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Research Article

## Kinetic evaluation of the stabilization efficiency of the phosphite and urea derivative based stabilizers against epoxy based stabilizers on the thermal degradation of plasticized poly (vinyl chloride)

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### Abstract

Poly(vinyl chloride) (PVC) is difficult to process because of its low thermal stability. Therefore, stabilizers are used. Epoxidized vegetable oils are environmentally friendly stabilizers, but they degrade at high temperatures, causing the polymer to become brittle and discolored. Also, unreacted double bonds in it can reduce the compatibility between plasticizer and PVC, causing greater migration of plasticizer from PVC. This study focuses on the evaluation of the effect of phosphite and urea derivative stabilizers against epoxy stabilizers on the thermal degradation of PVC and plasticizer diffusion from PVC. Plastisols were prepared by mixing plasticizers (di-octyl terephthalate and di-2-ethyl-hexyl phthalate), primary, and secondary stabilizers (epoxidized soybean oil (EPSO), epoxidized linseed oil (ELO), tri-phenyl phosphite (TPP) and diphenyl urea (DPU)) into PVC. Plastigels were cured and thermally aged. Thermal degradation in terms of color changes, oxidation index, and polyene concentration was investigated by using colorimetry, Fourier Transform Infrared Spectroscopy (FTIR) and Ultraviolet (UV)-visible spectroscopy, respectively. As a result, phosphite and urea derivative stabilizers provided better long-term stability than the EPSO. However, EPSO was more affected by the plasticizer migration than the others. An effort has been made in this study to shed light on the improvement of the thermal stability of PVC by means of non-toxic secondary stabilizers.

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## 1. Introduction

Poly(vinyl chloride) (PVC) is amongst the most widely used polymers worldwide since it is unique properties and low cost [1, 2]. However, PVC is difficult to process due to the high melt viscosity and rigid chain structure caused by polar chlorine atoms. As a result, the processing temperature increases and its thermal stability decreases [3-5]. Before its processing temperature reached, it will release hydrogen chloride (HCl) gas resulting in a performance decline [6]. The decomposition product, HCl, accelerates the degradation and plays a role in the autocatalytic process [7]. Degraded PVC is characterized by intense discoloration caused by the formation of conjugated double bonds (polyenes). When PVC has 4, 6, 8, and 11 polyenes in its chain, its color appears light yellow, yellow, orange, and red, respectively [8-10]. This problem can be solved by the use of plasticizers and thermal stabilizers [5, 11]. Stabilizers provide thermal stability by the absorption and neutralization of HCl gas, and thus prevents or delays the degradation process [7]. Conventional primary stabilizers such as calcium/zinc (Ca/Zn) stabilizers are widely used for thermal stabilization. However, it causes some problems in the long-term stability of PVC due to zinc chloride ( $ZnCl_2$ ) formed during the process and can catalyze the

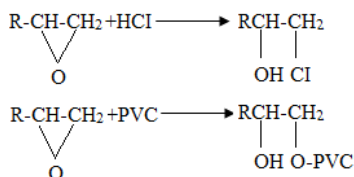
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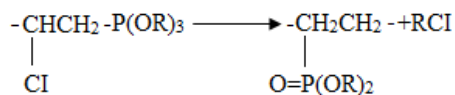
degradation of PVC. This causes a sudden zipper dehydrochlorination [6, 12]. When primary stabilizers and secondary stabilizers are used together, their stabilizing effects increase [6]. Ca/Zn stabilizers are supported by epoxidized vegetable oils as secondary stabilizers or by co-stabilizers because of their non-toxic structures [11, 13, 14]. Epoxidized vegetable oil based from renewable bio-resources, which are epoxidized triglyceride oils from rubber seed oil, sunflower oil, soybean oil, linseed oil, epoxidized cardanol, epoxidized triglyceride oils and oleic acid polyester with their low toxicity, they attract attention as PVC stabilizers or plasticizers [4, 5, 15]. The researches on epoxidized vegetable oils and their synergism with metal carboxylates for stabilization have been reported [3-5, 11, 16-19]. Ferrer et al. al., (2010) showed that PVC-based formulations containing different amounts of EPSO improved compatibility and thermal stability. They stated that the thermal stability of materials depends on the plasticizer concentration [11]. Karmalm et al., (2009) tested the effectiveness of EPSO as the primary plasticizer for PVC. They compared the stabilization of materials with different conventional stabilizers. They reported that the addition of traditional stabilizers for instance Ca/Zn-stearate, reduced the stability of PVC-EPSO [17]. Benaniba et al., (2003), studied PVC stabilization of epoxidized sunflower oil (ESO) with Ca/Zn stearate. They calculated the induction and dehydrochloride initial rates of dehydrochlorination before depletion of the stabilizers. The addition of this stabilizers increased the induction time and decreased the dehydrochlorination rate. The effectiveness of ESO found to depend on the amount of epoxy groups in the molecule and the high epoxy groups increased efficiency [18]. Scheme 1 represented the reaction with PVC in the presence of metal salts of epoxy thermal stabilizers [20]. Epoxy groups act as HCl scavengers and getting excellent thermal stability to PVC [5]. EPSO stabilization involves a reaction between the epoxide ring of EPSO and HCl. Then labile chlorine atoms return into the polymer chains. This reaction prevents further dehydrochlorination at high temperatures [17].



Scheme 1. Schematic representation of the reaction between epoxy thermal stabilizer with PVC in the presence of metal salts

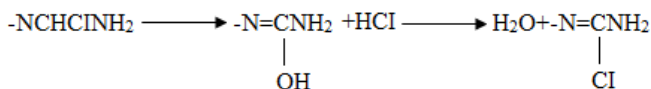
Such functional copolymers provide a strong auxiliary effect to the Ca/Zn-stabilizer system on the stabilization of PVC. This effect increasing with increasing hydroxy or epoxy group content. [13] but also problematic due to the tendency to degrade, causing the polymer to become brittle and discolored during heat aging. Also, many of vegetable oils are include of oleic, linoleic and linolenic acids containing conjugated double bonds. These oils are triglyceride mixtures formed by different unsaturated fatty acids [21]. The benefit of phosphite stabilizers is to prevent the chemical compounds resulting from chlorine disintegration, from causing color distortion and turbidity in the polymer. However, when organic phosphites used alone, they can cause metal chloride formation. Therefore, they used with metal heat stabilizers to prevent this. The most known organic phosphites are; triphenylphosphite and tris (nonylphenyl) phosphate [22]. Organic phosphites, reacts with hydroperoxides generated from the thermooxidative degradation of the polymer. The phosphite stabilizers can also act as metal-complexing agents. Therefore, phosphites classify as secondary antioxidants in these applications [23]. The effect of thermal stability

of organic phosphites showed in Scheme 2 [24]. Some phosphites increase the efficiency of other thermal stabilizers with anti-rust effect.



Scheme 2. Schematic representation of the thermal stability of organic phosphites

Urea derivatives have proven to be effective stabilizers for PVC when used with primary thermal stabilizers for PVC stabilization [25]. Phenyl urea and phenyl urea derivatives have a variety of functional groups that can interact with the evolved HCl gas released from degraded PVC. Due to their ability to form stable complexes with various metal ions, they react with metal chloride by-products formed during the thermal degradation of PVC stabilized with metallic stabilizers [19]. Urea derivatives act according to the mechanism in Scheme 3.



