Migration of Phthalate and Non-Phthalate Plasticizers Out of Plasticized PVC Films into Air

A. P. Tüzüm Demir,* S. Ulutan

Ege University, Faculty of Engineering, Department of Chemical Engineering, Bornova, Izmir, TR35100, Turkey
*Present address: Usak University, Faculty of Engineering, Department of Chemical Engineering, Usak, TR64200, Turkey
Correspondence to: A. P. Tüzüm Demir (E-mail: pinar.demir@usak.edu.tr) or (E-mail: apinar.tdemir@gmail.com)

ABSTRACT: The aim of the present work is to provide information about the migration of phthalate and non-phthalate plasticizers generally used in flexible polyvinyl chloride (PVC) applications. Plastisols (pastes) were prepared by mixing PVC, plasticizer, and thermal stabilizer. The plasticized PVC (p-PVC) films are obtained by gelation at 160°C for 15 min. The p-PVC films were heat treated at 50, 85, 100, 130, and 160°C up to 420 min to follow the mass loss to find out diffusivity of plasticizer out of films into air and to determine related activation energies. The films having di-octyl terephthalate (DOTP) and di-isononyl 1,2-cyclohexanedicarboxylic acid (DINCH) exhibited the lowest mass loss in general, among the phthalate and non-phthalate plasticizer having p-PVC films, respectively, as confirmed by FTIR investigation. The same tendency was observed for diffusion coefficients and for the activation energies of migration. The diffusion coefficients were found to be around 3.5×10^{-18}–2.1×10^{-17} m^2/sec for the studied plasticizers in PVC at 50°C and around 4.0×10^{-15}–9.9×10^{-14} m^2/sec at 160°C. The activation energies for 85–160°C interval were determined to be between 70 and 153 kJ/mol (0.72–1.58 eV) for the plasticizers used herein those could be treated as a homologous series as deduced from the related compensation factors. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Polyvinyl chloride (PVC) has a wide application area with several aspects such as its product performance, material processability, thermal stability, relatively low cost, and high versatility. It has inherent flame-retardant nature of its chlorine content, and it has been an excellent choice as insulation material for wire and cable.[1] PVC as cable jacket application has thermal rating as 60–90°C by IEEE (The Institute of Electrical and Electronics Engineers, Inc.) Std 1242-1999 cable guide. Its general properties are given as good for toughness, flexibility, flame resistance and water and weather resistance, excellent for ease of installation, heat resistance, and resistance to some chemicals except organic solvents.[2] However, atmospheric oxygen, UV radiation, temperature, moisture, and the electric field are the main factors from the environment that cause the ageing of the cables affecting the polymer structure and properties.[3] Electric fields are important in high voltage engineering due to performance of electric insulating material which is adversely affected by excessive electric field magnitudes.[4]

Additives are used in plastics to achieve the desired material properties, depending on the field of application.[5]

Plastisol is prepared by mixing process of PVC resin for paste application, plasticizer, and other additives.[6] Plasticizing additives in PVC break interchain dipole interaction providing a material with mobility and flexibility characteristics of a polymer with less interchain interaction.[7,8] When plastisols are heated (curing of plastisols up to 180–200°C), diffusion of plasticizer into PVC particles, swelling of the particles, and fusion of swollen particles to a solid mass occur simultaneously and a plastigel forms.[9,10]

Recent screening studies in industrialized countries for contaminants in human urine samples have revealed the extensive exposure of people to the group of phthalate plasticizers.[11–16] Because phthalates are not chemically bound to the products they easily diffuse to the surrounding media during its life-time, particularly those with high fat content.[12–22] As a consequence, phthalates contaminate indoor environments and human food and belong to the ubiquitous environmental contaminants and present difficulties in toys.[12,13,23] Several phthalates and especially di-ethyl hexylphthalate (DEHP) known as di-octyl phthalate, (DOP, as well) are suspected of having carcinogenic and toxic effects.[5,12–14,19,20,24–27] In 2008, dibutyl phthalate (DBP), DEHP, and benzyl butyl phthalate (BBP) were listed within the

14 SVHC (Substances of Very High Concern) by ECHA (European Chemicals Agency), as toxic for human infertility.[20,28] 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, trimelliates, and citrates) has taken place for the use in PVC applications.[11,20,21] DEHP is mainly replaced with the other phthalates such as di-isodecyl phthalate (DIDP) or di-isononyl phthalate (DINP) for wire and cable applications.[29]

Among the group of new general purpose plasticizers are terephthalates, especially dioctyl terephthalate (DOTP), which is also known as di-(2-ethylhexyl) terephthalate (DEHTP). The main fields of application for DOTP are coatings, vinyl floorings, electric connectors, vinyl water stops, and coatings for clothes, bottle caps, toys, and medical devices. As far as currently known, DOTP has no carcinogenic, genotoxic, or developmental effects.[11] Another new generation plasticizer is di-isononyl 1,2-cyclohexanedicarboxylic acid (DINCH) which has considerably lower specific migration rate than that of DEHP. DINCH is offered for a wide range of applications such as printing inks, can coatings, childcare articles, high solid paints, marine finishes, coil coatings, protective coatings, textile printings, and sport product, as well as for food contact applications, medical products, and toys.[11,21]

The aerobic ageing of plasticized PVC (p-PVC) involves three separate processes: dehydrochlorination, oxidation, and plasticizer loss by migration. The migration of plasticizer occurs through two processes as diffusion through the polymer matrix up to the surface of the material and transport from the polymer boundary to the surrounding medium. Both processes need to be considered when analyzing the rate of migration.[22,30] From an engineering point of view, the utilization of a parameter intrinsic to the migration process itself, as for example a diffusion coefficient, would be desirable. Evaporation of plasticizers with time and temperature is comparable with the lifetime of the polymer.[30,31] The service conditions for cables with p-PVC will tend to induce changes in the chemical and physical structures of the insulating materials, leading to irreversible changes in their electrical and mechanical properties, which are of importance for the safety of cable insulations to keep their functions under normal service conditions.[22]

The very long lifetimes (about 50 years) required of cables make the use of accelerated testing necessary.[22] The long intended lifetime of cables makes it important to monitor their deterioration with time.[6] The conventional methodology includes testing at elevated temperatures and extrapolation of high-temperature data to the normal service temperatures based on the Arrhenius equation.[22]

Activation energy is the kinetic component of the temperature dependence of permeation and is primarily determined by the penetrant size and shape of a polymer. Generally, it can be defined as the energy required to separate the polymer chains for a diffusional jump.[32] This methodology requires that the dominant ageing mechanism and the structure of the polymer remain essentially unchanged within the temperature interval considered. As an example, a PVC insulation rated as 60°C to be used under 300 V and 45°C having 0.92 eV degradation activation energy to simulate 15 and 30 years service life must be kept at 110°C for 456 and 888 h, respectively.[33]

The migration behavior of plasticizers is of importance since the phthalates soon will become out of use in order to alleviate the environmental contamination problems and ensure compliance with the recent environmental and health regulations of European Union. The present study, which is expected to serve for the protection of environment by means of data submission to the producers and users of plasticizers and for the development of new plasticizers, compares the migration behavior of a group of phthalate and non-phthalate plasticizer out of p-PVC into air. Therefore, the plasticizer migration data from PVC into air have been collected and treated by using the conventional methods. The mass losses from films were followed and FTIR spectra were taken, the diffusivity for different ageing times and temperatures and related activation energies were calculated. Compensation phenomenon is used to assess the behavior of the group of plasticizer taken under investigation herein, as well.

MATERIALS AND METHODS

Materials

A typical commercial PVC emulsion resin (paste type, <63 µm, K# 71–75; M_w 97,300–110,643 g/mol, Petkim, Turkey), characterized in detail elsewhere,[34] was used throughout the study mixing with plasticizers and synergic thermal stabilizers for plastisols preparation. All the plasticizers (DEHP, DINP, DIDP, di-octyl maleate (DOM), di-octyl adipate (DOA)) and the heat stabilizers (epoxidized soy bean oil (ESBO) and calcium–zinc stearate mixture ($CaSt_2$-$ZnSt_2$)) except DOTP (Aldrich, Germany) and DINCH (BASF, Germany) were kindly supplied by the producer, Plastifay Chemical Ind. (Turkey).

