

Degradation Kinetics of PVC Plasticized with Different Plasticizers Under Isothermal Conditions

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ABSTRACT: The aim of the present work is to elucidate the degradation kinetics of polyvinyl chloride (PVC) plasticized with some phthalate and nonphthalate plasticizers. A PVC thermomat instrument was utilized to maintain the isothermal degradation conditions at 140 and 160°C, and to suppress the oxidative degradation by means of nitrogen flow. The conductivity measurements were performed to follow hydrogen chloride (HCl) gas which is released upon PVC degradation and trapped in water. Dehydrochlorination of plasticized PVC films occurred with activation energies of about 23–160 and 26–117 kJ mol⁻¹ and the isokinetic temperatures, at which the dehydrochlorination rate constants of all p-PVC films would have the same value, were found to be 171 and 128°C for initial and linear regions of dehydrochlorination curve, respectively. Plasticizer incorporation contributes to the stability of the films particularly after the consumption of stabilizer due to the dehydrochlorination. Influence of temperature rise by 20°C on the degradation rate constant is the lowest for DINCH having p-PVC films as 0.36 and 0.42% increment at the initial region and linear region, respectively. On the other hand, DOTP reveals greater stability than the others do since the compensation ratio of the PVC film having DOTP is greater than the other films. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41579.

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INTRODUCTION

There is a debate on the environmental properties of the most common traditional plasticizer for polyvinyl chloride (PVC), di-2-ethylhexyl-phthalate (DEHP).¹ In 2008, dibutyl phthalate (DBP), DEHP and benzyl butyl phthalate (BBP) were listed within the 14 substances of very high concern (SVHC) by European Chemicals Agency (ECHA), as toxic for human fertility.^{1–3} Recently, many plasticizer producers promoted several alternatives in order to substitute DEHP due to the health effects as a shift from low to high molecular phthalates or even to other compound classes (adipates, succinates, glutarates, terephthalates, trimellitates, citrates) for the use in PVC applications.^{2,4,5} DEHP is mainly replaced with the other phthalates di-isodecyl phthalate (DIDP) or di-isononyl phthalate (DINP) for wire and cable applications.^{4,6} Among the group of new general purpose plasticizers are terephthalates, especially dioctyl terephthalate (DOTP), and di-isononyl 1,2-cyclohexanedicarboxylic acid (DINCH).^{4,5} When plasticized PVC (p-PVC) film is heated, plasticizer evaporates from the surface of the film and PVC degrades by the loss of hydrogen chloride (HCl) gas (dehydrochlorination) with the formation

of conjugated double bonds in the first stage of thermal decomposition.^{7–9} PVC could be stabilized by the substitution of allylic chlorines with stearates and no HCl is eliminated. However any HCl gas formed by dehydrochlorination may be scavenged by the heat stabilizers.¹⁰

Calcium and zinc stabilizers, which disperse more easily and uniformly in substrate, are widely used in the production of several nontoxic PVC articles, such as food contact packaging materials, children's toys and medical articles as well as of window profiles, pipes, wire, and cable.¹¹

Zinc chloride being a Lewis acid however accelerates dehydrochlorination reaction,¹⁰ formation of zinc chloride is retarded by the reaction of zinc chloride with calcium chloride forming stearic acid and calcium chloride. Thus the dispersion of heat stabilizers and mass transfer of the formed HCl gas from the plasticized system are important variables.¹²

The dehydrochlorination of PVC is initiated mainly by a tertiary chlorine atom and from chloroallylic labile structures, that arise as structural defects of PVC, created during its polymerization.¹³ Calcium and zinc stabilizer mixture has synergistic effect and

Table I. Identification of Substances Used in the Present Study

Chemical species	Abbreviation	Explanation	Specification
Poly(vinyl chloride)	PVC	Emulsion, <63 μm ; K# 71-75; M_w (97,300-110,643) g mol^{-1}	Petkim, Turkey. Characterized as in ref.22
1,2-Cyclohexane dicarboxylic acid, di-isononyl ester	DINCH®	$\text{C}_{26}\text{H}_{48}\text{O}_4$	Hexamoll®; BASF, Germany
Diocetyl terephthalate	DOTP, DEHTP	$\text{C}_{24}\text{H}_{38}\text{O}_4$	Purity >96%, Aldrich, Germany
Diocetylphthalate	DEHP, DOP	$\text{C}_{24}\text{H}_{38}\text{O}_4$	Plastifay Chemical Ind, Turkey
Diisononyl phthalate	DINP	$\text{C}_{26}\text{H}_{42}\text{O}_4$	Plastifay Chemical Ind, Turkey
Diisodecyl phthalate	DIDP	$\text{C}_{28}\text{H}_{46}\text{O}_4$	Plastifay Chemical Ind, Turkey
Diocetyl maleate	DOM	$\text{C}_{20}\text{H}_{36}\text{O}_4$	Plastifay Chemical Ind, Turkey
Diocetyl adipate	DOA	$\text{C}_{22}\text{H}_{42}\text{O}_4$	Plastifay Chemical Ind, Turkey
Epoxidised soybean oil	ESBO	$\text{C}_{57}\text{H}_{106}\text{O}_{10}$	Plastifay Chemical Ind, Turkey
Calcium-zinc stearate mixture	CaSt ₂ -ZnSt ₂ mixture	Thermal stabilizer	Plastifay Chemical Ind, Turkey
Tetrahydrofuran	THF	$\text{C}_4\text{H}_8\text{O}$	Merck, Germany

presents favorable stabilization¹⁴ through the carboxylate groups which substitute the tertiary and allylic chlorine atoms and stop the initiation of dehydrochlorination according to well known Frye and Horst mechanism.¹⁵

The generation of HCl gas causes contamination of all product streams with chlorinated organics, creates corrosion problems and produce harmful substances^{16,17} and discoloration of the resin occurs along with important changes in physical and chemical properties.

Because HCl is the main volatile product of PVC decomposition below 220°C, monitoring the amount of this acid that is evolved during the PVC thermal degradation allows determination of the rate of dehydrochlorination of the PVC.¹³ Most of the chlorine molecule is released as HCl that represents up to 99% of the total volatiles; this HCl is accompanied with a small amount of hydrocarbons, mainly aromatics such as benzene.⁷

There have been many studies for thermal decomposition of PVC due to its low thermal stability.^{7,8,16-19} Kosuda et al.⁹ studied the characteristics and reaction mechanism of the low temperature dehydrochlorination of PVC. In the thermal decomposition of PVC, the reaction behavior of the polyenes derived from the dehydrochlorination of PVC has an important influence on the yields and the species of the final products.¹⁶ Beltran and Marcilla,²⁰ applied several kinetic models to find out the thermal degradation kinetic parameters of PVC plastisols. They concluded that kinetic analysis of thermal gravimetric analysis (TGA) data was a very complicated process. It is difficult to differentiate between the mass loss due to the plasticizer evaporation and the one due to the dehydrochlorination as the degradation is monitored by means of TGA.²¹

Valorization of the PVC-containing wastes through the pyrolytic degradation promotes the generation of concentrated hydrochloric acid besides a carbon-rich residue and a synthesis gas.¹⁹

Although there are several studies related to the degradation of PVC, the ones monitoring dehydrochlorination of emulsion type PVC in plasticized systems is rare literature.

