 108.05 | $3.1 \times 10^9$ | 4.94 | |
| 23.2 | 83.75 | $3.6 \times 10^6$ | 5.54 | |
| 29.9 | 86.83 | $1.4 \times 10^7$ | 5.29 | |
| 39.9 | 75.41 | $5.2 \times 10^5$ | 5.72 | 5.37 |
| *PVC/DOA* | | | | |
| 10.9 | 69.11 | $1.1 \times 10^5$ | 5.94 | |
| 19.6 | 87.57 | $3.5 \times 10^7$ | 5.04 | |
| 29.2 | 76.46 | $1.5 \times 10^6$ | 5.37 | |
| 38.0 | 95.29 | $6.2 \times 10^8$ | 4.71 | 5.26 |
| *PVC/ESO* | | | | |
| 9.8 | 40.39 | 147 | 104.6 | |
| 19.4 | 19.54 | 1.91 | 3.71 | |
| 28.6 | 24.02 | 56.7 | 5.95 | |
| 39.3 | 31.15 | 6.37 | 2.68 | 4.11 |
| *PVC/Reofos* | | | | |
| 10 | 175.82 | $1.2 \times 10^{18}$ | 4.23 | |
| 20 | 115.84 | $4.8 \times 10^{10}$ | 4.70 | |
| 30 | 81.37 | $2.3 \times 10^6$ | 5.55 | 4.83 |
| *PVC/Reoplex* | | | | |
| 10 | 41.62 | $8.4 \times 10^2$ | 19.59 | |
| 20 | 80.37 | $1.1 \times 10^6$ | 5.78 | |
| 30 | 81.22 | $2.3 \times 10^6$ | 5.53 | 5.65 |

the degree of polymer crystallinity. If the polarity of the molecule of penetrant and polymer are also taken into account, it is clear why the effect of all these factors can sometimes act synergistically, but also interfering.

The values of activation energies for some tested samples, e.g. PVC/DOP [4], show the dependence on the initial concentration of plasticizer, which could be attributed to the influence of different mobility of macromolecule segments and/or different diffusion rates of plasticizer through the polymer. However, one can observe that pre-exponential factors change parallel with activation energies. So the change of the activation energy can be the result of influence of different experimental parameters on the samples, which have different physical states of polymer because of different concentrations of plasticizer.

For chemical processes, comparisons of $E$ are possible if $z$ and $f(\alpha)$ (kinetic model) are constant. To avoid the effect of experimental factors on the activation energy the introduction of compensation parameter $\mathrm{Sp}^* = E/\ln z$ is suggested [8], at which $\mathrm{Sp}^*$

represents the measure of reaction ability. The greater value of parameter means the lesser reactivity of the system.

With all the plasticized PVC samples (Table 4), the compensation parameters depend on the initial concentration of plasticizer. In comparison with the values of activation energy, Sp* shows greater regularity of that dependence. It is important to notice that with PVC/DOP, PVC/BBP, PVC/DOA and PVC/Reoplex samples, reaction ability (volatility) increases with the increase of initial concentration of plasticizers, and with PVC/DINP and PVC/Reofos, reactivity decreases with the increase of $c_0$. In the case of PVC/DINP plasticized samples this can be attributed to steric obstacles due to obvious branching of DINP molecules, while with PVC/Reofos folies, the possible reason might be poor thermal stability.

Apart from PVC/ESO and PVC/Reofos, where the plasticizer chemically reacts with the PVC (stabilizes and degrades PVC, respectively), reactivity (evaporation ability) rises in the sequence: PVC/Reoplex, PVC/DINP, PVC/DOP, PVC/BBP, PVC/DOA.

## 4. Conclusion

The weight loss of the investigated plasticized PVC folies increases with the increase of temperature in the selected temperature range from 120 to 150 °C. Also, at the chosen temperature, the weight loss increases with the increase of initial concentration of plasticizer in plasticized folies. The weight loss is comparable with the volatility of pure plasticizers.

The process of plasticizers' loss from plasticized PVC folies follows the kinetic laws of the first-order reaction. The suggested mathematical dependence shows that for the investigated system, the process of evaporation of plasticizers from the surface of plasticized article is the process, as it is slower, which determines the kinetics of plasticizers' weight loss. The rate constant of the process can be regarded as the characteristic of physical process of plasticizers' evaporation from plasticized articles. The values of rate constants of plasticizers' evaporation process increase with the increase of temperature in the range 120–150 °C approximately two times for each 10 °C. The rate constants of evaporation of pure plasticizers are much higher than those for the corresponding plasticized PVC folies at the same temperatures.

The rate constant of the process of evaporation of plasticizer from plasticized PVC depends on the temperature and the initial concentration of plasticizer. Thus, the influence of temperature is much more expressed than the influence of initial concentration. The value of the constant increases linearly with the increase of $c_0$ and the dependence is in the form of $k = k_0 c_0 + q$. The dependence of rate constant of the plasticizers' evaporation process on temperature is of exponential form, Arrhenius' type, so that on the basis of Arrhenius' equation, activation energies and pre-exponential factors were determined. The activation energies for the PVC plasticized by phthalate plasticizers as well as for PVC/DOA and PVC/Reoplex are within the range 70–108 kJ/mol. The activation energy for PVC/Reofos is significantly greater and it can be compared with the activation energy of thermal degradation of PVC plasticized by phosphate plasticizers.

The reaction ability (the ability of evaporation) expressed by compensation parameter depends on the initial concentration of plasticizers. Except PVC/ESO and PVC/Reofos, where the plasticizer chemically reacts with PVC (stabilizes or degradates PVC, respectively), reactivity increases in the sequence: PVC/Reoplex, PVC/DINP, PVC/DOP, PVC/BBP, PVC/DOA.

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