Scheme 3. Schematic representation of the thermal stability of  $\alpha$ -phenylindole and urea derivatives

The presence of chlorine in PVC resin increases the interchain attraction that makes PVC rigid and stiff [26]. Plasticizers are added to resin to lowering glass transition temperature ( $T_g$ ) and break up chain-chain interactions, leading to flexibility [4, 5, 26-28]. Low molecular weight monomeric plasticizers derived from phthalic acids are the most widely used plasticizers [26, 28]. Because of the high migration to contact media, some plasticizers, in particular phthalates, especially diethylhexyl phthalate (DEHP), (dioctyl phthalate, DOP), which are commonly used in PVC formulations has been questioned due to their potential toxicity risk to human health and the environment, food contaminations as well as deformation of material due to losing its flexibility [3, 4, 11, 14, 27, 28]. Therefore, many of the phthalate esters were restricted in the world are listed in the Substances of Very High Concern (SVCH) by European Chemicals Agency (ECHA). Therefore, there is a need for greener and safer alternatives [4, 5, 26, 29] or plasticizer migration must be controlled [28]. However, their plasticisation performance are similar, dioctyl terephthalate (DOTP) is less volatile than DEHP [5, 29]. DOTP are used for main fields of applications as coatings, floorings, electric connectors etc. As far as currently known, DOTP has no carcinogenic, or developmental effects [29]. As a result, PVC, is difficult to process, due to its low thermal stability. This problem is solved the use of stabilizers. Epoxidized vegetable oils are environmentally friendly but, it is problematic as it degrades at high temperatures, causing the polymer to become brittle and discolored upon thermal aging. Also, unreacted double bonds in it can reduce the compatibility between PVC and plasticizer, causing greater migration of the plasticizer from the PVC matrix to the environment. This study focuses on the evaluation of the effects of the phosphite and urea derivative stabilizers against epoxy stabilizers on the thermal degradation of plasticized-PVC (p-PVC) films and plasticizer diffusion from films. EPSO, ELSO, TPP and DPU were used as secondary stabilizers for p-PVC formulations and their thermal stabilization behaviour were investigated. The p-PVC films were prepared with DOTP and DEHP as plasticizers and their plasticizer diffusion efficiencies were investigated also. EPSO and DEHP were used for comparison at the same conditions in the

study. Thermal aging studies were carried out in an oven at 100 and 150°C up to 420 minute. This study focused on the decomposition of the films and plasticizer migration out of the films into air. Oxidation index were determined by FTIR spectroscopy. Stabilization behaviour as color changes and dehydrochlorination were investigated by colorimetry, and, UV-visible spectroscopy respectively. Diffusion coefficients of plasticizers were calculated from mass loss of the films. Conjugated double bonds (CDB) were determined by UV spectroscopy and degradation kinetics of the films were evaluated. The novelty of this study is the comparison study of the effect of phosphite and urea derivative stabilizers against epoxy stabilizers on the thermal degradation of PVC and their effect of migration of plasticizers to air from plasticized PVC composite films for use in flexible PVC cable sheath applications.

## 2. Materials and Methods

### 2.1. Materials

Emulsion-type PVC was purchased from Petkim Co., Aliğa, Izmir, Turkey. Dioctyl terephthalate (DOTP), dioctyl phthalate (DOP) ((di-2-ethyl hexyl phthalate (DEHP)), CaSt<sub>2</sub>, ZnSt<sub>2</sub>, epoxidized soy bean oil (EPSO), epoxidized linseed oil (ELSO), tri phenyl phosphite (TPP), diphenyl urea (DPU) were supplied by Sigma Aldrich, Germany. The additives and their molecular formulas are given in Table 1.

### 2.2. Methods

The experimental method mainly involves the preparation of p-PVC films by gelation of prepared plastisols, their thermal degradation under controlled conditions and the assessment of degradation and degradation kinetics by means of instrumental methods as well as the plasticizers migration and diffusion kinetics through mass loss measurements.

#### 2.2.1 Plastisol Preparation

Plastisols were produced by mixing 60 parts of plasticizer (DOTP and DEHP), 5 parts of secondary thermal stabilizers (EPSO, ELSO, TPP and DPU), and 3 parts of Ca-Zn St<sub>2</sub> mixture as primary stabilizers with 100 parts of PVC, on the mass basis. Formulations of the films and their codes are given in Table 2. Samples containing EPSO and DEHP (EP-DE) were used for comparison.

#### 2.2.2 Plastigel Preparation

P-PVC films which have 150µm thickness were drawn from plastisol and cured under the same conditions, as in our previous study [29].

#### 2.2.3 Thermal Degradation Studies

P-PVC films were cut into about 4x4cm<sup>2</sup> pieces and were heat treated at 100 and 150°C in an oven up to 420 minutes.

### 2.3. Analysis Methods

#### 2.3.1 Spectroscopic Analysis

Oxidation index values were analyzed using Perkin Elmer (Spectra 100) FTIR spectrometer.

Light absorbances of the films were determined by using a Perkin Elmer (Spectra 100) UV spectrophotometer.

Raman spectra of thermally degraded p-PVC films were recorded using a WITech alpha 300R Raman Microspectrometer. Diffraction grating was used in conjunction with air-

cooled DPSS laser source excitation up to 100mW at 532nm. The Raman spectra were acquired from 500 cm<sup>-1</sup> to 3500 cm<sup>-1</sup>. Raman analyzes were made by Atatürk University East Anatolia High Technology Application and Research Center, DAYTAM, Erzurum, Turkey. It has OECD ILU (GLP) conformity certificate.

Table 1. Additives used in the study

Material	Chemical Formula	Molecular Weight, g/mol	Molecular Formula
Polivinyll chloride, PVC, PETKIM Emulsion type	$-(C_2H_3Cl)_n-$	97300-110643	
Diocetyl terephthalate, DOTP	$C_{24}H_{38}O_4$	391	
Diethylhexyl phthalate, DEHP	$C_{24}H_{38}O_4$	390	
Calcium stearate, CaSt <sub>2</sub>	$C_{36}H_{70}O_4Ca$	607	
Zinc stearate, ZnSt <sub>2</sub>	$C_{36}H_{70}O_4Zn$	632.3	
Epoxidized soybean oil, EPSO (Epoxy value % 6.8-7.1)	$C_{57}H_{98}O_{12}$	975.5	
Epoxidized linseed oil, ELSO			
Triphenyl phosphite, TPP	$C_{18}H_{15}O_3P$	310.3	
Diphenyl ürea, DPU	$C_{13}H_{12}N_2O$	212.3	

### 2.3.2 Colorimetric Analysis

Yellowness index of the films were measured by placing the tip of the measuring head of B&W Tek Glacier X Model Color Spectrophotometer.

Table 2. Sample codes with respect to the variables as secondary thermal stabilizers and plasticisers in formulations of p-PVC plastisols

Secondary thermal stabilizer	Plasticizer/ Film codes	
	DOTP	DEHP
Epoxidized soybean oil, EPSO	EP -DO	EP-DE
Epoxidized linseed oil, ELSO	EL -DO	EL-DE
Triphenyl phosphite, TPP	TP-DO	TP-DE
Diphenyl urea, DPU	DP-DO	DP-DE

### 3. Theoretical

#### 3.1. Determination of Oxidation

The oxygen diffused into the polymer during decomposition reacts with the free radicals inside, causing further oxidation. As a result, the oxidized surface layer becomes thicker. This thickening is also assessed via the oxidation index ( $OI$ ), which is determined using infrared spectroscopy.

$OI$  values were calculated by using Eq (1) considering the absorbance of carbonyl band ( $C=O$ ) around  $1720\text{ cm}^{-1}$  and the absorbance of a reference group of  $-CH_2-$  at  $1363\text{ cm}^{-1}$ ,  $1420\text{ cm}^{-1}$  or  $2920\text{ cm}^{-1}$  band [9].

$$OI = \frac{A_{C=O}}{A_{ref}} = \frac{A_{[1722\text{ cm}^{-1}]}}{A_{[2920\text{ cm}^{-1}]}} \times 100 \quad (1)$$

#### 3.2. Following of Polyene Formation by Spectroscopic Method

Thermal stabilization behaviour in terms of concentration of polyenes formed due to the released HCl during thermal treatment were determined by spectroscopic technique. Concentration of polyenes were calculated using light absorbance by UV-visible spectroscopy [30]. There is a wide absorption peak at 200-350 nm for PVC in the UV spectrum. Dehydrochlorination rate can be determine using molar absorption coefficients from the concentration of conjugated dienes in the range of 268–447 nm in the UV spectrum [9]. Polyenes absorb light of a certain wavelength ( $\lambda$ ) with a certain molar absorption coefficient ( $\xi_\lambda$ ).