Emulsion PVC has different dehydrochlorination profile than that of suspension type which is frequently seen in literature.^{8,22,23} The emulsifying agents and the plasticizers have influence on the degradation route of PVC since each p-PVC system exhibits a different rate constant and activation energy to degradation.

Therefore, the objective of the present study is to shed some light on the degradation kinetics of highly plasticized PVC systems which are used mainly in cable sheaths. Accordingly, degradation kinetics of p-PVC films plasticized with some orthophthalate, terphthalate, and nonphthalate plasticizers were studied monitoring the evolved HCl gas to determine the kinetic parameters as the rate constants and activation energies. The HCl gas transferred into the deionised water was followed by means of the change in the electrical conductivity through a particular instrument, namely PVC Thermomat, serving for such analyses.

MATERIALS AND METHODS

Materials

The chemical components of p-PVC films, namely, powder PVC, liquid plasticizers, and the heat stabilizing system, are of technical grade and are the same as in our previous study.⁴ Powder PVC used in formulations is a typical commercial PVC emulsion resin (paste type, <63 μm , K# 71-75; M_w 97.300-110.643 g mol^{-1} , Petkim, Turkey, characterized in detail elsewhere²²). The unplasticized PVC (u-PVC) film is produced from the PVC powder simply cast in tetrahydrofuran (THF, stabilized with antioxidant and butylated hydroxytoluene (BHT)) as solvent.

On the other hand, p-PVC films were produced curing the plastisol formulations having plasticizers in addition to a synergic thermal stabilizers as epoxidized soy bean oil (ESBO) and calcium-zinc stearate (CaSt₂-ZnSt₂) mixture. While DEHP, DINP, DIDP, di-octyl maleate (DOM), and di-octyl adipate (DOA) were products of a domestic company, DOTP and DINCH were supplied from vendors.⁴ The chemical substances which were used throughout the study were given in Table I.

Production of p-PVC Films

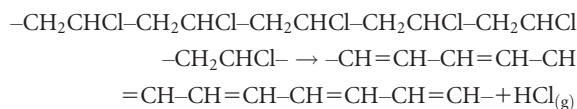
The method of p-PVC film production applied here was the same as the one in our previous study.⁴ Shortly, a hundred part of pre-dried PVC, 60 phr (phr: per hundred resin on the mass basis) plasticizer, 5 phr ESBO and 3 phr mixture of Ca and Zn stearates were thoroughly mixed to obtain a homogeneous mixture. Following the outgassing, small aliquots of plastisols spread at 120 μm thickness on glass plates were cured (gelled) for 15 min in an air-circulating oven set to 160°C. Then, the p-PVC films were cooled down and stripped off the glass plate.

Kinetic Study on Isothermal Degradation of PVC

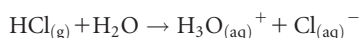
A Metrohm 763 PVC Thermomat instrument⁸ was utilized for the determination of dehydrochlorination of PVC on one test specimen of 3–4 mm² film pieces of each p-PVC sample. The film pieces were weighed and placed in the reactor vessel of the instrument previously set at constant temperature (140 and 160°C). Evolved HCl upon decomposition was swept with nitrogen gas having a flow rate of 6.9 cm³ min⁻¹ and dissolved in the deionised water of 60 \pm 0.02 cm³ in the measuring vessel of PVC thermomat. Conductivity of the water measured by a conductometer was recorded automatically throughout the experiment.

THEORETICAL

The thermal degradation of PVC occurs through the dehydrochlorination when heated during processing as shown below.^{19,22}



The dehydrochlorination of PVC is initiated mainly by a tertiary chlorine atom and from chloroallylic labile structures. The rate of dehydrochlorination of the PVC is determined monitoring the amount of HCl evolved during the thermal degradation.^{12,13} In a PVC Thermomat instrument, the released gas is transferred into water^{8,13,22,23} and HCl gas dissolves in water and gives H₃O_{aq}⁺ (simply taken as H⁺ in the following sections) and Cl⁻ ions as shown in the reaction scheme given below.



The concentration of hydrogen chloride evolved upon degradation of PVC is directly proportional to the change in the electrical conductivity of the aqueous solution.²⁴ For small inorganic ions, the ionic mobilities are quite small and generally lie between 4–8 $\times 10^{-8}$ m² V⁻¹ s⁻¹. However, H₃O_{aq}⁺ ion shows abnormally high value (36.3 $\times 10^{-8}$ m² V⁻¹ s⁻¹) due to its special jumping mechanism that operates in addition to the usual motion through the solution.²⁵

Determination of Thermal Dehydrochlorination Rate of PVC

Rate of dehydrochlorination depends on concentration of potential double bonds or concentration of unreacted HCl.

Considering the first order dehydrochlorination reaction of PVC,^{26,27} the rate equation can be given as follows [eq. (1)]:

$$\frac{dC_{\text{HCl}}}{dt} = k(C_o - C_{\text{HCl}}) \quad (1)$$

where dC_{HCl}/dt is the rate of dehydrochlorination ($\mu\text{mol g}^{-1}$ PVC.s), k is the rate constant of the reaction (s^{-1}), C_o is the potential number of double bond concentration form upon complete elimination of HCl per one gram of PVC, C_{HCl} is the concentration of evolved HCl from the sample. Because $C_{\text{HCl}} \ll C_o$, C_{HCl} is neglected and the rate of dehydrochlorination is expressed as follows [eq. (2)]:

$$\frac{dC_{\text{HCl}}}{dt} = kC_o \quad (2)$$

The change of conductivity of the aqueous solution in which the evolved HCl gas is transferred can be written in terms of concentration change in HCl [eq. (3)]^{8,13}

$$\Delta K = \sum F U_i |Z_i| \Delta C_i \quad (3)$$

where K is the conductivity, in S cm⁻¹, F is the Faraday's constant, U_i is the mobility of ion in water, Z_i is number density of ion charges, and, C_i is the concentration of ions that conduct the electricity.¹³

To find out the rate constant of the reaction, the rate of dehydrochlorination is calculated by taking the derivative of eq. (3). Because U_i is the sum of U_{H^+} and U_{Cl^-} which is equal to U_{HCl} and $|Z_i|=1$ for H⁺ and Cl⁻ ions, eq. (4) is obtained as follows.

$$\frac{dK}{dt} = F U_{\text{HCl}} \frac{dC_{\text{HCl}}}{dt} \quad (4)$$

where dK/dt is calculated from eq. (4) for each sample for both initial and linear regions of the curves to determine dC_{HCl}/dt in eq. (6).