Plastisol Preparation

The plastisols were prepared mixing 60 parts of plasticizer, five parts of ESBO, and three parts of liquid thermal stabilizer mixture, with 100 parts of PVC (named as phr; per hundred resins), on the mass basis. Firstly, PVC resin was dried about 60°C in an air-circulating oven (FN-500 Nuve) at about 6 h and mixed for 15 min with liquid ingredients by using a laboratory mixer to obtain a homogeneous mixture. Then, the plastisol obtained which is a paste was outgassed under vacuum in order to avoid the presence of air bubbles in the final product.

Preparation of p-PVC Films

Small aliquots of plastisols were applied on a glass plate in the form of films having 120 μ thickness, with the help of a film applicator. Then those films were cured (gelled) for 15 min to produce p-PVC films in an air-circulating oven which was previously set to 160°C. The films were stripped off the glass plate after cooling down to room temperature at ambient air.

Evaluation of Mass Change During the Heat Treatment in Air

The films were cut into about 4 × 4 cm^2 pieces to follow the mass losses with respect to time. The p-PVC films were heat treated in the oven which was previously set at 50, 85, 100, 130, and 160°C. Before and during the heat treatment up to 420 min, the films were weighed at certain intervals by using a digital balance with four digits.
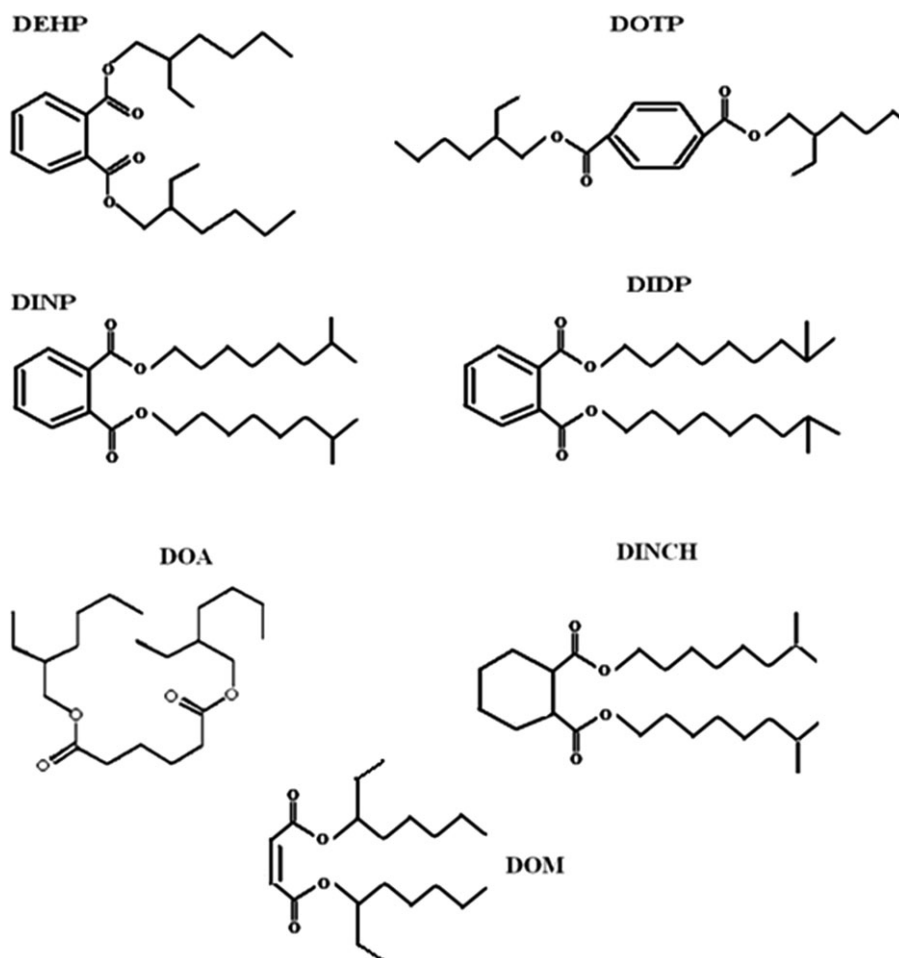
Figure 1. Structural formula of plasticizers.

Spectroscopic studies: FTIR

The raw materials as well as the p-PVC films were subjected to the Fourier transform infrared (FTIR) spectroscopic analyses taking their FTIR spectra as they are. A Perkin Elmer (Spectra 100) FTIR spectrometer equipped with Attenuated Total Reflectance (ATR) unit was used to take the spectra with a resolution of 4 cm^{-1}, 20 scans per sample on transition mode in the range of 4000–650 cm^{-1}.

RESULTS AND DISCUSSION

The characterization of the ingredients was performed taking their full FTIR spectra since the components of p-PVC were used as they are. Although their full spectra can be found elsewhere,[35,36] only some parts were submitted in the present study for the sake of simplicity.

Structural Analyses of the Components of p-PVC

Figure 1 shows the molecular structure of the studied plasticizers herein. DOTP is an aromatic terephthalate plasticizer while DEHP, DIDP, and DINP are all aromatic orthophthalates, DOM and DOA are aliphatic non-phthalates all having ethyl hexyl group, and DINCH is an alicyclic non-phthalate. The physical and chemical properties as well as the plasticization efficiency-related parameters of the plasticizers used throughout the study are given in Table I.

Mass Loss of the Films During Heat Treatment

Migration process depends on the molar mass, the molar volume, the polarity of the molecules, the nature and amount of the plasticizer, the plasticization process, and the homogeneity of the compound and the surrounding media, temperature, contact area, and other conditions.[10,23] When the plasticized article is exposed to air, the initial loss takes place by evaporation or volatilization of plasticizer from the surface. Mass loss percentages of p-PVC films during the heat treatment in the oven at 50, 85, 100, 130, and 160°C are given in Figures 2 and 3 for the films having phthalate and non-phthalate plasticizers, respectively, as the average of two sets of experiments. The mass loss of the film having DEHP takes place in both figures for comparison. Since the initial amount of the stearate mixture is very low, its contribution to the mass loss due to the consumption of heat stabilizers is thought to be negligible. ESBO, 8.3% mass of the plasticizer in the formulation used herein, has very high molar mass as 950 g/mol and has very low evaporation rate out of PVC; thus the mass loss belonging to ESBO is negligible.[35] The mass loss of PVC powder was determined to distinguish between the decomposition of PVC and evaporation of plasticizer. Even for the strongest heat treatment at 160°C (Figure 2), the mass loss is much below 2.7% although no heat stabilizer is added to neat PVC. Our previous study[34] revealed

**Table I.** Physical, Chemical, and Formulation Related Properties of Plasticizers Used in the Study

Property	DEHP	DINP	DIDP	DOTP	DOM	DOA	DINCH
Molar mass (g/mol)	390.6	420.6	446.7	390.6	340	371	425
Specific gravity (g/cm^3), (25°C)	0.983	0.975	0.968	0.984	0,940	0,925	0.947
Molar volume^a (cm^3/mol)	397.36	431.38	461.47	396.95	361.70	401.08	448.79
Phr minimum^{b,} x	45	48	51	45	39	42	49
Phr ratio = 60/x	1.33	1.25	1.18	1.33	1.54	1.43	1.22
Viscosity, cp, (20°C)	78-82	100-150	130	46	20	13	52
Boiling temperature (°C) at 4 mmHg	384	>400	250-257	400	229-239	417	240-250
Vapour pressure (mm Hg) at 25°C	10^{-8}	10^{-7}	10^{-7}	–	–	−67.8	–
Vapor pressure (mm Hg) at 200°C	1.2	0.5	0.35	0.99	–	10^{-7}	–

^{a}Calculated from molar mass and specific gravity data, ^{b}Calculated as given in Ref. 42.

that some species originating from emulsion polymerization process was imparting thermal stability to the PVC, as well.