The number of double bonds of the different lengths of polyenes were given in literature [31]. The concentrations of polyene sequences,  $C_n$  (mol/L), calculated by using Eq (2).

$$C_n = A / (\xi_\lambda \times b) \quad (2)$$

Where;  $A$  is the absorbance,  $b$  (cm) is the thickness of the films,  $\xi_\lambda$  (L/mol cm) is the molar absorption coefficient.

#### 3.3. Kinetic Evaluation of the Dehydrochlorination

The distribution values of  $n$  number of polyene sequences after dehydrochlorination is determined from its absorption spectra. The mol fraction of polyene sequences containing  $n$  conjugated double bonds are determined as Eq (3);

$$N_n = \frac{C_n}{C} \quad (3)$$

Where  $C$  is the concentration of vinyl chloride repeat units in films.  $N_{ps}$  is the mol fractions of polyene sequences and  $N_{db}$  (ND) is the mol fractions of the polyenes, are given by Eq (4) and Eq (5), respectively;

$$N_{ps} = \sum N_n \quad (4)$$

$$N_{db} = \sum n N_n \quad (5)$$

This is a first order reaction [32], Eq (6) was obtained;

$$-\ln(1 - N_{db}) = k_1 \times t \quad (6)$$

Where  $k_1$  is the reaction rate constant,  $t$  is time, and  $N_{db}$  is the mol fraction of polyenes. Plotting  $-\ln(1 - N_{db})$  versus time lines the rate constants can be determine [9].

### 3.4. Determination of Polyene Number Using Raman Spectroscopy

For excitation wavelengths from 425 nm to 625 nm to estimate the excitation wavelength for which the optimum resonance effect occurs derived an equation Eq (7) [33] as below.

$$\lambda = 700 - 537.7 \times \exp(-0.0768 \times n) \quad (7)$$

where,  $\lambda$  is excitation wavelength (nm) and  $n$  is the number of conjugated double bonds.

The other equation is related the wavenumber ( $\text{cm}^{-1}$ ) of the C=C stretching vibration between  $n$  (Eq (8)) [34].

$$\nu_{1521} = 1461 + 151.2 \times \exp(-0.07808 \times n) \quad (8)$$

### 3.5. Determination of Yellowness Index by Colorimetric Method

Color changes observed according to the numbers of polyenes formed from polymer degradation were determined by using tristimulus values of color. When PVC degrades as a result of thermal treatment, yellowing occurs. The coloration caused by the formation of polyenes is determined by the spectroscopy technique. The yellowness index ( $YI$ ) is a measure of color change compared to a white standard. PVC color is calculated with  $L^*a^*b^*$  color coordinates (tristimulus values) (Eq (9)) [35].

$$YI = (0.72a + 1.79b) \times [100/L] \quad (9)$$

### 3.6. Determination of the Plasticizer Migration

Aging of p-PVC involves dehydrochlorination, oxidation and loss of plasticizers by migration processes. When analyzing the migration of the plasticizer, it is necessary to analyze the diffusion through the polymer matrix to the surface of the material and the transporting from the surface to the surrounding environment [29]. For analyzing the rate of migration, diffusion coefficient would be desirable by Fick's law. Diffusion coefficient of the plasticizers calculates from the corresponding mass loss data when the other evaporating or decomposing components are negligible [29]. Eq (10) is able to explain the migration of plasticizer from p-PVC films [36].



$$\frac{M_t}{M_\infty} = (4/l) \times (D t/\pi)^{0.5} \tag{10}$$

Where  $M_t$  and  $M_\infty$  are the measured mass of plasticizer diffused at time  $t$  and after time infinite, respectively,  $D$  is the diffusivity and  $l$  is the film thickness.

#### 4. Results

The stabilizing efficiency of secondary stabilizers, the formation of polyene sequences, the yellowness index, and structural changes were evaluated. The degradation kinetics of the films were evaluated.

##### 4.1. Evaluation of the Structural Changes and Oxidation

During the decomposition, oxygen diffuses into the polymer, and the polymer is oxidized by the formation of free radicals. The oxidation is observed through the increase in OI values by the FTIR spectroscopy technique. Fig. 1 depicts the FT-IR spectrum of the films during heat treatment at 150°C for 420 minutes between 1800-1400  $\text{cm}^{-1}$  wave numbers. The intensity of the 1570 and 1530  $\text{cm}^{-1}$  bands belonging to the thermal stabilizers generally decreased after heat treatment due to their consumption. The bands at around 1720  $\text{cm}^{-1}$  belong to the carbonyl C=O vibrations of an ester plasticizer [29], and the decreasing peak height suggests the migration of the plasticizer by heat treatment in all films. However, in the films containing epoxy soybean oil (EP-DO and EP-DE) the peak height was reduced less than in the other films. When the effect of different thermal stabilizers on the migration of plasticizers is examined for DOTP and DEHP-containing films, the order of decrement of the ester peak during heat treatment is as follows: DP-DO = EL-DO = TP-DO > EP-DO and DP-DE = TP-DE = EL-DE > EP-DE, respectively. The oxidation index (OI) values given in Table 3 were calculated from the ratio of absorbance values of the 1720  $\text{cm}^{-1}$  carbonyl peak to the absorbance values of the reference group at 2920  $\text{cm}^{-1}$  using Eq (1).

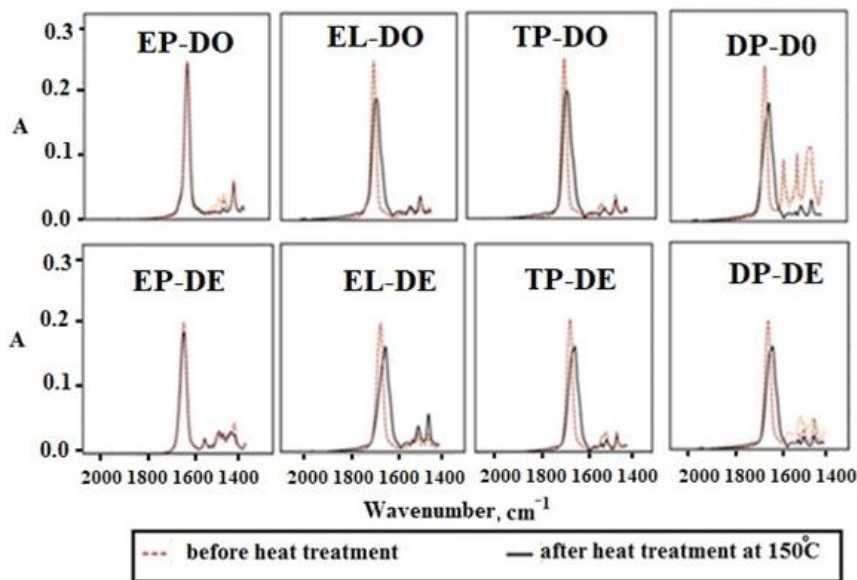


Fig. 1 Change of 1720  $\text{cm}^{-1}$  peaks of p- PVC films with temperature for 420 minutes

Table 3. OI values of the films during heat treatment

Time. min.	0	120	240	360	420	120	240	360	420
Films	OI (at 100°C)					OI (at 150°C)			
EP-DO	173.7	174.3	158.2	186.2	152.8	189.5	140.3	146.4	176.0
EL-DO	207.9	216.5	211.5	212.6	213.4	216.5	156.0	44.7	46.3
TP-DO	217.8	224.9	190.8	234.8	228.5	263.9	154.7	47.3	47.5
DP-DO	193.2	254.6	230.8	226.4	224.2	256.8	149.3	34.6	41.5
EP-DE	176.7	205.1	203.4	186.8	184.9	205.0	203.4	186.8	184.9
EL-DE	185.3	189.0	188.5	203.7	184.0	174.8	142.6	41.5	37.7
TP-DE	200.9	229.0	186.1	233.9	233.5	234.7	66.1	42.8	48.7
DP-DE	192.9	175.2	172.8	177.5	167.6	151.9	33.4	39.1	51.2

Change in OI values during the heat treatment process belongs to the plasticizer migration and degradation. Diffusion and carbonyl formation are two competing processes; while plasticizer diffusion results in decrementing carbonyl, its formation results in the increment of the same peak. This can be explained by the loss of ester resulting from plasticizer migration and the carbonyl formed as a result of decomposition on the same peak. Therefore, the observation of ester loss and carbonyl formation on the same peak made it difficult to explain the change in OI with heat treatment.

