Thermal Aging of Plasticized PVC. I. Weight Loss Kinetics in the PVC–Didecylphtalate System

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SYNOPSIS

Weight-loss kinetics were studied for 10 industrial extruded samples of poly(vinyl chloride) (PVC) plasticized by 20–30% by weight of didecylphtalate at 85, 95, 105, 110, and 120°C. For the most unstable samples, which contained a light coplasticizer, the weight-loss rate obeyed Fick's law. In the other cases, it was constant in the early period of exposure. The apparent Arrhenius parameters (i.e., preexponential factor and activation energy) were intercorrelated and varied strongly from one sample to another. This was explained by the existence of two distinct kinetic regimes corresponding, respectively, to diffusion or evaporation, the whole process being controlled by the slowest step, and a transition between both regimes occurring in the temperature range of exposure. In the proposed model, small changes of the preexponential factor of diffusion from one sample to another are sufficient to take into account the observed behavior.

INTRODUCTION

It is generally recognized that the plasticizer loss by evaporation plays a key role in the thermal aging at moderate temperatures (typically below 120°C) of plasticized poly(vinyl chloride) (PVC) used in electrical insulation. The main consequences of this phenomenon are well known: a progressive decrease of the ultimate elongation and a shift of the dielectric loss peak toward high temperatures.[1] Various kinetic models were proposed in the past half-century.[2-4] Some were simple linear functions of exposure time[3] and others were based on Fick's law,[4] whereas a more complex behavior was observed in certain cases.[5] Despite the relatively large amount of work published on this topic, a methodology for the choice of a kinetic model adapted to the case under study is still lacking. Our aim was first to compare the thermal aging kinetics of 10 industrial PVC–didecylphthalate (DDP) compounds for electrical insulation differing by the other composition parameters (fillers, coplasticizers, stabilizers, etc). The first part

of this paper is devoted to the weight-loss kinetics in the 85–120°C temperature range.

EXPERIMENTAL

Materials

The materials were supplied by five different French manufacturers as extruded ribbons of ~ 2 mm thickness. Their main characteristics are listed in Table I. All the formulations are industrial recipes for cable insulation. By steric exclusion chromatography (SEC), it was observed that only three systems (D, E, and K) contained a coplasticizer, presumably of the chlorinated hydrocarbon type. For D, its elution time was lower, e.g., its molecular weight higher than the DDP one, whereas the reverse was observed for E and K.

Dogbone samples according to the French Standard NFT 51034 were cut in the ribbons and used in the gravimetric study.

Aging

Ventilated ovens with a temperature regulation within ±1°C were used for exposure at 85, 95, 105,

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Table I Initial Characteristics of the Samples Under Study

Sample	Plasticizer (%)	Plasticizer[a]/PVC	Coplasticizer[b]	Thickness (mm)
A	26.8	0.500	No	1.66
B	25.5	0.450	No	1.63
C	19.9	0.500	No	1.28
D	23.3	0.541	Yes	1.41
E	21.4	0.435	Yes	1.67
F	27.1	0.434	No	1.76
G	23.9	0.480	No	2.10
H	27.9	0.460	No	2.13
K			Yes	
L			No	

[a] Mass fractions.
[b] From steric exclusion chromatographic data.

110, and 120°C. According to the French Standard NFC 32 201, charcoal was used as absorber in the bottom of the ovens. Despite this precaution, drops of plasticizer were found in many cases on the oven walls. The ratio PVC weight/oven volume was about 2.5×10^{-3} g/cm^3.

Weighting

An analytical balance of relative precision $\Delta m/m = 10^{-4}$ was used in the gravimetric study. The kinetic data will be generally expressed in terms of mass fraction:

$$w = \frac{m_0 - m}{m_0} \text{ (dimensionless)}$$

$$r = \frac{dw}{dt} \text{ (days}^{-1})$$

RESULTS

The experimental results are summarized as follows:

1. For all the systems under study except E and K, the weight-loss kinetic curves are linear in their initial part until typically a weight-loss value of 5%.
2. The linear part of the weight-loss kinetic curves intercepts the ordinate axis at a nonzero value, reaching to 0.35% in certain cases. This result can be attributed to the rapid evaporation of absorbed moisture.