In fact, the applied temperatures are lower than the decomposition temperature of PVC and the strong heat stabilizing system in p-PVC formulations prevents PVC decomposition and retards the release of dehydrochlorination products.[9] However, long heat treatment period about 420 min at 160°C in circulating air causes some decomposition most likely due to the consumption
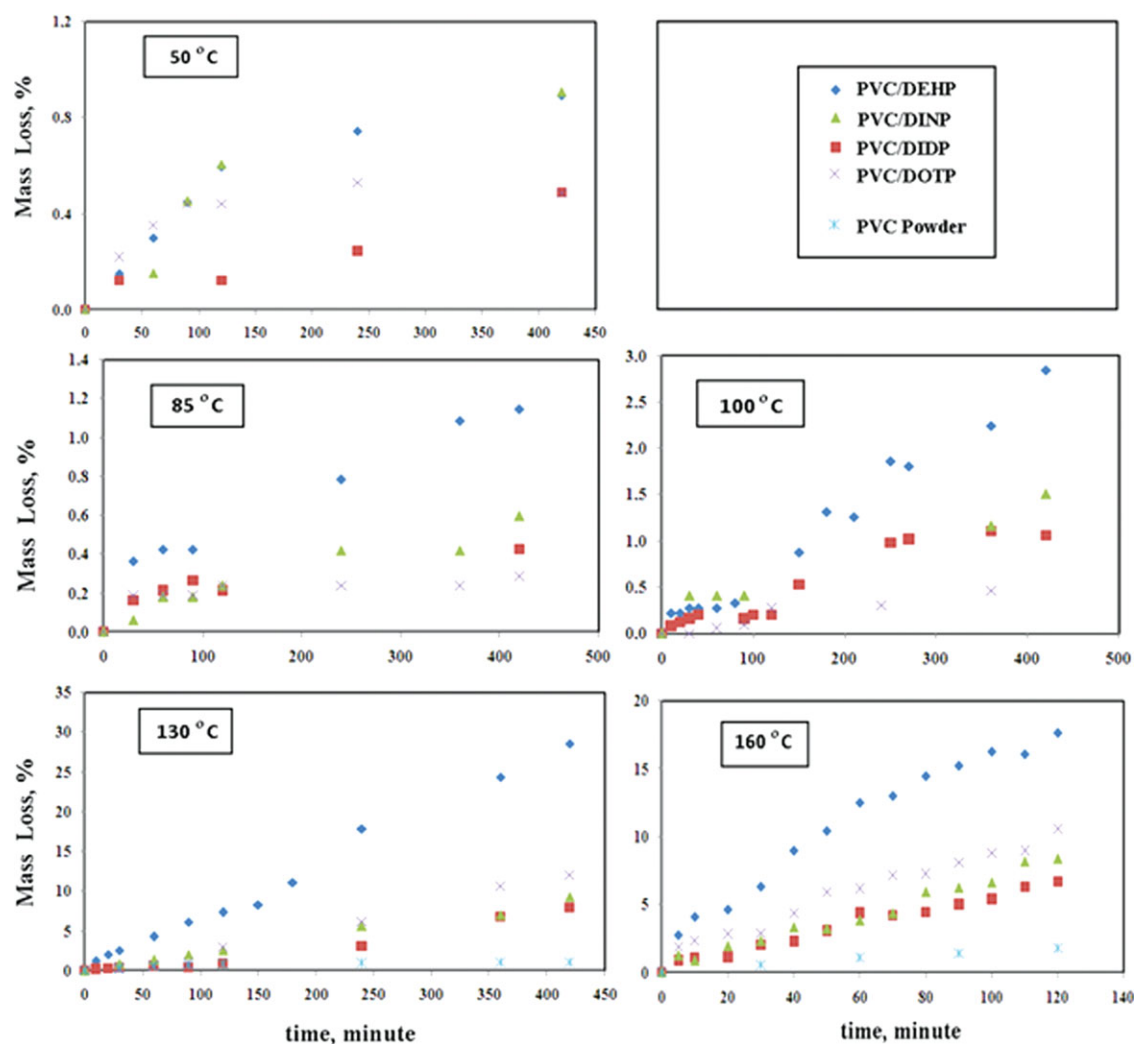
Figure 2. The mass loss (%) from the p-PVC films having the phthalate plasticizers and from neat PVC with respect to time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
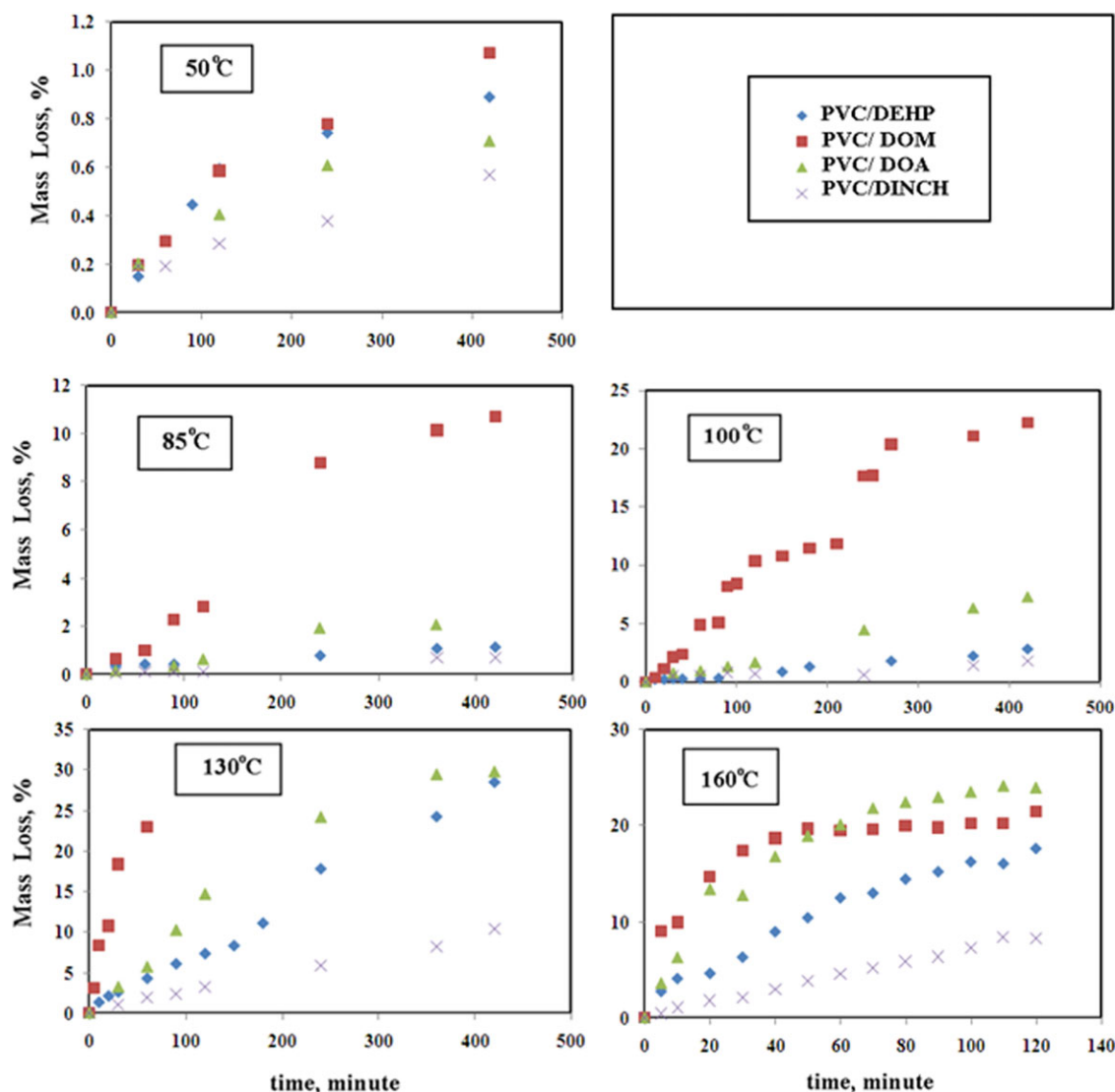
Figure 3. The mass loss (%) from the p-PVC films having DEHP and non-phthalate plasticizers with respect to time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of heat stabilizers. Therefore, the loss belonging to PVC decomposition would be assumed negligible compared to the mass loss occurring due to the plasticizer evaporation, especially the heat treatment periods which are not long. As an overall conclusion, the higher the temperature and the longer the thermal treatment periods, the higher is the mass loss out of the films. As the mass loss behaviors of phthalate plasticizers out of the p-PVC films are compared, DEHP exhibited the highest mass loss in all treatments in general. DINP and DIDP, which have higher molar masses than that of DEHP, lie between two octyl phthalates, namely, DEHP and DOTP as their mass losses are compared. While the mass loss at 420 min is 1.1% at 85°C for the film having DEHP, the mass losses are 0.6, 0.4, 0.3% for the films having DINP, DIDP, DOTP and at 130°C for the films with the same order as 28.6, 9.3, 7.9, 12.0, respectively (Figure 2). The different values for each plasticizer suggest that the loss of the films is extensively independent of loss from PVC. On

the other hand, the mass loss is inversely proportional to the molar mass of plasticizer except for DOTP. While DINP, DIDP, and DEHP are all orthophthalates, DOTP is a terephthalate and despite DOTP and DEHP have the same molar mass, planar spatial arrangement of DOTP most likely makes it more compatible with PVC polymer chain as confirmed with the lower mass loss of the film having DOTP than that of the one having DEHP. The geometric harmony of the plasticizer and PVC chain affects the migration of the plasticizer out of PVC, as well. The order of mass loss was determined in general as the non-phthalate plasticizer having films in comparison with DEHP as DOM > DOA > DEHP > DINCH (Figure 3). While the mass loss at 420 min for the films having DOM, DOA, and DINCH is 10.7, 2.2, 0.7% at 85°C, those rise to 27.6, 29.8, 10.4%, respectively at 130°C. The film having DINCH exhibited lowest molar mass in general, among the non-phthalate plasticizer having p-PVC films.