#### 4.2. Evaluation of Polyene Formation by UV-Visible Spectroscopy

Polyolefins are permeable in the UV zone. They give absorbance in the UV region depending on the color change after degradation. HCl is released by the dehydrochlorination of PVC during the heat treatment. Conjugated double bonds formed after degradation give maximum absorbance in the UV spectrum in the wavelength range of 268-447 nm. Between these wavelengths, namely at (268, 304, 334, 364, 390, 410, 428, and 447 nm), 3-10 conjugated polyenes are formed. The ratio of absorbance ( $A$ ) values to 1100 nm reference absorbance ( $A_{1100}$ ) values normalized the change in film thicknesses by heat treatment.  $A_{\lambda}/A_{1100}$  and polyene number during heat treatment at 100 and 150°C are depicted in Fig. 2 and 3, respectively. The number of polyenes increased with heat treatment. Three conjugated polyenes were observed at 268 nm wavelength even at 100°C and 3-10 double bonds were observed at 150°C. Although there are no major differences as compared to the one with DEHP, the film with DOTP formed a somewhat higher amount of shortest polyenes upon heat treatment. Diphenyl urea having a film had divergence from the others with lower absorbance, that is, a lower amount of conjugated double bonds. It was observed that the samples with the highest triple conjugated bond at 268 nm at 100°C are EL-DE and TP-DE, and at 150°C it is EP-DE. For the strongest heat treatment (at 150°C, 420 min), the lowest absorbance having sample was the one containing DP-DE, while the highest total absorbance having sample was the one containing EP-DO. While the order of the UV absorbance at 268-447 nm wavelength of the plasticizers DOTP>DEHP and of the secondary heat stabilizers is EPSO> ELSO> TPP> DPU, respectively. Fig. 4 shows the UV-vis relative total absorbances of the samples.

An increase in the slope of the relative UV absorbance curves of the films is due to the formation of polyene by heat treatment. The number of polyenes increases with heat treatment. Although total absorbance values increased in all films with heat treatment, the least change was observed in the film containing EL-DE, and the highest change was observed in the film containing EP-DO. The order of the UV total absorbance at the 268-447 nm wavelength of the plasticizers is as DOTP> DEHP. For the high heat treatment (at 150°C, 420 min), the lowest total absorbance value was observed in the sample containing DP-DE, while the highest was observed in the sample containing EP-DO. The order of the

total absorbance values for secondary heat stabilizers is  $ELSO > TPP > EPSO > DPU$  and  $EPSO > ELSO \approx TPP > DPU$  at 100 and 150°C, respectively. Diphenyl urea having film had divergence from the others with lower absorbance, that is, lower conjugated double bond amount. The stability of phenyl urea derivatives is high due to their chemical structure, which includes two amide linkages, two aromatic rings, a phthalimide moiety, and various substituent groups known to be thermally highly stable [37].

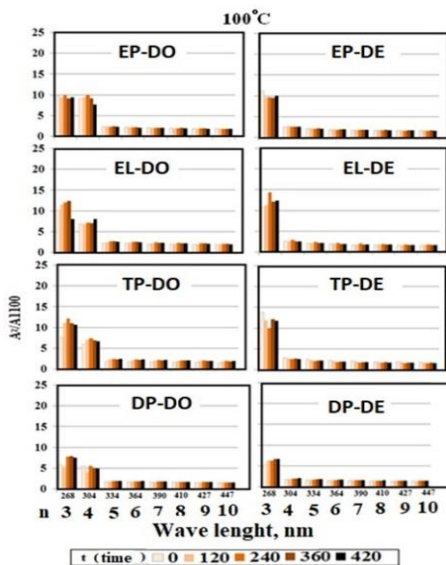


Fig. 2  $A_{\lambda}/A_{1100}$  values of the films at 100°C (n; number of conjugated polyene at specified wave length [31] (for 120, 240, 360, and 420 minutes)

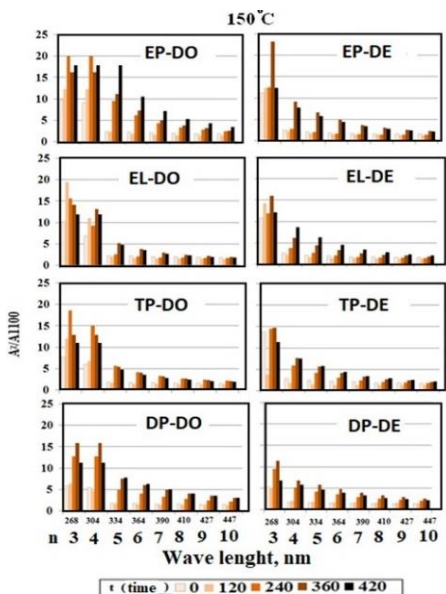


Fig. 3  $A_{\lambda}/A_{1100}$  values of the films at 150°C (n; number of conjugated polyene at specified wave length)

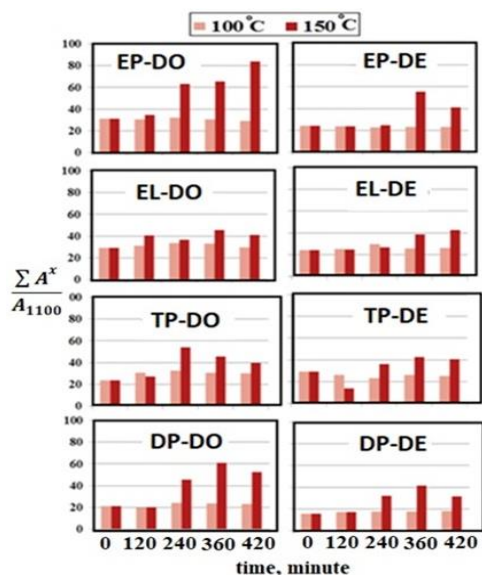


Fig. 4 Total relative absorbance values of P-PVC films

### 4.3. Evaluation of the Polyene Concentrations of Degraded p-PVC Films by UV/Visible Spectrum

Polyene concentrations,  $C_n$  (mol/L), were calculated by using Eq (2). In Table 4, the polyene concentrations of the films were given. The mol fraction of polyenes at each  $n$  value and the mol fractions of conjugated double bond ( $x_{cdlb}$ ) were given in our previous study [9]. The concentration of the polyenes formed after degradation in films increased with temperature. The concentration of polyenes formed in heat-treated films up to 420 minutes at 150°C at 268 nm wavelength (the number of conjugated dienes formed at this wavelength is three) in the UV spectrum was mostly observed in films containing EP-DE. Whereas it was observed that they were the lowest in EL-DO-containing films. However, the highest increase in triple conjugated double bond concentrations compared to the initial values was observed in EP-DO film, while the least increase was observed in DP-DE film. The order of the increment of the concentration at 268 nm wavelength for the films is as follows: EP-DO > TP-DO > EL-DO > EL-DE > EP-DE > DP-DO > TP-DE > DP-DE. The order of the increment of the concentration at 268 nm wavelength for the films in terms of plasticizers is DOTP > DEHP. Fig. 5 shows the total concentration of the polyenes. With the increase in heat treatment time and temperature, the total concentrations of polyenes observed in the wavelength range of 268-447 nm in all films increased. The total concentration of polyenes formed in the films at 150°C for 420 minute remained in the range of 14-22  $10^{-3}$  mol/L. In general, the total concentration of polyenes formed as a result of degradation was higher in films containing DOTP than in films containing DEHP plasticizers. The order of the total polyene concentration of the films is as follows: EP-DO > TP-DO > EP-DE > TP-DE > DP-DO > EL-DE > EL-DO > DP-DE. Mohamed et al. (2014) suggested that the stabilizing effect of various maleimido phenyl urea stabilizers is due to a radical mechanism that blocks the single electron sites formed in PVC chains [38].