3. For samples E and K, which appear as the most unstable ones (using a gravimetric criterium), the weight loss is a linear function of the square root of time. To illustrate the difference between both types of kinetic behavior, the weight loss was plotted against time and square root of time, respectively, for the most stable (L) and for the most unstable K samples (Fig. 1).
4. The initial rate of plasticizer loss was graphically determined from the weight-loss kinetic curves. It seems to obey the Arrhenius law. The values of weight-loss rates r and the corresponding values of the logarithm of the preexponential factor ln r_0 and apparent activation energy E_a are listed in Table II.
5. For all the samples except E and K, there is a close correlation between ln r_0 and E_0 (Fig. 2):

$$\ln r_0 = a + b \cdot E_a \qquad (1)$$

where $a = -5.4$ and $b = 0.342$ mol kJ^{-1}, the correlation coefficient for the linear regression being higher than .995.

Samples E and K display the same tendencies, e.g., ln r_0 increases with E_a, but the corresponding points are not located on the same straight line as are other samples (Fig. 2).
6. Only sample C displayed a noticeable thermochemical instability in the aging conditions under study. It became quickly black, whereas all the other samples were slightly discolored at the end of their exposure, whatever the temperature.
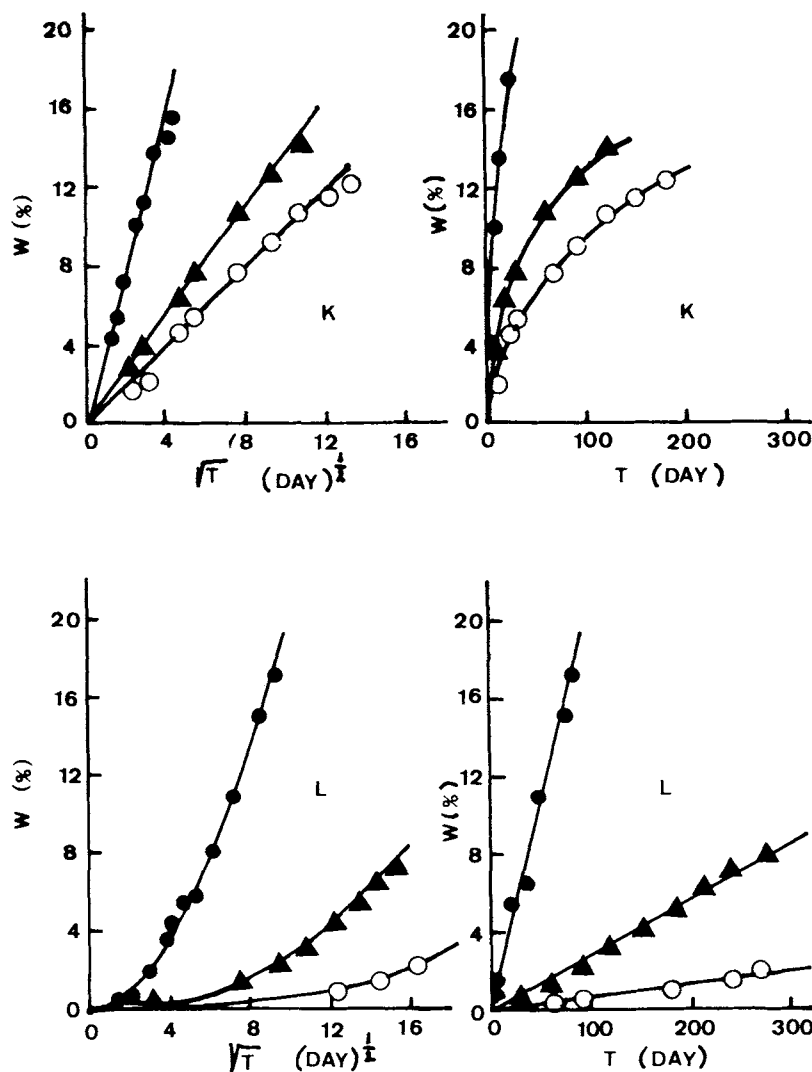
Figure 1 Weight loss against square root of time (left) and time (right) for samples K (top) and L (bottom): (●) 110°C; (▲) 95°C; (○) 85°C.