Diffusion Coefficient of Plasticizer Migrating Out of p-PVC Films into Air

Plasticizer loss from the surface causes surface depletion and sets up a concentration gradient. Further loss can occur only by diffusion of the plasticizer along this gradient, to replenish the surface from the bulk. Diffusion coefficient of the plasticizers can be calculated from the corresponding mass loss data when the other evaporating or decomposing components are negligible.[1,18]

The process of diffusion of additives from the bulk to the surface of polymeric material is described by Fick's law of diffusion.[30] Diffusion of relatively small molecules through rubbery polymers in one dimension is given in eq. (1).

$$\frac{\partial CA}{\partial t} = D \times \frac{\partial^2 CA}{\partial^2 X} \qquad (1)$$

where, D is the diffusion coefficient, C is the concentration of the diffusion substance, A is the migrating species, t is the time, and X is the coordinate perpendicular to the section.[16,38,39] For the diffusion of an additive from bulk film which has two faces open to the ambient, the coordinate perpendicular to the section is taken as half thickness (l) of the film. Crank[40] has shown that if $M_t/M_\infty < 0.5$ at short times, the solution of eq. (1) for the layer geometry (thickness of 2 l) is as given in eq. (2).[39]

$$\frac{M_t}{M_\infty} = \left(\frac{4}{l}\right) \times \left(D\frac{t}{\pi}\right)^{0.5} \qquad (2)$$

where M_t and M_∞ are the masses of diffusing substance from a distance of l at time t, and, at equilibrium of sorption attained theoretically after infinite time, respectively. Hence, diffusion coefficient, D, or more correctly effective diffusion coefficient, D_e, can be calculated from the slope (θ) of initial portion of M_t/M_∞ versus square root of time plots using eq. (3).

$$D_e = \pi \times \left(l\frac{\theta}{4}\right)^2 \qquad (3)$$

The data as the mass loss of the films during the heat treatment (used in Figures 2 and 3) were evaluated to calculate fractional loss (M_t/M_∞) by using eq. (4), where the m_o and m_t are initial mass and the mass at any instant time t, respectively. The m_∞ is the mass at equilibrium, which is considered as the maximum amount of evaporable plasticizer and corresponds in this study to 0.357 g plasticizer/g film, for all samples. This amount can be calculated from the presented data in the article.

$$\frac{M_t}{M_\infty} = \frac{m_o - m_t}{m_o - m_\infty} \qquad (4)$$

Diffusion coefficient of the migrating molecule out of a polymer film was estimated from the slope θ of the linear portion of the graph of fractional loss versus $t^{0.5}$, by using eqs. (2) and (3). The linearity of M_t/M_∞ versus $t^{0.5}$ plots in the region of $M_t/M_\infty < 0.5$ where the model is valid (Figures 4 and 5) revealed a good fit to the Fickian diffusion kinetics which is confirmed by the correlation coefficient for diffusion, R^2_{diff}, as reported in Table II together with the diffusion coefficients, D_{eff}, for the migration of plasticizers out of p-PVC films into air.

The effective diffusion coefficients of plasticizer increased with temperature as expected, and decreased with increasing molar mass of plasticizers for phthalate-type plasticizer except for DOTP (Table II). Some deviations are common for that kind of studies since the very low values are involved, i.e., 10^{-14}–10^{-18} m^2/sec. DEHP exhibited highest diffusivity values among phthalates in all treatments, in general. While the effective diffusion coefficient is 2.7×10^{-17} m^2/sec at 85°C for DEHP, this value has the order of 10^{-18} m^2/sec for the other phthalates. The diffusivity values belonging to the plasticizers in the films subjected to other thermal treatments have the same order of the diffusivity values. The order of effective diffusivity of phthalates out of p-PVC films into air is determined as DEHP > DINP > DIDP > DOTP, in general.

As the diffusion behaviors of non-phthalate plasticizers are considered in comparison with DEHP in the film (Figure 5), the order of diffusivity values of plasticizer was determined in general as of DOM > DOA > DEHP > DINCH. DINCH generally exhibited the lowest diffusivity values, among the non-phthalate plasticizer. Therefore, the diffusivity results are in line with the mass loss data since the films are identical except differences arising from the type of plasticizer. Although there is no study in literature spanning all the plasticizers studied herein in a temperature range, Ekelund et al.[6] reported that the migration of DEHP from p-PVC films to air at 120 and 155°C is controlled by diffusion, while it was controlled by the evaporative boundary conditions where the evaporation rate was initially constant and independent of DEHP concentration at 80 and 100°C.[6] Such a behavior needs to be confirmed with a detailed study for all the plasticizers considered.

Diffusion Behavior and Structure Relationship of the Plasticizers

The performance of a plasticizer in a flexible PVC compound depends upon polarity, molar mass, and structure. While the phthalates are aromatic esters, the adipate and maleate plasticizers are aliphatic and DINCH is an alicyclic ester. Phthalates have an intermediate polarity due to the presence of two polar groups and their aromatic character, which imparts high stability.[10,41] Adipates have a linear aliphatic structure and lower polarity than the phthalates have, which results in a delay in the gelation process. The dicarboxylate-type plasticizer, DINCH, has similar structure and almost equal molar mass to DINP. In fact, DINCH is produced from DINP modifying the aromatic ring of phthalate structure to the cyclic one. The stability is slightly sacrificed as the phthalate structure is eliminated. However, DINCH is superior with the lowest mass loss to the non-phthalate ones which have neither aromatic nor cyclic structure. Another issue might be considered is the molar volume difference about 4% as calculated from molar mass and specific gravity values given in Table I. The larger molar volume of DINCH suggests the higher free volume introduced into the p-PVC, than that is achieved by DINP. As the mass loss at 120°C is calculated as an example, about 18% higher loss was determined for the film having DINCH than the one having DINP. The higher the polarity of the employed plasticizer, the higher is its interaction capacity with the polymer.[41] So, DINCH seems less compatible with PVC than DINP is, as a result of the lower
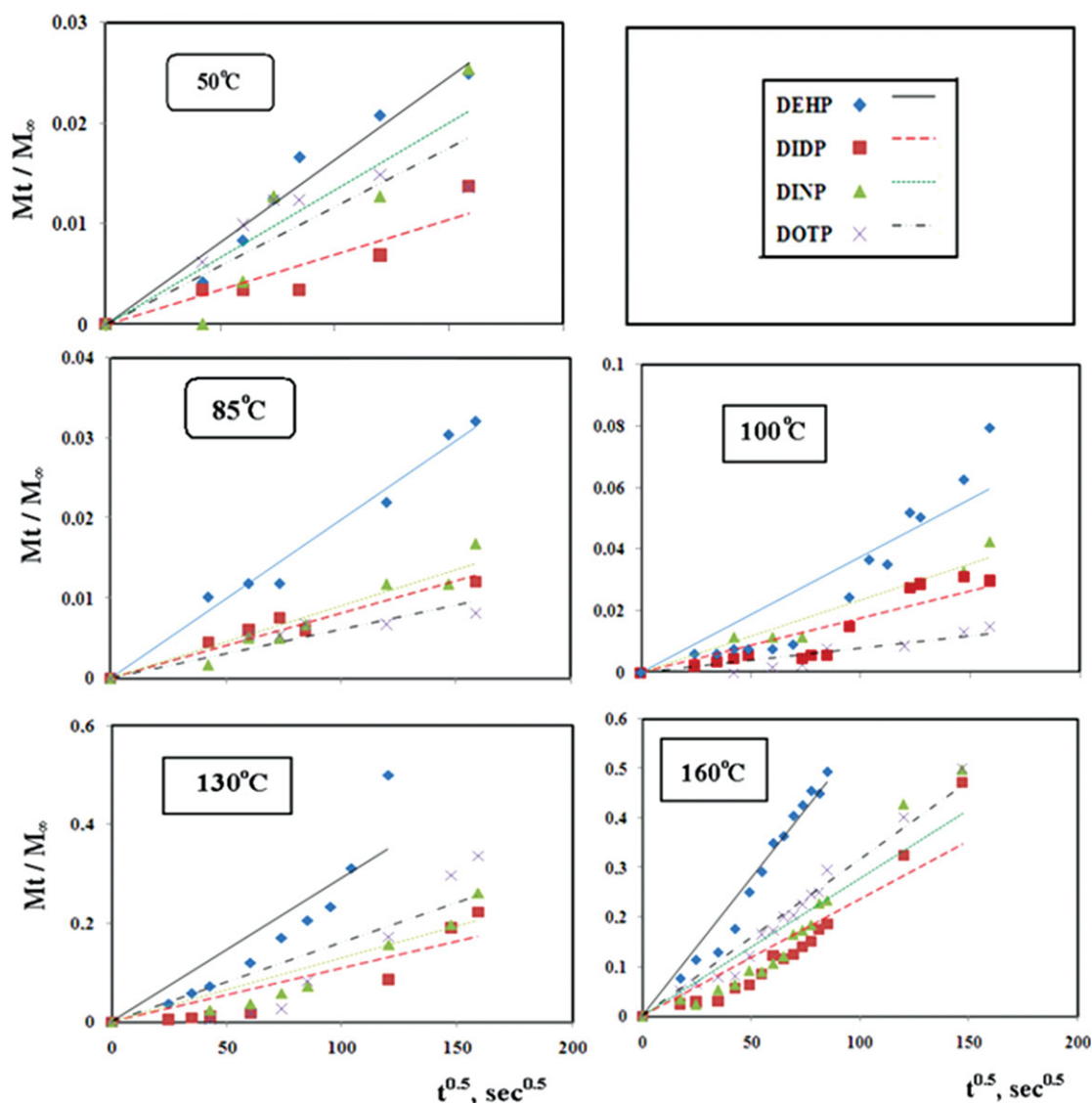
Figure 4. Fractional loss from p-PVC films having phthalate plasticizers at 50–160°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polarity of the alicyclic structure of DINCH than that of the aromatic ring of DINP.[10]