### 4.4. Degradation Kinetics for Dehydrochlorination Reaction of PVC

The mol fractions of polyene sequences formed after degradation were determined from their UV spectra. These values for each films containing  $n$  polyene ( $N_n$ ) were determined

by using Eq (3). Mol fractions of polyene sequences and double bonds ( $N_{ps}$  and  $N_{db}$ ) were calculated by using Eq (4) and Eq (5). These values were given in Table 5. Then, the degradation rate constants for each film were calculated at 15 (°C up to 420 minutes by using Eq (6). Thermal dehydrochlorination is a first order reaction [9]. Therefore Eq (6) was used for the reaction rate constant calculation. The polyene formation rate constants for each film were determined by plotting  $-\ln(1-N_{db})$  versus time lines. The dehydrochlorination rate constants (Table 6) were calculated using the slope of these curves (Fig. 6). Polyene formation rate constants calculated from the slopes of the lines in Fig. 6. These are between  $1.68 \cdot 10^{-4}$ - $2.34 \cdot 10^{-4} \text{ min}^{-1}$  at  $150^\circ\text{C}$  (as given in Table 6). The degradation rate constant of the film containing EPSO is higher than that of the other stabilizers.

Table 4. Concentration of polyenes,  $C_n \cdot 10^3, \text{ mol/L}$

N, number of polyene raysı		Polyene concentration, $C_n \cdot 10^3, \text{ mol/L}$								$\sum C_n \times 10^3, \text{ mol/L}$
		3	4	5	6	7	8	9	10	
T, °C	A Film	A <sub>268</sub>	A <sub>304</sub>	A <sub>334</sub>	A <sub>364</sub>	A <sub>390</sub>	A <sub>410</sub>	A <sub>428</sub>	A <sub>447</sub>	
25	EP-DO	5.93	2.65	0.41	0.34	0.25	0.24	0.17	0.15	10.14
100		9.40	3.66	0.65	0.53	0.40	0.38	0.28	0.24	15.54
150		10.05	4.83	2.87	1.48	0.80	0.59	0.36	0.26	21.24
25	EL-DO	5.99	1.92	0.39	0.32	0.24	0.23	0.17	0.14	9.4
100		8.03	3.86	0.73	0.61	0.45	0.43	0.31	0.26	14.68
150		9.25	4.44	1.08	0.69	0.42	0.35	0.23	0.18	16.64
25	TP-DO	6.68	2.50	0.47	0.39	0.30	0.29	0.21	0.18	11.02
100		9.55	2.88	0.62	0.51	0.38	0.37	0.27	0.23	14.81
150		11.12	5.34	1.37	0.90	0.57	0.48	0.32	0.25	20.35
25	DP-DO	7.92	3.54	0.70	0.59	0.45	0.43	0.32	0.27	14.22
100		9.18	2.87	0.70	0.58	0.44	0.42	0.31	0.26	14.76
150		9.71	4.67	1.91	1.37	0.86	0.70	0.46	0.36	20.04
25	EP-DE	9.63	1.04	0.51	0.41	0.30	0.29	0.21	0.18	12.57
100		10.61	1.31	0.64	0.51	0.38	0.36	0.26	0.23	14.3
150		12.04	3.67	1.63	1.08	0.67	0.55	0.36	0.28	20.28
25	EL-DE	8.38	0.97	0.48	0.38	0.28	0.27	0.19	0.16	11.11
100		11.01	1.10	0.56	0.44	0.33	0.31	0.23	0.19	14.17
150		11.01	3.80	1.63	1.05	0.63	0.50	0.32	0.25	19.19
25	TP-DE	9.88	1.00	0.51	0.40	0.30	0.28	0.20	0.17	12.74
100		11.22	1.15	0.58	0.46	0.34	0.33	0.24	0.21	14.53
150		11.68	3.70	1.70	1.13	0.70	0.59	0.39	0.30	20.19
25	DP-DE	9.18	1.51	0.82	0.67	0.51	0.49	0.36	0.31	13.85
100		9.63	1.42	0.76	0.61	0.46	0.44	0.32	0.28	13.92
150		9.92	2.84	1.36	1.02	0.67	0.56	0.38	0.30	17.05