Assuming all of the evolved HCl from PVC is dissolved in the water having a volume of $V_{\text{H}_2\text{O}}$, then the total moles of released HCl, n_{HCl} , gas is expressed as in eq. (5):

$$\frac{dn_{\text{HCl}}}{dt} = V_{\text{H}_2\text{O}} \frac{dC_{\text{HCl}}}{dt} \quad (5)$$

Then the rate of dehydrochlorination is expressed in terms of total moles of released HCl gas and the rate constant of the reaction is obtained [eq. (6)]:

$$k = \frac{1}{C_o} \frac{dC_{\text{HCl}}}{dt} = \frac{1}{C_o m \varphi_f} \frac{dn_{\text{HCl}}}{dt} \quad (6)$$

where m is the mass of film in reaction vessel, and φ_f is the fraction of PVC in the plastisol.

Determination of the Temperature Dependence of PVC Dehydrochlorination

Degradation process is often observed as a thermally activated process, so that the degradation rate constant can be expressed in the Arrhenius form in eq. (7).

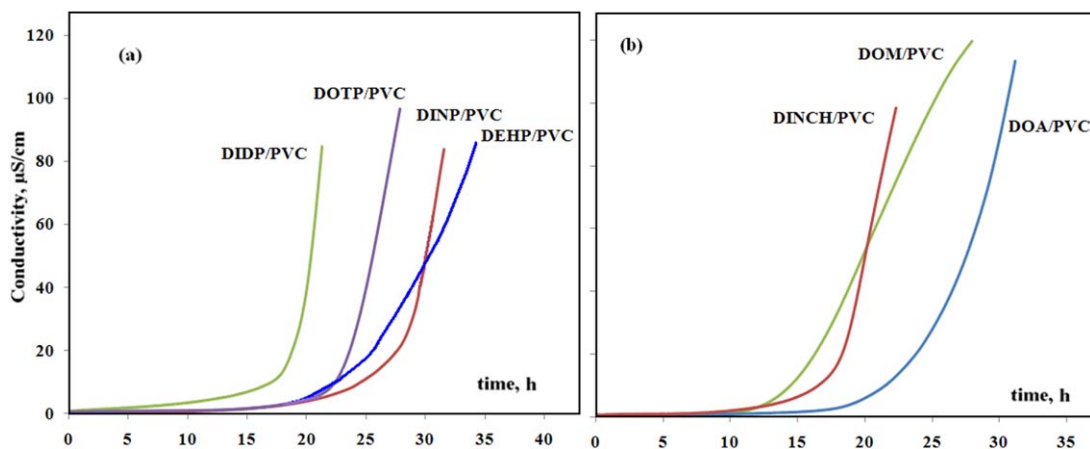


Figure 1. Conductivity of aqueous solutions having hydrogen chloride released at 140°C from p-PVC films containing (a) phthalate (b) non phthalate plasticizers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$k = A e^{-\frac{E_A}{RT}} \quad (7)$$

where k is rate constant, A is preexponential factor, R is gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and the apparent activation energy, E_A (J mol^{-1}), for the degradation is estimated through the Arrhenius equation carrying out the reaction at two temperatures those between the E_A is assumed to be constant applying the eq. (8).²³

$$\ln \frac{k_2}{k_1} = -\frac{E_A}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (8)$$

where k_1 and k_2 are the rate constants at T_1 and T_2 temperatures, respectively.

For many heterogeneous chemical reactions, a linear relationship between exponential and preexponential factor of Arrhenius equation, namely E_A and A , has been found. This correlation is called “compensation law,” “compensation effect,” “isokinetic effect,” or “ θ rule.”^{4,28}

For the thermally stimulated experiments, the origin of the compensation phenomenon is attributed to^{4,29}:

- i. The physical aspects of the considered system which are based on molecular interpretations assigned such as cooperative nature of relaxational process. The enthalpy–entropy relationship, the relation between entropy of transition and change in the energy levels of the transition state, the simultaneous occurrence of reactions on the surface centers involving different activation energies, the existence of interrelated kinetic behavior within a group of rate processes are some reasons likely to be involved in.
- ii. Experimental propagation errors or intrinsic mathematical consequences of the physical description of the process.

As the compensation effect which is due to the complexity of the degradation process is considered, it is one of the most controversial problems in the field of thermal decomposition of solids.^{4,28} The compensation ratio (S_p , kJ mol^{-1}) given by eq. (9) is used to describe the reactivity of the system since the greater the compensation value, the greater the stability is.

$$S_p = \frac{E_A}{\ln A} \quad (9)$$

The isokinetic effect is expressed as eq. (10) where the isokinetic temperature (T_{iso} in Kelvin) represents the temperature at which the rate constants of all reactions of the series have the same value and k_{iso} is the isokinetic rate constant.²⁸

$$\ln A = \ln k_{\text{iso}} + \frac{E_A}{RT_{\text{iso}}} \quad (10)$$

Definitions Belonging to the Thermal Degradation Rate of PVC

PVC thermomat tests give information about dehydrochlorination reactions following the released HCl evolving on heating of PVC. In the thermomat experiment, the flow of nitrogen gas in the course of heating of PVC sample carries released HCl gas into a conductivity cell filled with water. Conductivity of the original distilled water increases with time as the acidic species are released. Conductivity of an electrolyte solution, depends on the charge of each species, and on their mobilities. Thus the change of conductivity of aqueous solution upon dehydrochlorination of PVC with respect to time is plotted. The slopes of the curves are related to the rate of change of the conductivity (K) of the solution with respect to time. It also depends on the concentration of ions in the solution, C_i , given by eq. (3). Assuming that all of the evolved HCl from PVC dissolves in water ($V_{\text{H}_2\text{O}}$, m^3), then the rate constant of the reaction is obtained from eq. (6).

The conductivity versus time curve reveals two dehydrochlorination rate regions and the transition between these regions.¹³ “Induction time” and “stabilization time” are the definitions belonging to the conductivity versus time curve of PVC decomposition.