DISCUSSION

It is clear that, for the PVC–DDP system, in the 85–120°C temperature range, the plasticizer loss is the only significant source of weight change, but at least two distinct kinetic regimes are involved.

For samples E and K, whose unstability is increased by the presence of a light coplasticizer, it is logical to attribute the fact that w is proportional to $t^{1/2}$ to the kinetic control by diffusion according to Fick's law.

More difficult to explain is the case of the other samples, but it appears that the only possible rate-determining step of the plasticizer loss process is the evaporation. In principle, when the whole pro-

cess is kinetically controlled by evaporation, the plasticizer concentration must remain homogeneously distributed in the sample thickness and a decrease of the weight-loss rate must result in the decrease of the plasticizer concentration in the superficial layer. In the case under study, the constancy of the weight-loss rate (at least in the early period of exposure) suggests that the PVC–DDP system is far from an ideal solution, as previously quoted for other polymer–additive systems.[6] It could be supposed that an almost continuous plasticizer monolayer exists at the sample surface, making the evaporation rate practically insensitive to the plasticizer bulk concentration. Indeed, when this latter decreases, the free volume fraction and, thus, the plas-

Table II   Kinetic Data on Weight Loss in the Early Period of Exposure

Sample	Weight-loss Rate r (10^3 Days^{-1}) at (°C)					ln r_0	E_a
	120	110	105	95	85		(kJ mol^{-1})
A	650	—	138	77	9.9	42.36	140
B	720	—	148	43	11.3	42.16	139
C	520	—	109	38	12.7	37.31	124
D	250	—	80	31	5.3	34.92	119
E	1100	—	355	103	40.0	33.99	111
F	620	—	129	31	9.1	42.70	141
G	400	—	200	37	9.0	39.64	132
H	300	—	60	30	9.1	39.72	117
K	—	1750	—	375	200.0	32.72	103
L	—	210	—	29	7.6	45.96	151

ticizer diffusivity decreases and can reach to a critical value beyond which the whole process becomes diffusion-controlled. A simple kinetic model cannot, therefore, describe the whole plasticizer-loss process.
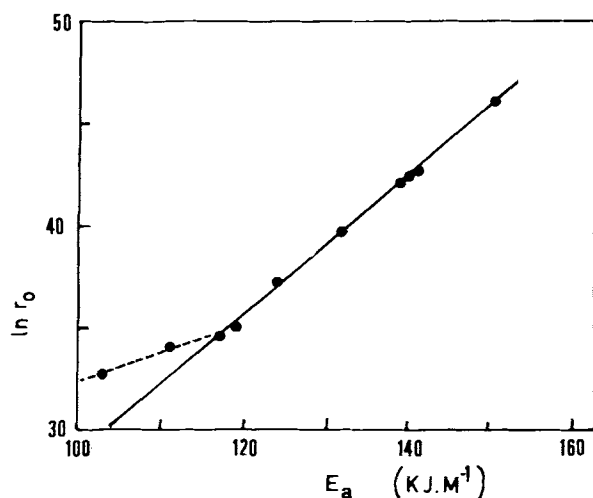
Concerning now the early period of exposure, the existence of a close correlation between the Arrhenius parameters ln r_0 and E_a, often called the compensation effect,[7-9] calls for the following comments:

From eq. (1), the Arrhenius equation can be rewritten:

$$r = \exp a \cdot \exp - \left[\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_c} \right) \right] \qquad (2)$$

where

$$T_c = 1/bR \qquad (3)$$

Figure 2 Logarithm of the preexponential factor against activation energy.

T_c is named "compensation" or "isokinetic" temperature. $(T_c)^{-1}$ and ln a are the coordinates of the "isokinetic" point located at the intersection of all the Arrhenius straight lines. In this study, $T_c = 351$ K, e.g., it lies slightly below the temperature range of exposure.

The existence of a compensation effect is usually interpreted in terms of correlation between the enthalpy and entropy of activation.[10] Here, however, the variation of r_0 and E_a are very large, which seems physically difficult to justify for systems of very close compositions (Table I).