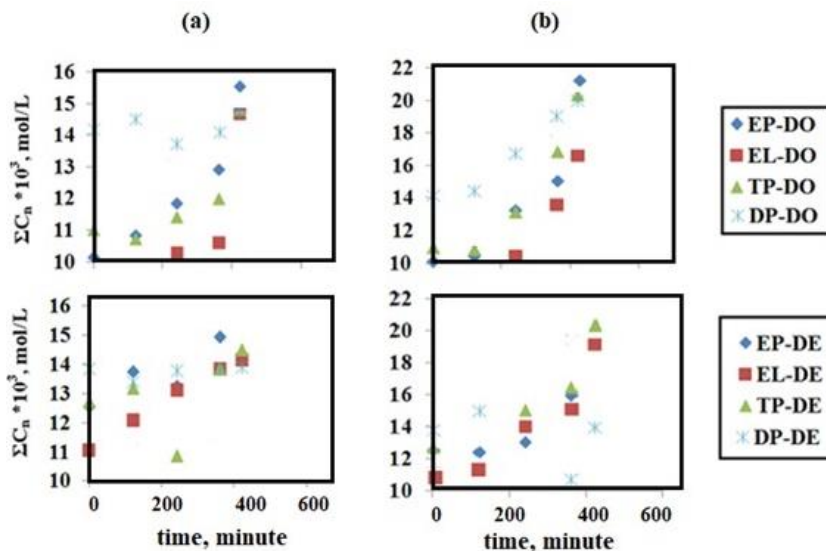


Fig. 5 Total concentration of polyenes at (a) 100°C and (b) 150°C for 420 minute

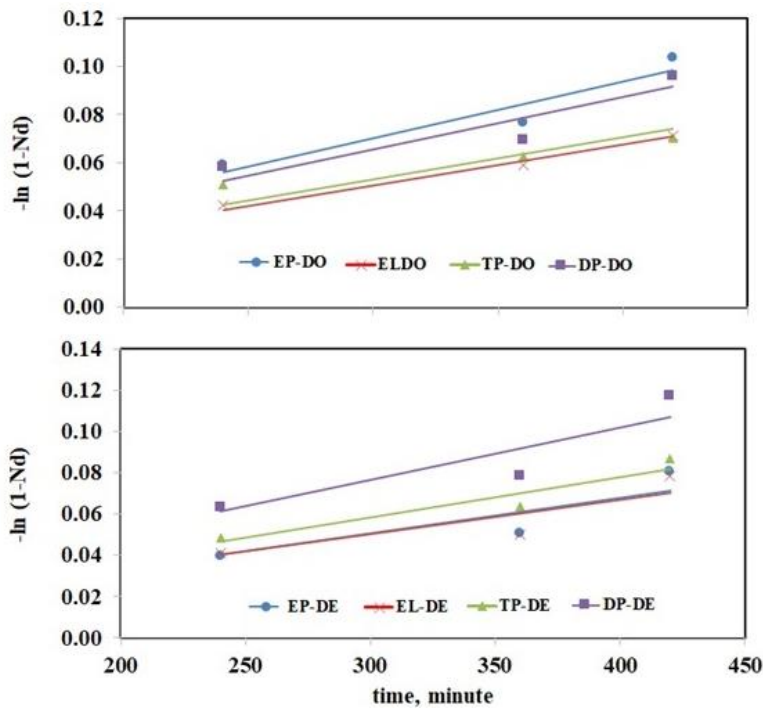


Fig. 6 Time dependence of the mole fraction of polyenes

Table 5. Mol fraction of the polyene sequences for each films at 150°C

Film code	time .min	$N_3 \cdot 10^4$	$N_4 \cdot 10^4$	$N_5 \cdot 10^4$	$N_6 \cdot 10^4$	$N_7 \cdot 10^4$	$N_8 \cdot 10^4$	$N_9 \cdot 10^4$	$N_{10} \cdot 10^4$	$N_{ps} \cdot 10^4$	$N_{db} \cdot 10^4$
EP -DO	0	7.34	3.28	0.51	0.42	0.31	0.30	0.22	0.184735	12.56	48.57
	120	7.54	3.62	0.40	0.28	0.19	0.18	0.13	0.112418	12.47	45.94
	240	8.22	3.95	1.12	0.63	0.35	0.27	0.17	0.131063	14.85	57.36
	360	9.41	4.52	1.85	1.05	0.58	0.44	0.27	0.200257	18.32	73.86
	420	11.12	5.34	3.18	1.64	0.88	0.65	0.40	0.287200	23.50	98.28
EL -DO	0	7.34	2.36	0.48	0.40	0.30	0.28	0.20	0.173983	11.53	44.12
	120	7.59	2.06	0.23	0.17	0.13	0.12	0.09	0.076427	10.46	36.58
	240	7.98	2.27	0.37	0.27	0.19	0.18	0.13	0.110738	11.50	41.55
	360	8.60	3.84	0.90	0.57	0.35	0.29	0.20	0.155737	14.91	57.21
	420	9.83	4.72	1.15	0.73	0.44	0.37	0.25	0.195383	17.69	68.77
TP-DO	0	7.34	2.75	0.52	0.43	0.33	0.31	0.23	0.196947	12.11	47.05
	120	7.54	2.04	0.30	0.23	0.18	0.17	0.13	0.108669	10.69	38.49
	240	8.10	3.15	0.72	0.46	0.28	0.24	0.16	0.123662	13.22	49.76
	360	8.54	4.10	1.02	0.67	0.42	0.35	0.23	0.178177	15.49	60.61
	420	9.41	4.52	1.16	0.77	0.48	0.40	0.27	0.212139	17.23	67.86
DP-DO	0	7.34	3.28	0.65	0.55	0.42	0.40	0.29	0.251949	13.18	52.98
	120	7.65	2.70	0.58	0.47	0.35	0.34	0.25	0.215568	12.56	49.05
	240	7.92	3.81	0.88	0.64	0.40	0.34	0.23	0.182921	14.40	56.68
	360	8.88	4.27	1.21	0.85	0.54	0.45	0.29	0.224912	16.71	67.10
	420	10.49	5.04	2.06	1.48	0.93	0.75	0.50	0.383177	21.62	91.57
EP-DE	0	7.34	0.79	0.39	0.31	0.23	0.22	0.16	0.137323	9.58	35.19
	120	7.75	0.66	0.30	0.24	0.18	0.18	0.13	0.110908	9.55	33.77
	240	8.54	0.92	0.40	0.29	0.21	0.20	0.15	0.127120	10.84	38.75
	360	9.49	1.80	0.79	0.51	0.30	0.25	0.16	0.122712	13.42	49.42
	420	11.59	3.54	1.57	1.04	0.64	0.52	0.34	0.265530	19.52	77.46
EL-DE	0	7.34	0.85	0.42	0.33	0.24	0.23	0.17	0.144207	9.73	36.03
	120	7.86	0.57	0.26	0.21	0.15	0.15	0.11	0.095499	9.41	32.62
	240	8.16	1.25	0.53	0.35	0.24	0.22	0.15	0.130552	11.02	40.30
	360	9.33	1.75	0.75	0.48	0.30	0.26	0.18	0.143454	13.19	48.85
	420	10.90	3.76	1.62	1.03	0.62	0.49	0.32	0.246071	18.99	75.63
TP-DE	0	7.34	0.75	0.38	0.30	0.22	0.20	0.15	0.125160	9.46	34.44
	120	8.04	0.51	0.25	0.20	0.15	0.15	0.11	0.097244	9.50	32.81
	240	8.88	1.75	0.74	0.47	0.30	0.26	0.18	0.144458	12.72	47.37
	360	10.29	2.57	1.13	0.73	0.45	0.38	0.25	0.195817	16.00	61.60
	420	11.97	3.79	1.74	1.16	0.72	0.60	0.40	0.307941	20.68	83.21
DP-DE	0	7.34	1.21	0.65	0.54	0.41	0.39	0.29	0.251487	11.09	44.50
	120	8.60	1.75	0.92	0.75	0.56	0.54	0.39	0.342034	13.86	57.13
	240	9.10	2.37	1.15	0.86	0.56	0.48	0.33	0.265470	15.13	61.14
	360	10.69	3.02	1.53	1.12	0.72	0.61	0.41	0.321782	18.42	75.35
	420	12.66	5.19	2.48	1.86	1.22	1.02	0.69	0.554517	25.67	110.75

Table 6. Polyene formation rate constants

p-PVC films	$k_1 \cdot 10^4, \text{min}^{-1}$	$R^2$
EP-DO	2.34	0.91
EL-DO	1.69	0.98
TP-DO	1.77	0.52
DP-DO	2.18	0.82
EP-DE	1.69	0.78
EL-DE	1.68	0.77
TP-DE	1.95	0.90
DP-DE	2.25	0.82

#### 4.5. Degradation of PVC Using Raman Spectroscopy

Raman spectroscopy is a very useful technique for detecting polyenes in PVC. Degraded PVC contains polyene sequences of various lengths, which chain lengths of 10–30 exhibit various absorption bands in the spectrum [34]. Typically, the wavenumbers of the C-C and C=C stretching vibrations are denoted as 1122 and 1500  $\text{cm}^{-1}$ , respectively [33, 34]. These correspond to polyene sequences in the Raman spectrum of p-PVC films shown in Fig. 7. Therefore these peaks reflect PVC degradation. Measurements were obtained by dividing the absorbance peak at 1122  $\text{cm}^{-1}$  by the peak at 2911  $\text{cm}^{-1}$ , which is unaffected by degradation due to C-H to eliminate effects of film thickness and instrument variation on this peak value [33]. An increase in the peak intensities of C-C and C=C was observed with heat treatment. However, due to strong Raman scattering due to darkening of the color of the samples at high heat treatment time, the spectrum was as in Fig. 7 (c). Using Eq (7), it is found that polyene sequence lengths for excitation wavelengths from 425 to 625 nm correspond to 9 to 26 [33]. In this work, for the laser light wavelength of 532 nm, polyene lengths were 15. Calculations were made for this polyene length. When 1122  $\text{cm}^{-1}$  peak (C-C) was divided by 2911  $\text{cm}^{-1}$  reference peak (C-H), 92.5 % increase in peak intensity was observed as a result of heat treatment at 150°C for 240 minutes. When 1500  $\text{cm}^{-1}$  peak (C=C) was divided by 2911  $\text{cm}^{-1}$  reference peak (C-H), 79.3 % increase in peak intensity was observed as a result of heat treatment at 150°C for 240 minutes.