The induction time is the time at which the release of HCl gas is started out of the PVC material upon degradation. While the induction time corresponds to the period before the inflection point of the conductivity versus time curve, the stabilization time corresponds to the $50 \mu\text{S cm}^{-1}$ conductivity value for

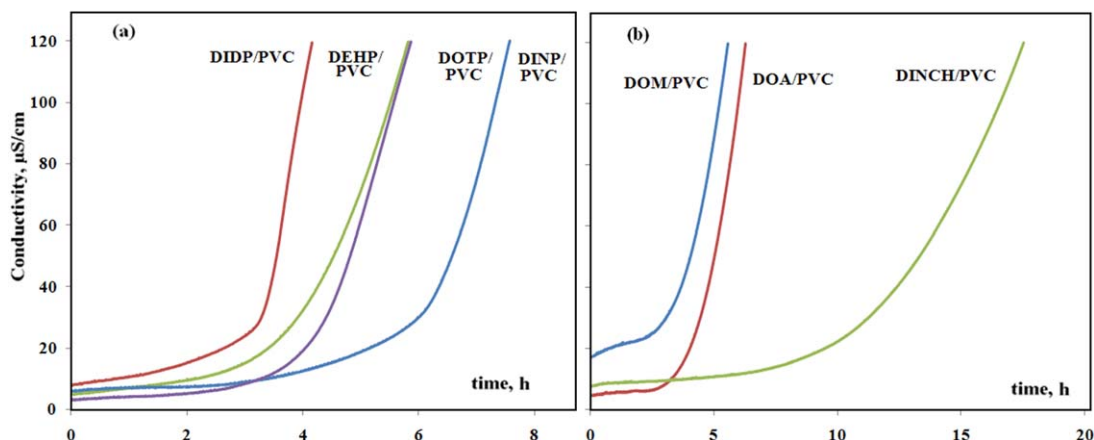


Figure 2. Conductivity of aqueous solutions having hydrogen chloride released at 160°C from p-PVC films containing (a) phthalate (b) non phthalate plasticizers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

500 ± 5 mg PVC content²² which covers most PVC samples and therefore is taken as standard in the thermomat experiments.

RESULTS

The study presented herein focuses on the degradation behavior of a commonly stabilized and plasticized PVC system in comparison with pristine PVC powder and u-PVC film. Therefore, the study mainly reveals the influence of different plasticizers onto PVC degradation kinetics and the achievement of the stabilization of this system.

Change of Conductivity upon Release of HCl Gas from PVC

As the dehydrochlorination of PVC has occurred, the HCl gas has evolved and the conductivity of the aqueous solution has changed as depicted in Figures 1 and 2 at 140 and 160°C, respectively.

The rate of dehydrochlorination of PVC has been determined from the conductivity of the solution using the amount of HCl transferred into the deionized water. The procedure followed for the calculation of the rate has been given in Appendix section.

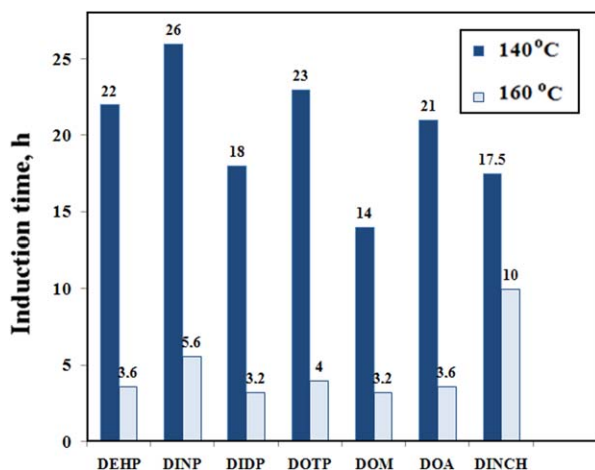


Figure 3. The induction time for dehydrochlorination of p-PVC samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Induction Time and Stabilization Time for Dehydrochlorination of PVC

Induction and stabilization times of the films determined by using the conductivity versus time data have been given in Figures 3 and 4, respectively. In fact, it is hard to determine the exact induction point due to the complex effects of the release of HCl gas into the water on the conductivity. These effects belong to the simultaneous and/or subsequent mass transfer as HCl gas from the bulk sample to the liquid environment, diffusion of HCl into the water, as well as to slight change in water temperature due to the dissolution of HCl in it. Therefore, the cross section of the lines extrapolated from the initial and linear region parts of the conductivity versus time curve is considered as the “induction time” for the sake of evenly data collection for the calculations.

The induction time values for p-PVC films (Figure 3) were found to be 14–26 h and 3.2–10 h for 140 and 160°C treatments, respectively. The same films have the stabilization time 20–30 h and 4–13 h, at 140 and 160°C, respectively (Figure 4).

Degradation starts much more earlier at high temperatures as compared to low temperatures. All p-PVC films processed at

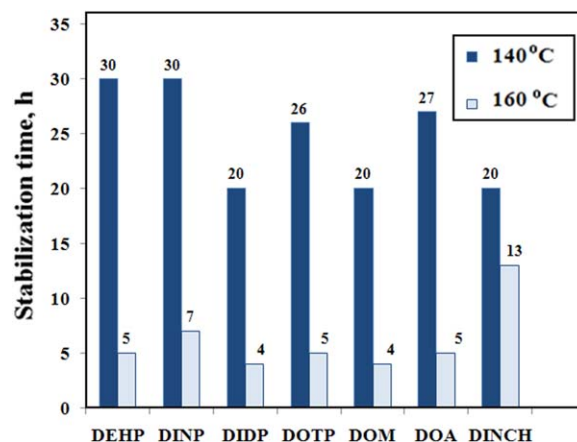


Figure 4. The stabilization time for dehydrochlorination of p-PVC samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Induction and Stabilization Time for PVC Samples

	140°C			160°C		
	Powder PVC	u-PVC	p-PVC films	Powder PVC	u-PVC	p-PVC films
Induction time, h	4.1	1.3	14-26	0.9	0.3	3.2-10
Stabilization time, h	8.5	4.1	20-30	1.9	0.7	4-13

160°C exhibited shorter induction and stability time than those processed at 140°C as expected under the light of literature.²¹

The film containing DINCH as plasticizer showed minimal change suggesting that it was the least affected by the temperature. However the others exhibited about 80% decrement both in induction and stabilization time, DINCH having p-PVC film exhibited only about 40% decrement most likely because of a better geometric harmony of PVC with DINCH than those with the other plasticizers.

In our former study²² the induction and stabilization time values for PVC without stabilizers as PVC powder and u-PVC film were reported. Yet the PVC samples either with or without stabilization additive should have tiny amount of emulsion process additives not completely removed and acting as stabilizer to them. While the induction (and stabilization in parenthesis) times were 4.1 (8.5) h and 1.3 (4.1) h respectively, at 140°C, they were 0.9 (1.9) h and 0.3 (0.7) h at 160°C. Induction time gets shorter with increasing temperature (Table II).

It is obvious that the induction time and the stabilization time for plastisols are longer than those for the PVC without stabilizers, namely, PVC powder and u-PVC film thanks to the presence of added stabilizers (Table II). These results suggest that the presence of plasticizer most likely retards the decomposition of PVC.

As the powder PVC and u-PVC are compared, the shorter decomposition time values of u-PVC than those belonging to

powder PVC suggest the presence of species carried along with the solvent used in the production of solvent cast u-PVC film. Although contamination with THF, which is used to cast the film, accelerates the decomposition of PVC,³⁰ BHT carried along with THF used as antioxidant in it may retard decomposition of u-PVC films cast from THF.²⁵

Previous to the induction time, no release of HCl gas out of the film occurs since it is scavenged by the stearates to stabilize PVC. The length of the induction period may be considered as a measure of the heat stability of PVC and the binding capacity of the stabilizer.³¹ However in this study, the amount of heat stabilizer in the formulation is constant in all p-PVC films.