These variations can be explained on the following basis[11]:

(a) It is considered that the plasticizer loss results from a sequence of two distinct steps (diffusion and evaporation) and is kinetically controlled by the slowest one (Fig. 3).

(b) Both steps obey the Arrhenius law. For the simplicity of demonstration, it will be supposed that both steps are zero-order processes of respective Arrhenius parameters: r_{01} and E_{a1} (evaporation) and r_{02} and E_{a2} (diffusion). The coordinates of the intersection of the corresponding Arrhenius straight lines are $(T_x)^{-1}$ and ln r_x.

(c) T_x is located within the temperature range of exposure so that the transition from evaporation-controlled to diffusion-controlled kinetic regime is experimentally observed.

(d) Since the lowest apparent activation energies (samples E and K) correspond presumably to a Fickian process, it is logical to attribute the lower values of r_0 and E_a to the diffusion process. In this case, when $T \ll T_x$, the process would be evaporation-controlled, and
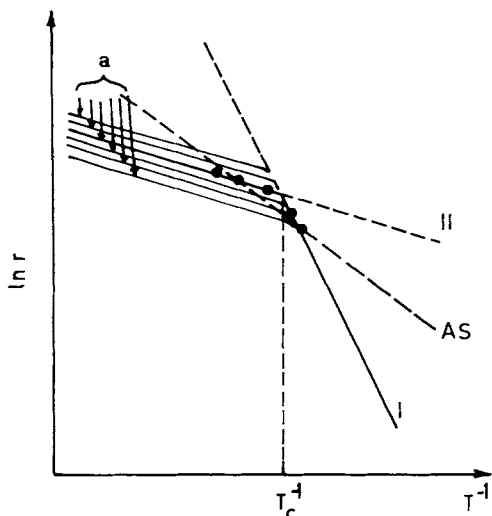
Figure 3 Schematization of the Arrhenius plot for kinetics controlled by evaporation (I) below T_x and by diffusion (II) above T_x. Arrows curves corresponding to various values of the preexponential factor of diffusion.

when $T > T_x$, the diffusion would be kinetic-controlled.

In these conditions, small changes of the true kinetic parameters can lead to strong changes of the

apparent ones, as demonstrated by the following model:

Evaporation rate: $r_1 = \exp 46$

$$\times \exp - (150{,}000/RT)$$

Diffusion rate: $r_2 = \exp A \cdot \exp - (100{,}000/RT)$

Only A varies from one sample to another, as schematized in Figure 4. The numerical application of this model for the five temperatures under study and five values of A (30.0, 29.5, 29.0, 28.5, and 28.0) is given in Table III. It can be seen that

(i) In the narrow temperature range under study, the changes of the kinetic regime are difficult to detect. The Arrhenius plot can be considered linear within experimental scatter, whereas it is in reality composed of two straight lines.

(ii) The apparent kinetic parameters ln r_0 and E_a undergo very large variations and remain intercorrelated. The apparent isokinetic point is located near to the lowest exposure temperature (Fig. 4), as experimentally observed ($T_c = 351$ K).
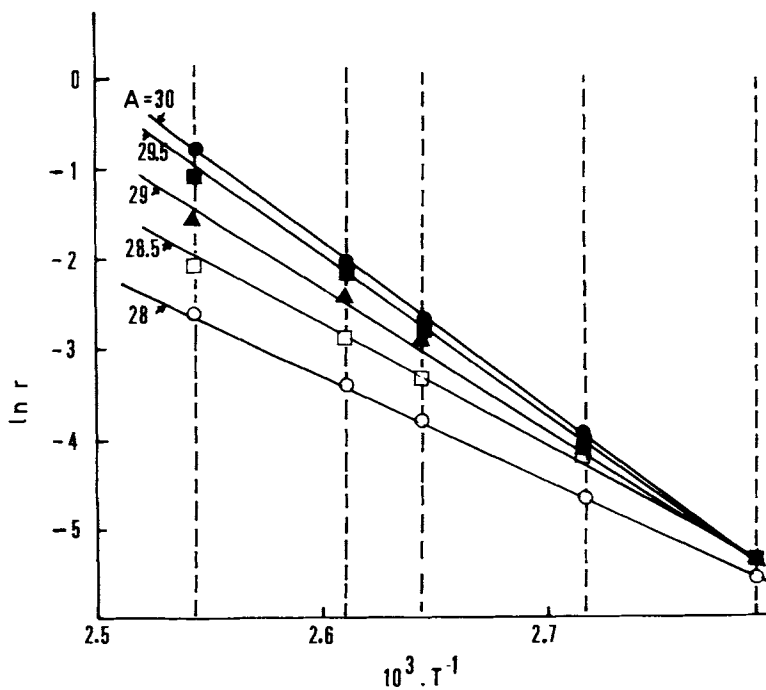
Figure 4 Arrhenius plot for the proposed model (see text). The values of the preexponential factor of diffusion (all other parameters being constant) are the numbers in the figure.