Another issue is the processing condition which influences gelation and therefore, the migration behavior of plasticizer. Different plasticizers may involve different gelation conditions, which may explain quite different values found in literature. In addition, the minimum plasticizer amount as a measure of plasticizer efficiency for the fully plasticization differs with the molar mass of plasticizer.

As the mass percentage of plasticizer per mol is calculated taking 875 g per one helical segment of PVC,[42] 60 phr plasticizer is 1.33 times of the minimum amount for DEHP and 1.18–1.54 times for all plasticizers studied (Table I). In addition to different plasticizer efficiency, molar volume could be of help to explain why molecules of a similar polarity show different gelation behavior. Because branching is somehow related to molar volume, it can also influence the gelation conditions.[41]

Temperature Effect on Diffusion of Plasticizers and Activation Energies

Product lifetime is controlled mainly by the plasticizer migration.[22] The smaller the plasticizer molecule, the easier is its entrance into the PVC matrix; the larger molecules require more energy than the smaller ones required to establish desired interaction with polymer. Since the activation energy is necessary to separate the plasticizers from the polymer chains, activation energy of plasticizers for diffusion is expected to be inversely proportional to the diffusivity values. Diffusion is often observed as a thermally activated process, so that the diffusion coefficient can be expressed in the Arrhenius form in eq. (5).

$$D_e = D_o \times e^{\frac{-E_A}{RT}} \qquad (5)$$

where D_e is the effective diffusion coefficient (m²/sec), D_o is a constant defined as pre-exponential factor which is the
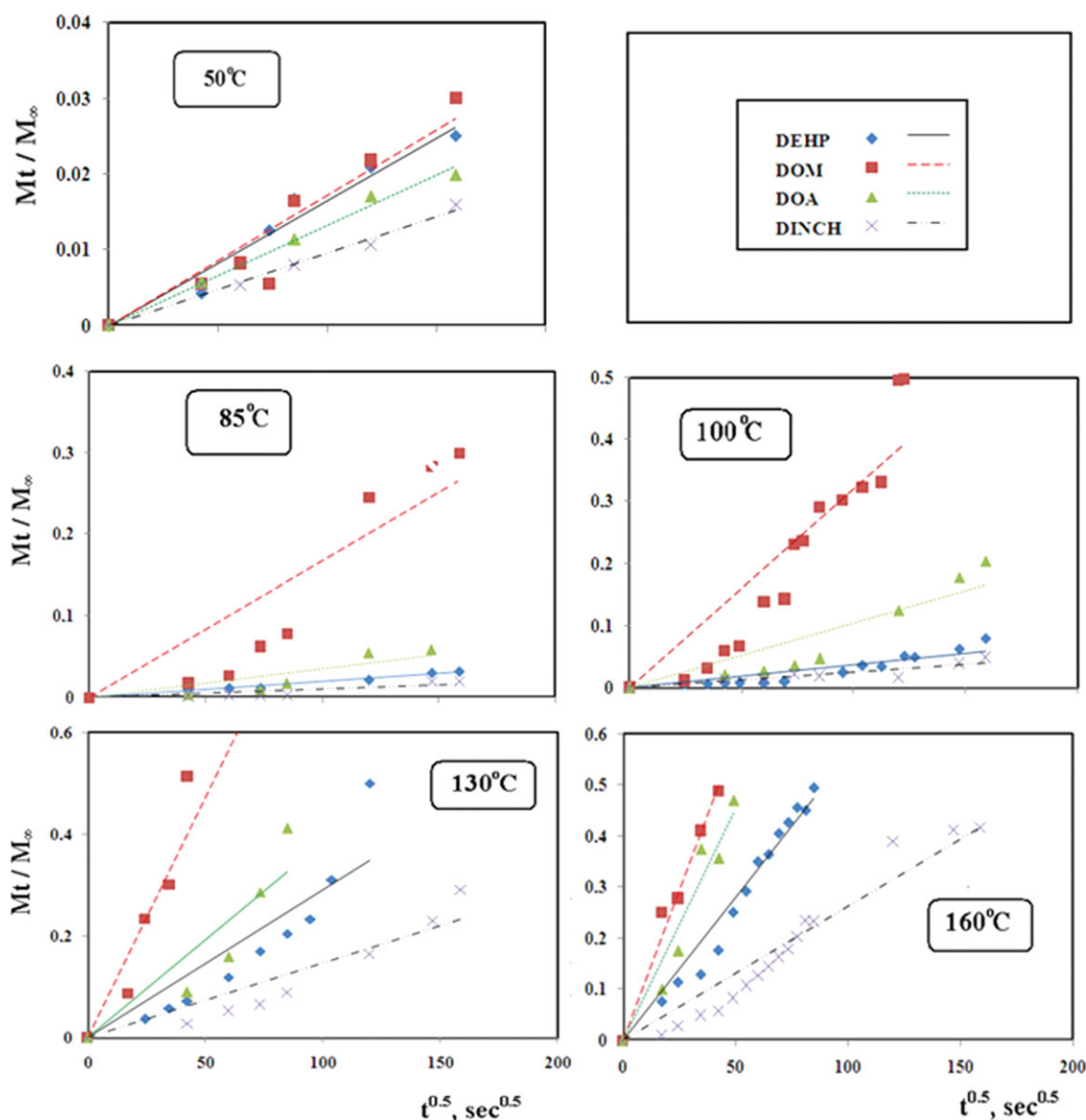
Figure 5. Fractional loss from p-PVC films having DEHP and non-phthalate plasticizers at 50–160°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

theoretically maximum diffusion coefficient at infinitely high temperature, E_A is the activation energy for diffusion, R is the universal gas constant (8.314 J/mol K), and T is the temperature studied. This equation assumes that the diffusion process is controlled by a rate proportional to $\exp(-E_A/RT)$. The exponential part of eq. (5) is given as the ratio of activation energy to kT, as well, where k is the Boltzmann constant, which relates energy at the individual particle level with temperature, and found from the division of universal gas constant by Avogadro number. Therefore, activation energies are found directly as electron volt (eV) values instead of J/mol. An Arrhenius plot may show a change in slope associated with a change in the dominant deterioration process or with a phase transition of the material.[22] Therefore, the activation energy (E_A, J/mol) values and regression coefficients (Table II) were calculated from the slope of Arrhenius plots of the present data as $\ln D_e$ versus reciprocal of Kelvin tem-

perature, $1/T$ as K^{-1} (Figure 6). Since the results of studies at 50°C did not profoundly differ from those at 85°C, they did not plot on these graphs but yet give an idea about the migration behavior. Very low slope value for 50–85°C region would give the exponential value in eq. (5) negligible compared to D_o value. This suggests the migration was controlled by the evaporation with constant rate. The constant slopes with regression coefficients high enough for 85–160°C interval suggest that deterioration process through the dehydrochlorination is not dominant in the p-PVC films.[6,22] In fact, the presence of the plasticizer is thought to suppress the dehydrochlorination to a certain level, and therefore, the degradation process is not prevailing even at 160°C. Different mobility and/or different diffusion rates of plasticizer through the polymer lead to different E_A values.[37]