In the present study, amongst the DEHP, DINP, and, DIDP having eight, nine, and ten carbon atoms respectively in aliphatic arms of orthophthalates as a homologous series, DIDP having samples exhibited the shortest induction and stabilization time values. This result suggests that the longer branching having phthalate plasticizer imparts less hindrance to PVC for dehydrochlorination.

Rate Constants for Dehydrochlorination Reaction of PVC

Two rate constants were calculated for each dehydrochlorination reaction step: Initial region rate constant (IRRC) belongs to the initial region of the conductivity curve where release of HCl gas starts. Linear region rate constant (LRRC) is evaluated from the following step where the acceleration effect of evolved HCl^{8,13,23} and the products formed after the dehydrochlorination could be detected.

Table III. Kinetic Parameters^a for Dehydrochlorination of PVC

Sample	Initial region parameters			Linear region parameters		
	$k^a \times 10^5, \text{min}^{-1}$		$E_A^a, \text{kJ mol}^{-1}$	$k^a \times 10^5, \text{min}^{-1}$		$E_A^a, \text{kJ mol}^{-1}$
	140°C	160°C		140°C	160°C	
DEHP/PVC	0.6	5.1	159.1	2.3	12.0	112.8
DINP/PVC	0.9	3.4	103.1	4.9	16.0	88.0
DIDP/PVC	1.6	6.1	99.5	7.9	38.0	116.8
DOTP/PVC	1.6	4.5	76.9	5.1	17.0	89.5
DOM/PVC	1.0	4.0	103.1	2.8	12.0	108.2
DOA/PVC	0.8	3.6	112.8	4.5	13.0	78.9
DINCH/PVC	1.1	1.5	23.1	5.9	8.4	26.3
PVC powder ^b	0.2	1.1	126.7	1.4	1.8	18.7
u-PVC ^b	2.3	11.4	110.9	5.7	20.8	89.7

^a k : rate constant, E_A : activation energy.

^bCalculated using the data of Ref. 22.

The rate constants for dehydrochlorination reaction (Table III) were calculated using the slope of tangent line belonging to the initial and linear region of the curves of conductivity versus time graphs and applying eq. (6). P-PVC film having DINCH presents lower degradation rate constants at 160°C than the others do.

In fact according to Table III, k values are different at each T as expected since the rate constant increases with temperature. T_1 and T_2 are close enough temperatures for this context to take the related enthalpy almost constant. Therefore, as we believe E_A values are acceptable as represented in the Table III.

The LRRC were higher than the IRRRC because of the autoacceleration effect of HCl and also more rapid dehydrochlorination occurred after the consumption of the stabilizers.³² The degradation of p-PVC films were faster at 160°C than at 140°C which increase the release of HCl.

The LRRC of PVC powder (calculated using the data also in Ref. 22) was lower than that of p-PVC films in all regions (Table III). As seen on the curves in Figure 1, an initial slow rate of HCl evolution at the beginning of the heat treatment followed by a more rapid dehydrochlorination after consumption of the stabilizers.^{22,23} Yet the lowest degradation rate constants of PVC powder prevent its degradation to a certain extend.

As the temperature raised by 20°C, degradation rate constants of the films except DINCH having one increased by 1.8–7.5% and 1.2–4.9% at the initial region and linear region, respectively. However, DINCH having p-PVC films exhibited only 0.36 and 0.42% increment with the same order which is the lowest influence of temperature rise.

Activation Energy for Dehydrochlorination of PVC in Stabilized Plastisol Systems

Activation energy, the independent variable, is equal to the energy barrier that must be exceeded for the degradation reaction to occur. Table III depicts the activation energies of the dehydrochlorination reactions calculated herein by using the data at two temperatures as 140 and 160°C in eq. (8).

The stabilizer should be consumed during the thermomat measurement at high temperatures and therefore the films should become more prone to dehydrochlorination besides the acceleration of dehydrochlorination due to the evolved HCl.^{8,13,23} However DIDP, DOTP, DOM, and DINCH having films exhibit the slight rise of E_A , DEHP, DINP, and, DOA having films exhibit lower E_A values in linear region than those in initial region which proves this expectation.

While the process is complex enough with stabilization and dehydrochlorination mechanisms, plasticizer evaporation accompanying to them makes the process hard to understand. Therefore, each plasticizer system should be studied since the molecular structure of the plasticizer, which is the only difference in the present films, may have a governing role on the dehydrochlorination.

The steep decrease in E_A of PVC powder from initial to linear region suggests that PVC itself is really prone to dehydrochlori-

nation as long as it is not stabilized for manufacturing processes.

The activation energy values of the films except DINCH having one in both region were found to be 77–159 kJ mol⁻¹ for the 140–160°C interval. However, DINCH having p-PVC film exhibited the activation energies as 23–26 kJ mol⁻¹ suggesting easy pass of the degradation threshold. This occurs most likely due to the retardation of PVC degradation at the beginning in the presence of calcium and zinc stabilizers. The chemical composition of the metal stabilizers change upon their reaction with PVC and the species formed in turn accelerates decomposition. Therefore, PVC powder decomposes faster than p-PVC films do at linear regions because of the activation energy values of the PVC powder relatively lower than others.

The activation energies of the dehydrochlorination reactions for initial regions were found to be about 100–160 kJ mol⁻¹ and 23–113 kJ mol⁻¹ for the samples having orthophthalate and nonphthalates plasticizers, respectively, while those for linear regions were found to be about 88–117 kJ mol⁻¹ and 26–108 kJ mol⁻¹, respectively. DOTP, which is a terephthalate, exhibited values laying between orthophthalates and nonphthalates.

It seems that, activation energies of dehydrochlorination for the samples having phthalate plasticizers are higher than those having nonphthalate plasticizers.

The energy required for a chlorine atom abstraction with a subsequent attack on the neighboring hydrogen and leading to HCl elimination is 159.1 kJ mol⁻¹ (1.64 eV) and 112.8 kJ mol⁻¹ (1.17 eV) for initial and linear region dehydrochlorination of PVC film having DEHP, respectively (Table III).

Krongauz et al.,²¹ reported that the degradation activation energies of PVC plasticized with DEHP and non-plasticized PVC powder determined by means of spectroscopic analysis and TGA were remarkably close as 147 and 153 kJ mol⁻¹, respectively. In our study these values were found to be 112.8 and 18.7 kJ mol⁻¹, respectively for the linear region.

Marcilla and Beltran,³³ determined the activation energy of the degradation of PVC plastisol having 65 phr DEHP to be between 85 and 131 kJ mol⁻¹ in several models they applied to their TGA analyses. They suggested that higher homogeneity of the sample and the interaction between the plasticizer and resin at high concentrations of plasticizer results in more hindered diffusion of evolved HCl and accordingly decelerates the decomposition of the resin. So the activation energy increase with plasticizer concentration. Possibly having no thermal stabilizers in the system made the decomposition of their plastisols easier although the plasticizer amount is slightly higher than those in ours.