#### 4.6. Evaluation of Discoloration of the Films

The colors of the films were evaluated by the yellowness index (YI) measurements (Eq (9)) calculated using Tristimulus (L.a.b) values. Fig. 8 shows the YI values of the films at 100 and 150°C. The yellowing of the films indicates that dehydrochlorination has taken place with the formation of polyenes. Color changes were observed in all films as a result of decomposition due to the increase in heat treatment time and temperature. This can be seen from the increase in the YI values. The YI values of all films increased with heat treatment. In general the YI values and YI increments of films containing DOTP as a plasticizer were higher than those containing DEHP. The order of the YI values at 150°C for 420 minutes was determined to be DP-DO > DP-DE > TP-DO > TP-DE > EP-DO > EL-DO > EL-DE > EP-DE. The order of the YI increment at 150°C for 420 minute is as follows: EP-DO > EP-DE > EL-DE > TP-DO > DP-DO > TP-DE > DP-DE. EPSO including films that consisted of the highest number of polyenes, had YI values were also high. However, the film including diphenyl urea consisted of the lowest number of polyenes. According to the initial values, the highest increment in yellowness index values during the long heat treatment process was observed in the film including EPSO. The lowest increment in yellowness index values during the long heat treatment process was observed in films including DPU (Fig. 9). The photographs of films given in Fig. 10 showed the discoloration on the films, which were plasticized with two different plasticizers and contained four different secondary



stabilizers during heat treatment. No significant change in the color of the films was observed at low temperatures, while no darkening was observed at 150°C. The films began to turn yellow and brown during heat treatment. The types of stabilizers have shown a difference. After 150°C 240 minutes, yellowing was observed on the films due to heat treatment. During the 150°C 240-minute heat treatment, the maximum yellowing was observed in films containing EPSO, while the least yellowing was observed in ELSO, including films. The film containing ELSO did not show early color change compared to other films. The yellowing of the films proves that dehydrochlorination occurs via polyene formation. In many applications, in addition to thermal stability, stability against discoloration caused by the action of light is desirable. Butler et al. (1968) have found that monophenyl urea and diphenyl urea have a good light stabilising effect [39].

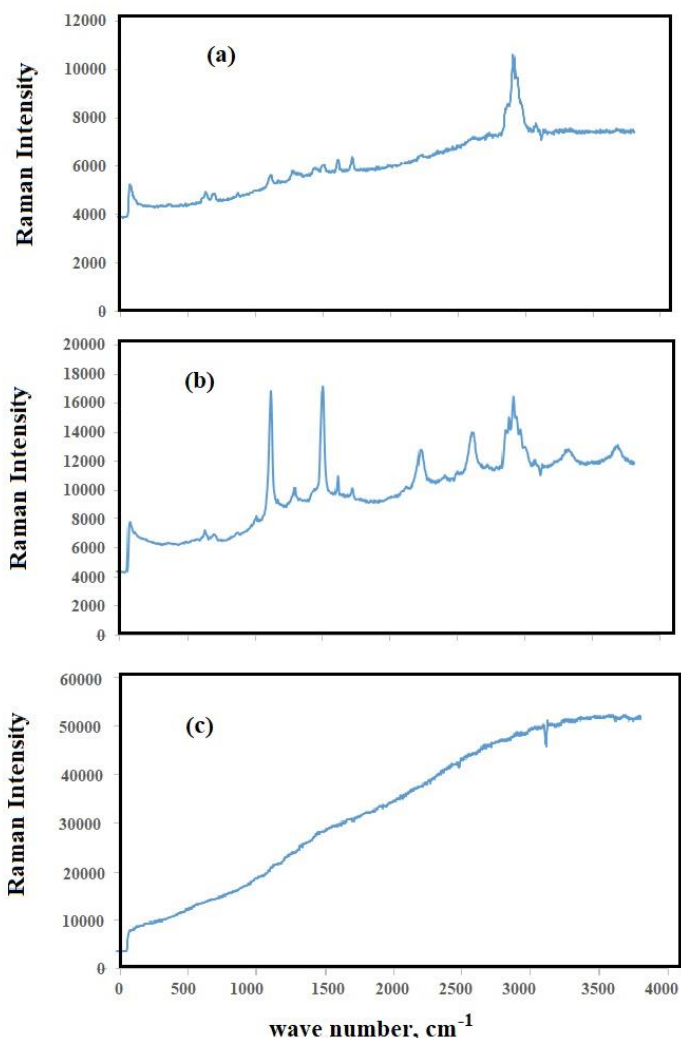


Fig. 7 Resonance Raman spectrum of thermally degraded p-PVC film (DP-DO) a) before heat treatment b, and c) after heat treatment at 150°C for 240, and 420 minute, respectively (using 532 nm laser).

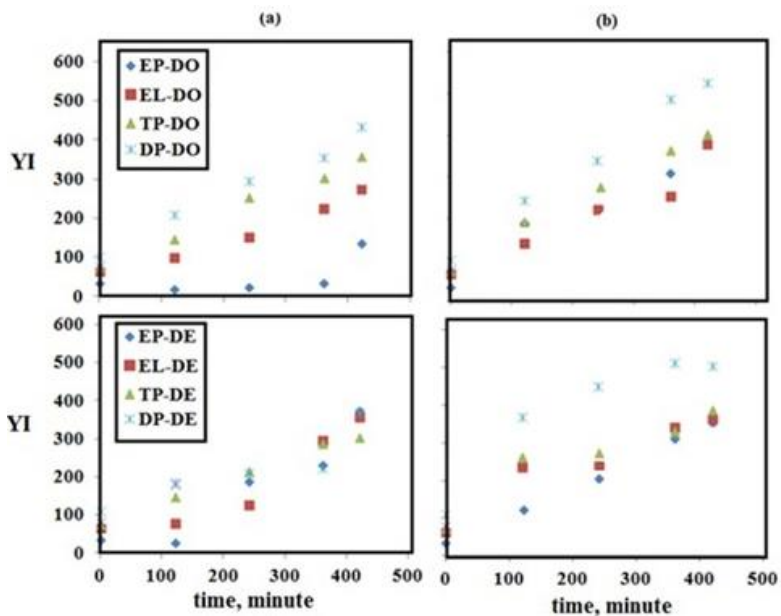


Fig. 8 YI values of the films (a) at 100°C and (b) at 150°C

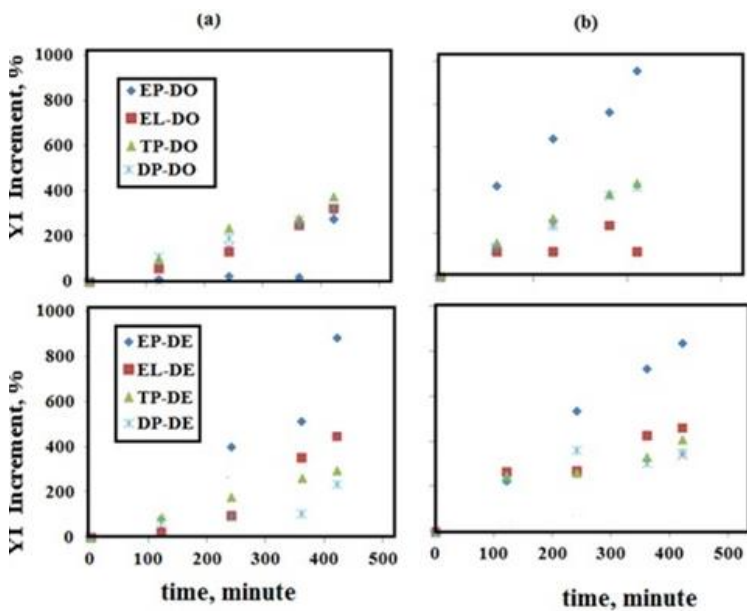


Fig. 9 YI increment (%) values of the films during thermal treatment (a) at 100°C and (b) at 150°C