For the phthalate plasticizers in PVC films, the activation energy is 122.3 kJ/mol (1.27 eV) for DEHP, these values are 120.5,

Table II. Diffusion Coefficients and Arrhenius Equations for the Diffusion of Plasticizers From p-PVC Films into Air

Plasticizer	Temp. (°C)	D_e (m²/sec)	R^2_{diff}	Arrhenius equation [eq. (5)]	R^2_{arrh}
DEHP	50	1.9×10^{-17}	0.96	$D = 19.07 \times e^{\frac{-1.2 \times 10^5}{RT}}$	0.97
	85	2.7×10^{-17}	0.98		
	100	9.9×10^{-17}	0.83		
	130	6.0×10^{-15}	0.82		
	160	2.2×10^{-14}	0.97		
DIDP	50	3.5×10^{-18}	0.85	$D = 2.05 \times e^{\frac{-1.2 \times 10^5}{RT}}$	0.98
	85	4.6×10^{-18}	0.92		
	100	2.2×10^{-17}	0.80		
	130	8.5×10^{-16}	0.82		
	160	4.0×10^{-15}	0.85		
DINP	50	1.3×10^{-17}	0.83	$D = 2.7 \times e^{\frac{-1.2 \times 10^5}{RT}}$	0.98
	85	5.7×10^{-18}	0.92		
	100	3.9×10^{-17}	0.94		
	130	1.2×10^{-15}	0.860		
	160	5.5×10^{-15}	0.87		
DOTP	50	9.7×10^{-18}	0.76	$D = 3.5 \times 10^4 \times e^{\frac{-1.5 \times 10^5}{RT}}$	0.93
	85	2.5×10^{-18}	0.77		
	100	4.4×10^{-18}	0.84		
	130	1.8×10^{-15}	0.75		
	160	7.1×10^{-15}	0.97		
DOM	50	2.1×10^{-17}	0.9	$D = 3.4 \times 10^{-5} \times e^{\frac{-6.9 \times 10^4}{RT}}$	0.94
	85	2.0×10^{-15}	0.82		
	100	7.3×10^{-15}	0.84		
	130	6.3×10^{-14}	0.94		
	160	9.9×10^{-14}	0.98		
DOA	50	1.2×10^{-17}	0.99	$D = 1.7 \times e^{\frac{-1.1 \times 10^5}{RT}}$	0.98
	85	8.5×10^{-17}	0.78		
	100	7.7×10^{-16}	0.83		
	130	1.1×10^{-14}	0.83		
	160	5.8×10^{-14}	0.94		
DINCH	50	6.5×10^{-18}	0.98	$D = 2.1 \times e^{\frac{-1.1 \times 10^5}{RT}}$	0.97
	85	7.9×10^{-18}	0.78		
	100	4.5×10^{-17}	0.82		
	130	1.5×10^{-15}	0.88		
	160	4.9×10^{-15}	0.94		

120.7, and 153 kJ/mol (1.25, 1.25, and 1.58 eV) for DINP, DIDP, and DOTP, respectively. For the non-phthalate plasticizers, these values are 69.4, 110.7, and 114.4 kJ/mol (0.72, 1.15, and 1.18 eV) for DOM, DOA, and DINCH, respectively. At higher temperatures, DOM has the highest migration tendency with lowest activation energy. Kovacic and Mirclic[37] found that the values of activation energies for the phthalate plasticizers in p-PVC lie within the range 70–108 kJ/mol in 120–150°C range by using isothermal thermogravimetry. Another study[22] reports the activation energies at 80–180°C for 36.5 phr DEHP in PVC gives about 93.2 kJ/mol (0.97 eV) by linear interpolation, which is at about the same order found in the present study. The

divergence is possibly due to the differences between the compositions, type of PVC, and different production methods. Activation energy gets higher as the molecule of plasticizer is larger and branching of the molecule is greater.[37] In the present study, exactly equal molecular weight having DOTP exhibits greater activation energy than that of DEHP, which suggests the planar arrangement of terephthalate structure leads to better alignment between polymer molecules than orthophthalate structure of DEHP does, suggesting that the governing effect is the molecular structure of plasticizer.

The D_o values, which theoretically correspond to the diffusivity at infinitely high temperature span a broad interval yet large
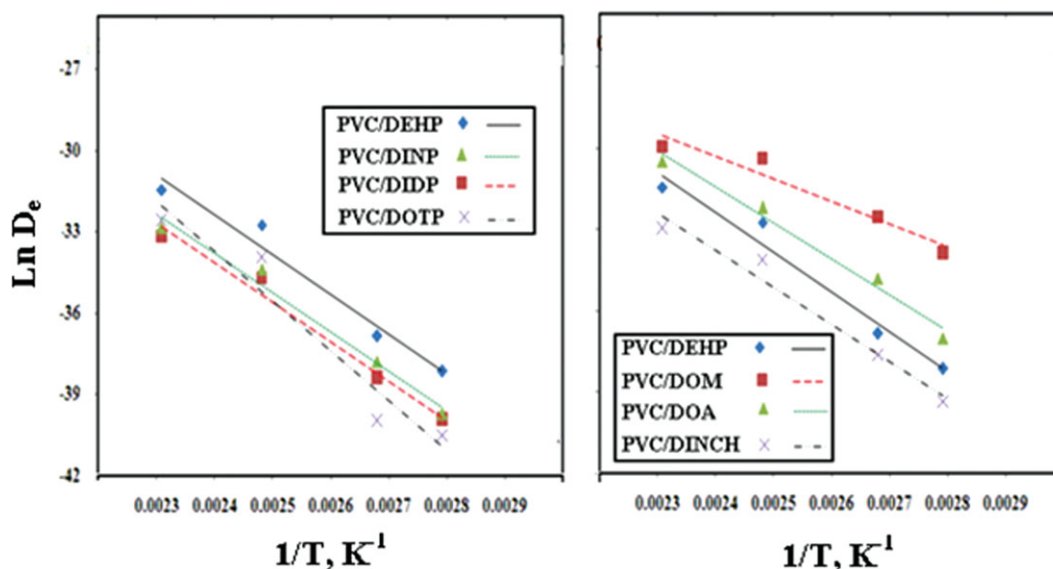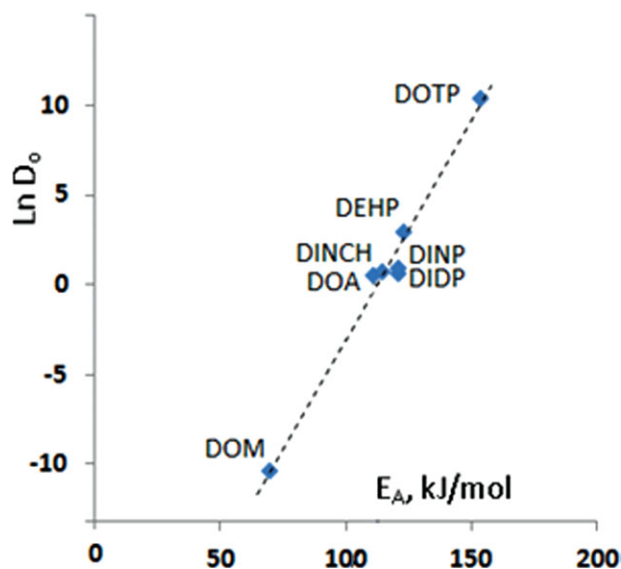
Figure 6. $\ln D_e$ versus $1/T$ (K^{-1}) graphs for migration of several plasticizers out of p-PVC films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