Table III   Logarithm of the Weight-loss Rate for Five Values of the Logarithm of the Preexponential Factor of Diffusion[a]

	ln r at (K)					ln r_0	E_a (kJ)	R
A	393	383	378	368	358			
30.0	−0.792	−2.014	−2.649	−3.971	−5.367	46.00	153	0.999
29.5	−1.083	−2.014	−2.649	−3.971	−5.367	43.48	146	0.997
29.0	−1.583	−2.382	−2.797	−3.971	−5.367	37.49	127	0.990
28.5	−2.083	−2.882	−3.297	−4.161	−5.367	31.21	109	0.995
28.0	−2.583	−3.382	−3.797	−4.661	−5.573	28.00	100	0.999

[a] The other kinetic parameters are E_a of diffusion = 100 kJ mol^{-1}; E_a of evaporation = 150 kJ mol^{-1}; preexponential factor of evaporation = exp 46; and ln r_0 and E_a are the calculated apparent Arrhenius parameters and R is the correlation coefficient.

Physically small variations of the preexponential factor of the diffusion process are easy to justify by variations of the sample thickness, filler content, polymer molecular weight, etc., whereas variations of the evaporation kinetic parameters would be more difficult to explain and would lead to a compensation temperature near to the high limit of the temperature range of exposure.

The peculiarities of the weight-loss kinetics for the PVC–DDP system between 85 and 120°C can be thus be reasonably explained by the existence of a transition between the diffusion-controlled and the evaporation-controlled kinetic regimes in the temperature range under investigation. In these conditions, a small change of an elementary rate constant results in a large variation of apparent Arrhenius parameters.

From a practical viewpoint, the following comments can be made:

(i) The "temperature window" for such experiments is practically fixed by experimental constraints: Above 120°C, the polymer and plasticizer degradation process can complicate the kinetics. Below 85°C, exposure durations longer than 1 year would be required.

(ii) As shown in the schematic representation of Figure 3, a lifetime prediction by application of the Arrhenius equation to experimental results would lead to an underestimation.

REFERENCES

1. Review in S. K. Sears and J. R. Darby, *The Technology of Plasticizer*, Wiley, New York, 1982.
2. H. A. Liebapsky, A. L. Marshall, and F. Verhoek, *Ind. Eng. Chem.*, **34**, 704 (1942).
3. M. C. Reed and L. Connor, *Ind. Eng. Chem.*, **40**, 1414 (1948).
4. H. N. Quackembos, *Ind. Eng. Chem.*, **46**, 1335 (1954).
5. A. M. Husson, F. C. Husson, and G. Merle, in *2nd International Symposium on PVC*, Lyon, July 5–9, 1976, p. 247.
6. N. C. Billingham and P. D. Calvert, in *Developments in Polymer Stabilization*, G. Scott, Ed., Applied Science, London, 1980, Vol. 3.
7. C. Lacabanne, D. Chatain, J. C. Monpagens, A. Hiltner, and E. Baer, *Solid State*, **27**, 1065 (1978).
8. J. P. Crine, *J. Macromol. Sci. Phys.*, **B23**, 210 (1984).
9. F. K. David, *IEEE Trans. Elect. Insul.*, **22**(3), 229 (1988).
10. J. D. Hoffmann, G. Williams, and E. Passaglia, *J. Polym. Sci. C*, **14**, 173 (1966).
11. L. Audouin and J. Verdu, *Polym. Deg. Stab.*, **31**, 335 (1991).