The lower is the activation energy, the more susceptible the material is to degradation. Noting that the linear region commences after the consumption of the stabilizer, the differing activation energies suggests that the plasticizer type and structure affect the stabilizer consumption and degradation of PVC. Orthophthalate type plasticizer as DEHP, DINP, and DIDP having films generally have higher activation energies than the others have, suggesting that their stability was high.

Table IV. Preexponential Factor (A) and Compensation Ratio (S_p) for Dehydrochlorination of PVC

Sample	Initial region		Linear region	
	A, min^{-1}	S_p	A, min^{-1}	S_p
DEHP/PVC	8.0×10^{14}	4.64	4.3×10^9	5.09
DINP/PVC	9.9×10^7	5.60	6.6×10^6	5.60
DIDP/PVC	6.2×10^7	5.55	4.7×10^{10}	4.75
DOTP/PVC	8.5×10^4	6.78	1.1×10^7	5.52
DOM/PVC	1.1×10^8	5.57	1.4×10^9	5.14
DOA/PVC	1.5×10^9	5.34	4.3×10^5	6.08
DINCH/PVC	9.2×10^{-3}	-4.93	1.0×10^{-1}	-11.4
PVC powder	2.1×10^{10}	5.33	3.3×10^{-3}	-3.27
u-PVC	2.5×10^9	5.12	1.3×10^7	5.48

The Mechanism of Dehydrochlorination of p-PVC Films and its Relation with the Structure of Plasticizer

The activation energy of a complex process like polymer degradation is not a parameter enough to describe the degradation process by itself, without the preexponential factor.²⁸

Although the values of preexponential factor A are quite scattered within a series of species due to different experimental conditions, $\ln A$ and E_A pairs, are linearly correlated. While the $\ln A$ versus E_A as a straight line indicates that the reaction follows the same mechanism, any deviation from the straight line indicates a different mechanism.²⁸

Kovacic and Mirlicic,³⁴ studied the compensation effect by using rate constants of plasticizer evaporation from PVC to make clear if there is any resemblance in their behavior as if a homologous series could have.

Suggesting an analogy between the compensation concept and dehydrochlorination of PVC, we adapted the compensation ratio ($S_p, \text{kJ mol}^{-1}$) to the present dehydrochlorination mechanism with its own activation energy and preexponential factor.

Therefore, the preexponential factors and then, the compensation ratios belonging to initial and linear region for PVC powder and p-PVC films given in Table IV were calculated using eqs. (7) and (9), respectively.

The A values of p-PVC films except the one having DINCH plasticizer spanning a broad range from 10^4 to 10^{14} in initial region and 10^5 to 10^{10} in linear region in the present study is attributed to somewhat different structure of the plasticizers taken under investigation. Then going a step forward, $\ln A$ values were plotted against E_A in Figure 5 and this plot was found to have the characteristics of the straight compensation line. Therefore, even though the structural differences were present, the plasticizers taken under investigation were belonging to the same group and the mechanism of degradation of PVC did not change with the plasticizer type herein. On the other hand, the compensation ratio of p-PVC film having DOTP as plasticizer is greater than the other films, suggesting that DOTP impart greater stability to PVC than the others do. The compensation ratio of p-PVC film having DINCH is lower than those of the other films. The absence of heat stabilizers and plasticizers in powder PVC is thought to make its compensation ratio shorter than those for p-PVC films.

The intermolecular interaction between the polar parts of the plasticizer (carbonyl group) and the PVC (carbon–chlorine bond) slightly weakens the intramolecular bonding forces in the interacting functional groups.³⁵ The use of Hansen solubility parameter (HSP) integrates the interactions in polymer solutions, which requires the use of thermodynamic theories and interactions parameters, with compatibility concepts. Kurt-Comlekci³⁶ calculated the relative energy distance (RED) for DIDP, DINP, DEHP, DOM, and, DOA by using the HSP and concluded that all were compatible with PVC.³⁶

The size and shape of plasticizer molecules are of importance for solubility, diffusion and chemical resistance phenomena. Smaller molecules tend to be more readily soluble than larger ones. The Hildebrand solubility parameter theory points to smaller molar volume solvents as being better than those with larger molar volumes, even though they may have identical solubility parameters. This fact is known from the Flory–Huggins

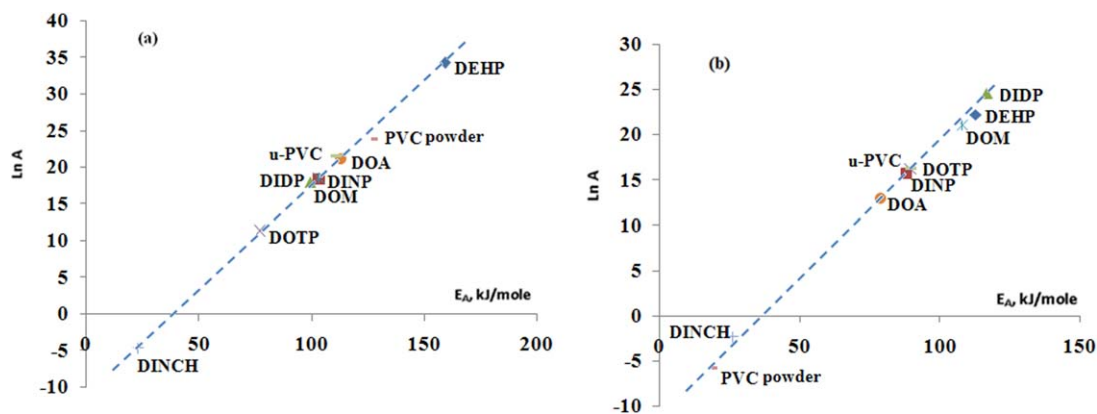


Figure 5. The change of preexponential factor with respect to the dehydrochlorination activation energy of PVC samples belonging to (a) initial region, (b) linear region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