enough to support the case increasing diffusivity with increasing temperature. The D_o values spanning a broad range from 10^{-5} to 10^{+4} in the present study can be attributed to somewhat different structure of the plasticizers taken under investigation. As their molar volumes and molar masses are considered to sort the D_o values, DINP, DINCH, and DIDP have the same order and almost one-tenth of DEHP has. The DOA has the closest diffusivity value to those they have while DOM and DOTP has considerable deviation from the values belonging to the other plasticizers. DINCH and DIDP have very close boiling temperatures (given at 4 mmHg; Table I), as well. However DINP and DOTP have the same boiling temperatures, their D_o values have quite different order. The same molar volume and molar mass having species DOTP and DEHP have quite different D_o values possibly due to their different molecular structure. Therefore, going a step forward, ln D_o values were plotted against E_A in Figure 7. Although DOTP and DOM are at distinct placements, they are on the same line with all the other plasticizers. It was long noticed that although D_o values are quite scattered within a series of species due to different experimental conditions, $\ln D_o$ and E_A pairs are linearly correlated. This correlation is called "compensation law" or "isokinetic effect."[43] For the thermally stimulated experiments, the origin of the compensation phenomenon is attributed to meaningful physical aspects of the system under study, based on molecular interpretations assigned such as cooperative nature of relaxational process as well as to pure experimental propagation errors or to intrinsic mathematical consequences of the physical description of the process.[44]

Kovacic and Mirclic,[37] studied the compensation effect by using rate constants of plasticizer evaporation from PVC. The pre-exponential factor of Arrhenius relations changes parallel with activation energies in homologous/systematic series of species. However, to make clear whether there is any resemblance in their behavior as if a homologous series could have, the compensation concept which is also a measure of the evaporation

ability of plasticizer[37] is considered. Suggesting an analogy with the compensation concept which also compensates the experimental errors and related to activation energy for diffusion,[37] we defined a compensation factor (S_P, kJ/mol) equal to ($-E_a/\ln D_o$). Then, S_P was plotted against intrinsic properties of plasticizer as molar volume, molar mass, and boiling point of plasticizers (Figure 8). Keeping DOA aside, which gave totally different values, S_P values gave regression coefficients as 0.95 and 0.85, as plotted against molar volume and molar mass, respectively. On the other hand, no relation of S_P is found with boiling temperature of the plasticizers. These findings suggest that the DOA exhibits totally different behavior from the others. In

Figure 7. $\ln D_o$ versus E_A graphs for migration of several plasticizers out of p-PVC films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
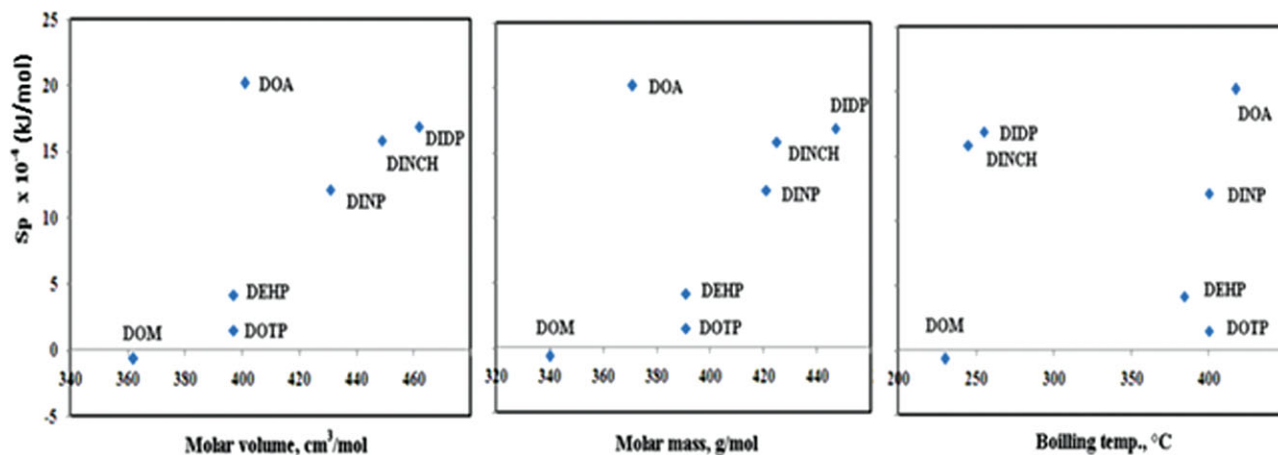
Figure 8. Compensation factor with respect to intrinsic plasticizer properties. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fact, the DEHP (DOP), DOA (DEHA), DOM (DEHM), and DOTP (DEHTP) all have the diethylhexyl (DEH) structures. As the aromatic diesters DEHP (and DOTP), DINP, and DIDP are considered, they belong to a homologous series with 8, 9, and 10 carbons 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.

### FTIR Analysis of p-PVC Films Before and After Heat Treatment

The migration of plasticizer is followed by FTIR spectrum over the band in 1803–1655 cm^{-1} attributed to carbonyl (C=O) group of the plasticizer which is not present in PVC.[45] Figures 9 and 10 depict the FTIR spectra of the films before and after heat treatment at 160°C for 420 min. The 1570 and 1530 cm^{-1} bands are observed on the spectrum of stabilizer mixture as well, and

they are attributed to zinc and calcium stabilizers.[45] The intensity decrease of these bands upon heat treatment reveals that the stabilizers are consumed, and similar behavior was observed in all films since the amount of stabilizer was fixed. The peak at around 1720 cm^{-1} is attributed to the C=O vibrations belonging to an ester plasticizer. The 3400 cm^{-1} peak belongs to —OH stretching vibration due to the formation of hydroperoxides under thermal treatment by the air oxygen.[46] The bands at around 1720 cm^{-1} is attributed to the C=O vibrations belonging to an ester plasticizer.[46] The decrement of 1720 cm^{-1} peak height suggests the plasticizer migration. The 3400 cm^{-1} peak belongs to —OH stretching vibration due to the formation of hydroperoxides under thermal treatment by the air oxygen.[45]

The peak height (in fact, since the y axis is transmittance rather than absorbance; they recognized as well depth) increment at
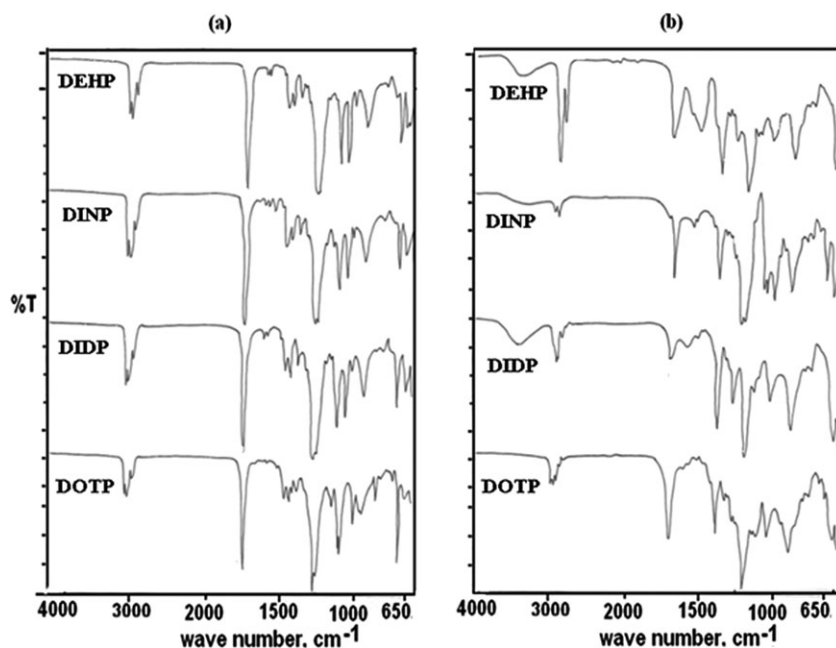

Figure 9. FTIR spectra of p-PVC films having phthalate plasticizers (a) before and (b) after thermal treatment period of 420 min at 160°C.
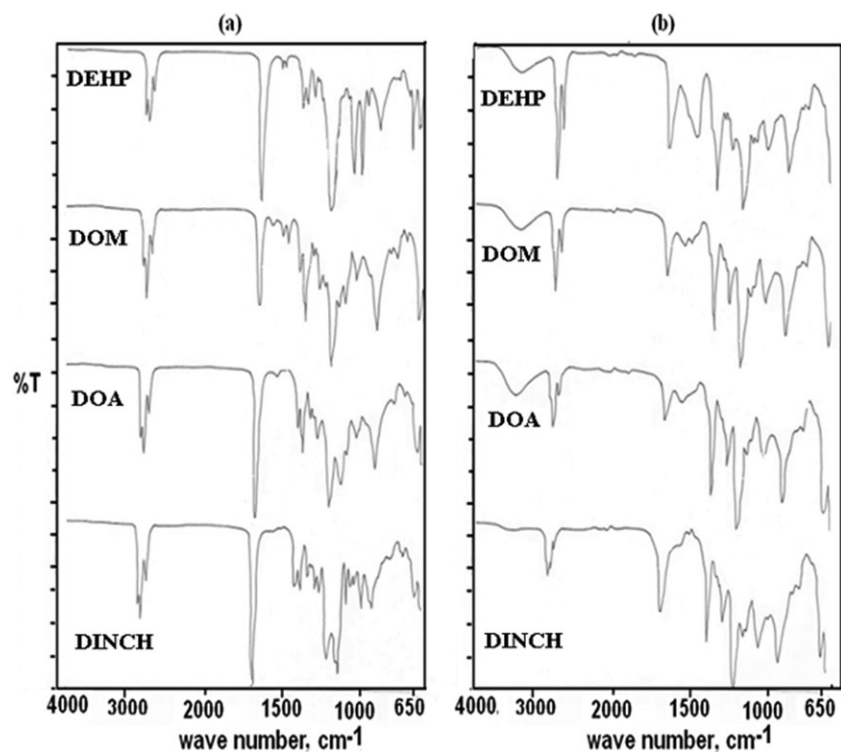
Figure 10. FTIR spectra of p-PVC films having DEHP and non-phthalate plasticizers (a) before and (b) after thermal treatment period of 420 min at 160°C.

3400 cm^{-1} on IR spectra of p-PVC films having DOP, DINP, and DIDP showed almost the same trend. Those belonging to the films having DOA and DOM exhibited higher peak heights than the films having phthalate group having ones did. However, those belonging to the films having DOTP and DINCH showed almost no peak evolution with the heat treatment. Therefore, hydroperoxide formation after heat treatment was deduced to be negligible for the films plasticized with DOTP and DINCH.
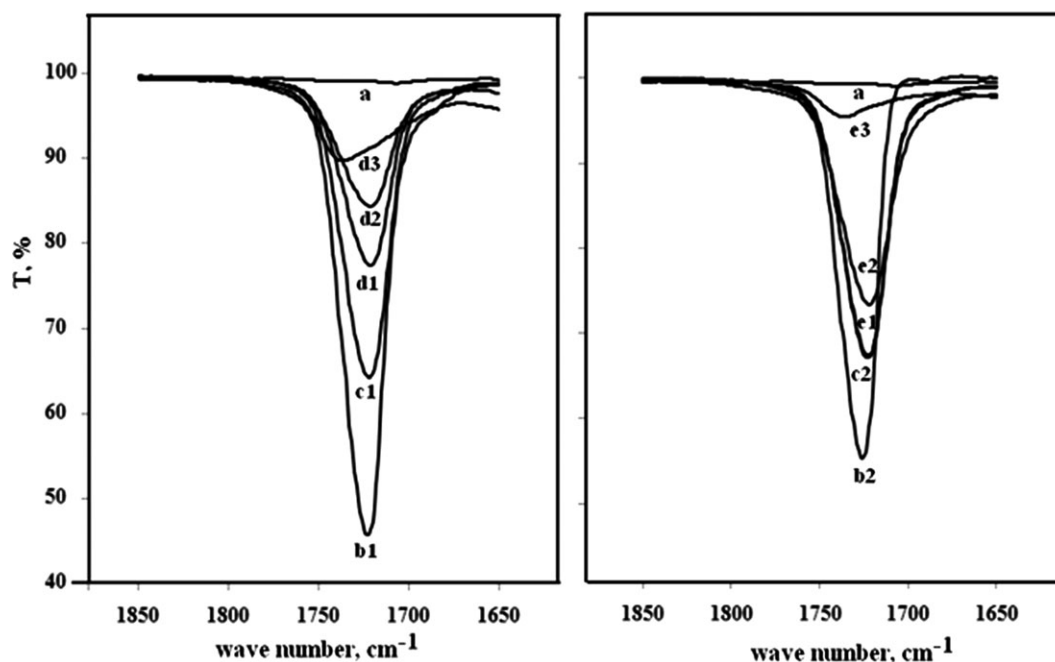
Figure 11. FTIR spectra of the raw materials as (a) PVC; (b1) DEHP; (b2) DIDP and of the films as (c1) fresh PVC/DEHP, (c2) fresh PVC/DIDP (d, e) 420-min aged films as PVC/DEHP and PVC/DIDP, respectively, at (1) 100°C, (2) 130°C, and (3) 160°C.

The peak height change at 1720 cm^{-1} due to the migration of plasticizer from p-PVC is observed with the order of the films having DIDP > DOP > DINP > DOTP and DOA > DOM > DOP > DINCH. While the order of effective diffusivity of phthalates out of p-PVC films into air was DEHP > DINP > DIDP > DOTP, the changing rank surprised us. PVC/DIDP film is expected to have lower migration than PVC/DEHP did in contrast to the results found herein. In addition, DIDP molecular characteristics make this plasticizer the choice for wire and cable applications that require less plasticizer loss. Therefore, these two plasticizers were taken for further investigation. Figure 11 shows the IR band around 1720 cm^{-1} belonging to p-PVC films having DEHP and DIDP films, the films after 420 min heat treatment at 100, 130, and 160°C in addition to the band belonging to neat PVC, DEHP, and DIDP. As seen in Figure 11(a), PVC has no peak at about 1720–1740 cm^{-1} region; however, DEHP and DIDP do. Both DEHP and DIDP evaporation increase regularly as the aging temperature increases.

At 100 and 130°C DIDP evaporates less than DEHP do, however, it reveals a different behavior at 160°C shifting the band to higher wavenumbers pointing another issue needs further investigation. With the help of the present data in hand, it can be concluded as it is due to two competing processes having opposite directions which becomes comparable at such a high temperature: Migration of plasticizer and formation of carbonyl are the competing processes, while the plasticizer loss is observed as decrement, carbonyl formation is observed as the increment of the same peak.

Clearly, if the aging at and below 130°C would be compared, which are quite suffice for PVC in cable jacket application having thermal rating as 60–90°C (IEEE), migration of DEHP would be found higher than DIDP did. In fact, for life time prediction experiments, 110°C was an appropriate aging temperature.[33] Summing up, the FTIR investigations reveal that DOTP and DINCH are the low migration plasticizers among the plasticizers studied.

The p-PVC films with other plasticizers were checked for the same phenomena, as well. Those FTIR investigations having many details are planned to submit in another paper. However, the order of migration, which is the questionable in the present work, did not show a change with temperature.

CONCLUSION

The physical structure and the quality of a flexible PVC product change in its service life, mainly due to the plasticizer migration. Choice of less migrating plasticizers gains importance in many applications of flexible PVC. The plasticizer migration out of PVC films results in deterioration and may be harmful for the environment and human health through contamination. Although the relatively low temperatures (>50°C) are involved in many applications, aging experiments are useful to predict the product lifespan.

The present study provides some information about the mass loss, diffusivity, activation energy, compensation issue, and FTIR findings revealing the migration behavior of a group of plasticizers out of p-PVC films. When the same plasticizers fam-

ily is studied, it can be roughly stated that an increment in the molar mass of the plasticizer tends to decrease the migration level of plasticizer. Despite DOTP and DEHP having the same molar mass, DOTP is more compatible to PVC polymer chain due to its physical structure to be more linear. Because of this, DOTP exhibits lower migration and involves higher activation energy than that of DEHP. The diffusion coefficients were found to be around 3.5×10^{-18}–2.1×10^{-17} m^2/sec for the studied plasticizers in PVC at 50°C and around 4.0×10^{-15}–9.9×10^{-14} m^2/sec at 160°C. The activation energies for 85–160°C interval were determined as 70–153 kJ/mol (0.72–1.58 eV). The compensation factors, S_p, gave good correlation with both molar volume and molar mass except p-PVC film having DOA suggesting that the plasticizers taken under investigation herein have somewhat similar structures. Finally, it is expected that adjusting the formulation considering the minimum plasticizing level for the plasticizer involved, and processing/gelation conditions for the chosen plasticizer will result in better performance properties.

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