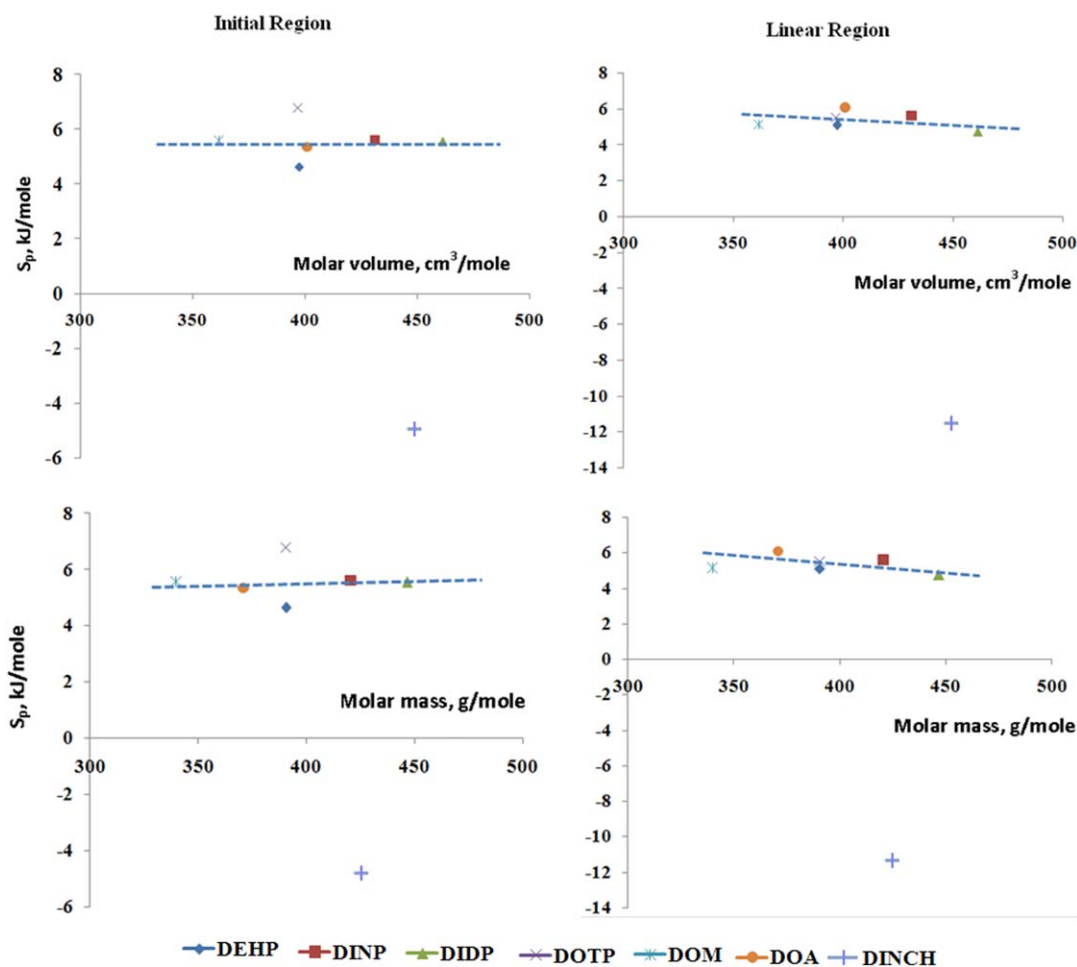


Figure 6. Compensation ratio with respect to molar volume and molar mass of plasticizer in p-PVC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

theory of polymer solutions, as well. Smaller and more linear molecules diffuse more rapidly than larger and more bulky ones.³⁷

Then, S_p values were plotted against intrinsic properties of plasticizers as molar volume and molar mass (Figure 6). These findings suggest that the DINCH as plasticizer exhibits totally different behavior from the others.

As their molar volumes and molar masses are considered to sort the A values, DINP, DIDP, DOM, and DOA have the same order. The DOTP and DEHP which have the closest values to each other considerably deviates from the values belonging to the other plasticizers. The DINCH has the totally different behavior from the others. The same molar volume and molar mass having species, namely, DOTP and DEHP have substantially different A values possibly due to their different molecular structure. DOTP, however has a planar spatial arrangement, is a terephthalate and have the same molar mass as DEHP has. This structure of DOTP most likely hinders the stabilizer movement through the plastisol to maintain the thermal stability and makes it more compatible with PVC polymer chain than DEHP is. In the previous study similar tendencies were

observed for the mass loss because of plasticizer migration and its diffusivity in air.⁴

In fact, the DEHP (DOP), DOA (DEHA), DOM (DEHM), and DOTP (DEHTP) all have the diethylhexyl (DEH) structures. On the other hand, aromatic diesters DEHP (and DOTP), DINP and DIDP belong to a homologous series with 8, 9, and 10 carbon having groups in their alkyl part. DINP and DINCH are similar except the aromatic ring of the first one exchanged with alicyclic structure in the latter.

Besides compensation ratio, the isokinetic rate constant, k_{iso} , and isokinetic temperature, T_{iso} , values are other two values representing common kinetic behavior of the species belonging to the same family. Therefore, the k_{iso} and T_{iso} values were calculated from the intercept and the slope of the $\ln A$ versus E_A plots given in Figure 5 by using eq. (10). The common dehydrochlorination rate constant of the p-PVC films under investigation at the isokinetic temperatures has been found to be $4.54 \times 10^{-5} \text{ min}^{-1}$ for both regions. The isokinetic temperatures have been found to be 444.5 K (171.3°C) and 400.9 K (127.7°C) with high regression coefficients as 0.997 and 0.998, for initial and linear regions, respectively. Therefore, one may

suggest that the rate constants will have the same value for the present films at about 171°C for the initial region, and at about 128°C for the linear region. The activation energies found from 140 and 160°C data should be valid about 15–20°C beyond those temperatures and T_{iso} values is thought to be validation of the present results confirming the similarity of dehydrochlorination mechanisms of the present p-PVC films and in turn, confirming that the plasticizers do not have a broad departure from each other in terms of their structural behavior to substantially change the reaction kinetics.

Another fact worth to mention herein is about the amount of plasticizer which is the same as 60 phr of PVC. However, the minimum plasticizer amount as a measure of plasticizer efficiency for the fully plasticization differs with the molar mass of plasticizer. Therefore, a phr ratio which changes from 1.18 to 1.54 for all the considered plasticizers is obtained dividing 60 phr value by the minimum phr amount.⁴ The phr ratio of DINP and DIDP are 1.25 and 1.18, respectively and therefore, the higher amount of DINP may explain its better prevention from dehydrochlorination. Although the longer alkyl length in the same orthophthalate family is expected to give higher free volume, DINP imparts higher stability than DIDP does. The phr ratio of DINP and DIDP are 1.25 and 1.18, respectively and therefore, the higher amount of DINP may explain its better prevention from dehydrochlorination. On the other hand, DOTP has lower stability contribution to the stability of PVC than DEHP has. Because both have exactly the same phr ratio (1.33), it can be attributed to the planar structure of terephthalate which most likely contributes less to mobility and therefore to the free volume.

CONCLUSION

The present study monitors the release of HCl making use of the PVC Thermomat instrument under isothermal conditions and nitrogen flow. Therefore, it is superior to the methods which cannot suppress the oxidative degradations and cannot distinguish between plasticizer evaporation and dehydrochlorination.

Many kinetic parameters have been determined from the conductivity data obtained simply from dehydrochlorination under nitrogen flow applied to a group of p-PVC at two temperatures in the present study. Therefore, one can conduct similar studies for several reasons such as to determine the processing/manufacturing conditions and the limits of a new generation plasticizer, to compare the plasticizers for a particular application area and to validate the material in the waste stream.

However the amount of stabilizer is fixed in the present study, each plasticizer affects degradation in a different way. The difference in structure, spatial arrangement, and, free volume contribution of each plasticizer may change the route of degradation therefore the commencement of degradation may be detected at a different instant and with a different kinetic scheme before and after that instant.

The induction time results reveal the orders of plasticizers to be DINP > DOTP > DEHP > DOA > DIDP > DINCH > DOM

at 140°C and DINCH > DINP > DOTP > (DEHP ≈ DOA) > (DIDP ≈ DOM) at 160°C from the highest to the lowest stability effect. The same assessment through the stabilization time reveals these orders as (DEHP ≈ DINP) > DOA > DOTP > (DIDP ≈ DOM ≈ DINCH) at 140°C and DINCH > DINP > (DEHP ≈ DOTP ≈ DOA) > (DIDP ≈ DOM) at 160°C.

The plasticizers are thought to hinder some zipping mechanisms which are common in PVC degradation,^{2,3} particularly after the consumption of stabilizers through their free volume contribution. Therefore, the initial region and linear region parameters have been evaluated separately. As the influence of plasticizers on stability is evaluated through the kinetic parameters basis, namely k and E_a , and from the compensation ratio, main improvement occurs at the linear region, where the stabilizers are consumed so that the degradation commences.

The rate constant order of plasticizers from the highest to the lowest stability effect are found to be (DOTP ≈ DIDP) > DINCH > DOM > DINP > DOA > DEHP at 140°C and, DIDP > DEHP > DOTP > DOM > DOA > DINP > DINCH at 160°C for the initial region. The same assessment for the linear region reveals the order as DIDP > DINCH > DOTP > DINP > DOA > DOM > DEHP at 140°C and DIDP > DOTP > DINP > DOA > (DOM ≈ DEHP) > DINCH at 160°C.

The activation energy order of plasticizers are found to be DEHP > DOA > (DINP ≈ DOM) > DIDP > DOTP > DINCH at initial region and DIDP > DEHP > DOM > DOTP > DINP > DOA > DINCH at linear region.

These results are in accordance with each other as low rate constant and high activation energy for the low degradation tendency and the opposite is for the high one. On the other hand, the influence of temperature rise by 20°C on the degradation rate constant is the lowest for DINCH having p-PVC films as 0.36 and 0.42% increment at the initial region and linear region, respectively.

The compensation ratio order of plasticizers are found to be DOTP > DINP > DOM > DIDP > DOA > DEHP >> DINCH at initial region and DOA > DINP > DOTP > DOM > DEHP > DIDP >> DINCH at linear region. As deduced from the compensation ratio, DINCH imparts the lowest stability to the PVC films at both regions, while DOTP and DOA impart the greatest stability at initial and linear region, respectively.

Although the amount of plasticizer is constant as 0.60 g g⁻¹ PVC, it somewhat differs as converted into per mol PVC since molar mass of each plasticizer is different. Nevertheless, it can be said that all of the considered plasticizers impart stability to PVC to some extent, as an overall evaluation based on induction and stabilization time as well as on kinetic parameters.

APPENDIX

The procedure followed to determine kinetic constants and activation energies has been given on an example. The thermomat test considered herein is the one conducted at 160°C on p-PVC film having DOTP as plasticizer.

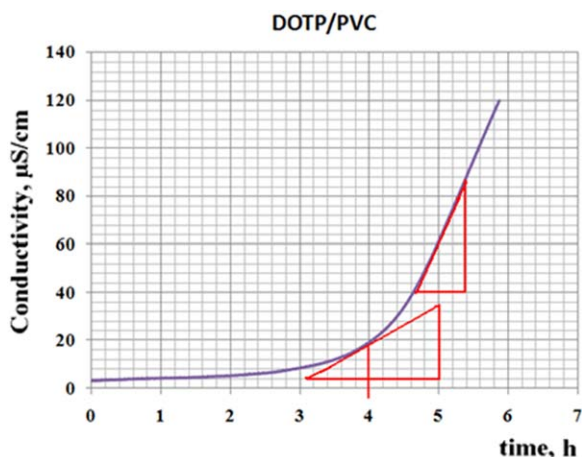


Figure 7. Conductivity of aqueous solution having hydrogen chloride released at 160°C from p-PVC films having DOTP as plasticizer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The initial region rate constant has been calculated from dK/dt which is the slope of the tangent line drawn at deflection point of the curve of conductivity versus time graph. For the determination of deflection point two lines referring to the two linear portions, namely, one at initial, and the other at the linear region were plotted on the excel file. The “induction time” is considered as the cross section of those lines which is found herein to be 14,400 s = 4.0 h, as shown in Figure 7.

Calculation of rate constant, k, by using eq. (6)

$$k = \frac{1}{C_0 m \varphi_f} \frac{dn_{\text{HCl}}}{dt} \quad (\text{A1})$$

where C_0 , the potential number of double bond concentration, has been calculated as $1.65 \times 10^4 \mu\text{mol g}^{-1}$, mass of the sample, m , 0.500 g and, φ_f , mass fraction of PVC in p-PVC.

Then, eqs. (4) and (5) are combined to find out $\frac{dn_{\text{HCl}}}{dt}$;

$$\frac{dn_{\text{HCl}}}{dt} = \frac{V_{\text{H}_2\text{O}}}{FU_{\text{HCl}}} \frac{dK}{dt}$$

$V_{\text{H}_2\text{O}} = 6.0 \times 10^{-5} \text{ m}^3$ in the present system and Faraday constant; $F = 9.6485 \times 10^4 \text{ C mol}^{-1}$.

The sum of mobility of each ion ($U_{\text{H}^+} + U_{\text{Cl}^-}$) gives the total mobility of HCl evolved;

$$U_{\text{HCl}} = 4.4163 \times 10^{-7} \text{ m}^2 \text{Vs}^{-1}$$

$$\frac{dK}{dt} = 4.39 \times 10^{-3} \mu\text{S cm}^{-1} \text{ s}^{-1} \quad (\text{From the tangent in Figure 7})$$

Therefore;

$$\frac{dn_{\text{HCl}}}{dt} = 2.39 \times 10^{-8} \text{ mols}^{-1};$$

Substituting $\frac{dn_{\text{HCl}}}{dt}$ in eq. (6); the initial region rate constant is found as;

$k = 2.9 \times 10^{-6} \text{ s}^{-1} \times 60 \text{ min}^{-1} = 1.7 \times 10^{-4} \text{ min}^{-1}$ for p-PVC having DOTP, at 160°C

The procedure has been repeated for each sample at each temperature and both for the initial and linear regions.

Then using the k values at 140 and 160°C in the equation below derived from eq. (8) as k_1 and k_2 , respectively, activation energies, E_A have been calculated:

$$E_A = R \cdot \left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \frac{k_2}{k_1}$$

The rate constants for dehydrochlorination reaction were calculated using the slope of tangent line belonging to the initial and linear region of the curves of conductivity versus time graphs.

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