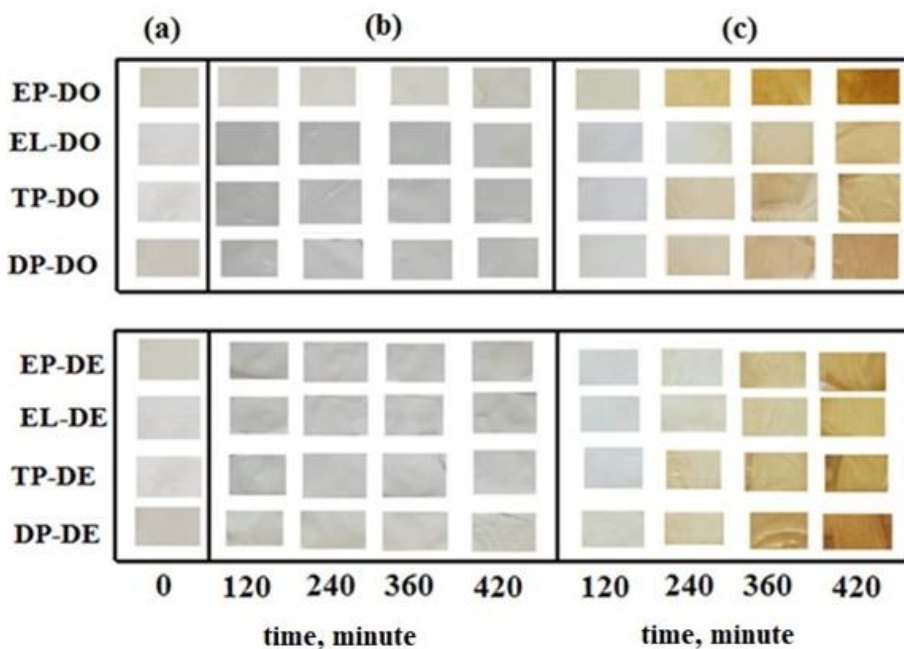


Fig. 10 The photographs of the films during heat treatment

#### 4.7. Determination of Mass Loss and Diffusion Coefficient

When the plasticized PVC films are exposed to air, mass loss occurs by evaporating the plasticizer from the surface. The mass loss of the films having DOTP and DEHP during the heat treatment at 100 and 150°C are given in Fig. 11 (a) and (b), respectively. Since the amount of the initial primary and secondary stabilizers are very low, 5% and 8.3% of the plasticizer mass, respectively, in the formulation used herein, and they have very high molar masses, their contribution to mass loss due to the consumption of heat stabilizers is negligible [40]. However, long heat treatments at high temperatures cause decomposition, most likely due to the consumption of heat stabilizers. Therefore, it is suggested that the mass loss of the films during short to medium heat treatment periods depends mainly on the evaporation of plasticizers [29]. The mass loss of the films increased with heat treatment. While the mass loss for EP-DO, EL-DO, TP-DO, DP-DO having films for 420 minutes at 100°C are 0.8, 0.5, 0.9, and 1.0 %, those at 150°C 11.7, 8.4, 12.9, and 12.0 %, respectively. While the mass losses for EP-DE, EL-DE, TP-DE, and DP-DE having films for 420 minutes at 100°C are 1.0, 0.9, 1.6, and 0.8 %, those at 150°C 20.2, 18.3, 23.2, and 23.5 %, respectively. The mass loss of the films containing DEHP was higher compared to the DOTP-containing films. Considering the effect of secondary thermal stabilizers on the mass loss of the films, it was observed that films containing tri phenyl phosphite (TP) were higher at high temperature than others, whereas the films having epoxidized linseed oil (EL) were lower. The order of the mass loss was determined as TP-DO > DP-DO > EP-DO > EL-DO at 150°C for DOTP-containing films. Similarly, the order of the mass loss is TP-DE > DP-DE > EP-DE > EL-DE for DEHP-containing films at 150°C. For examining the migration behavior of plasticizers from p-PVC films into air, diffusion coefficients were calculated by plotting against  $Mt/M_\infty$  versus  $t^{0.5}$  at 100°C and 150°C, as given in Fig. 12 (a) and (b), respectively. From the slope of the linear part of this graph, the diffusivity of the molecules diffused from the polymeric membrane is also calculated. Diffusion coefficients calculated from Eq (8) are given in Table 7. The effective diffusivity of plasticizer increased with heat

treatment. The migration of plasticizers from films containing DEHP was higher than that of DOTP- containing films. Parameters such as molar mass, polarity of molecules, nature and amount of plasticizer, contact medium, and temperature affect plasticizer migration [29, 41]. Table 1 shows the molecular structure of plasticizers. DOTP is an aromatic terephthalate plasticizer, while DEHP is an aromatic ortho phthalate. Although DOTP and DEHP have the same molar mass, the planar spatial arrangement of DOTP likely makes it more compatible with PVC polymer chains. Therefore, the mass loss of DOTP film is thought to be less than that of DEHP [29]. Considering the effect of secondary thermal stabilizers on the effective diffusion of plasticizers from p-PVC films, it was observed that diffusion coefficients of the films having triphenyl phosphite (TP) were higher than the others at high temperatures. Whereas the films having epoxidized linseed oil (EL) were the lowest. Due to the linear structure of ELSO, it is thought to result in lower plasticizer diffusion. Plasticizer migration from the films having DEHP was higher than that from the films having DOTP. For example, while the effective diffusion coefficient of the p-PVC films at 150°C is  $1.4 \times 10^{-14} \text{ m}^2/\text{sec}$  for EP-DO, and  $4.0 \times 10^{-14} \text{ m}^2/\text{sec}$  for EP-DE. The order of the diffusion coefficients was determined as TP-DO > DP-DO > EP-DO > EL-DO at 150°C for DOTP containing films as plasticizers. Similarly, the order of the diffusion coefficients was determined as the TP-DE > DP-DE > EP-DE > EL-DE at 150°C for DEHP- containing films as plasticizer. The diffusivity values belonging to the films subjected to 100°C thermal treatments also have the same order. Although they have a similar chemical formula, the use of DOTP as a plasticizer instead of DEHP due to its linear structure would be advantageous in terms of plasticizer migration in PVC. Because the films are identical, the diffusivity results are in line with the mass loss, except for differences arising from the type of plasticizer and secondary heat stabilizer.

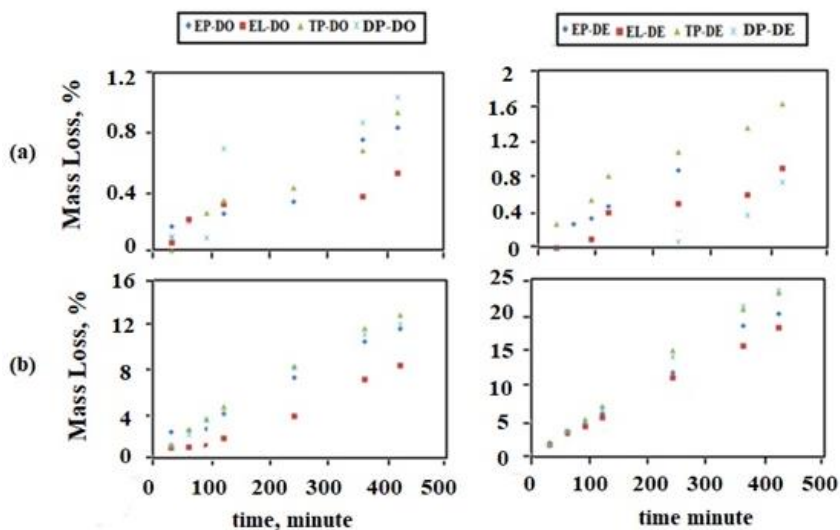


Fig. 11 The mass loss of the films

Ekelund et al. (2008) reported that the diffusion of plasticizer from PVC films to air was controlled by diffusion, where the evaporation rate was independent of plasticizer amount at low temperatures [42]. When examined in terms of thermal stability, DPU and TPP showed higher stability than EPSO and ELSO due to the phenyl rings in their chemical structures, while the linear structures of EPSO and ELSO ensured less plasticizer migration from PVC when examined in terms of the effects of thermal stabilizers on plasticizer

migration. However, the phenyl groups in the structures of DPU and TPP opened the interchain spaces, causing more plasticizer migration.

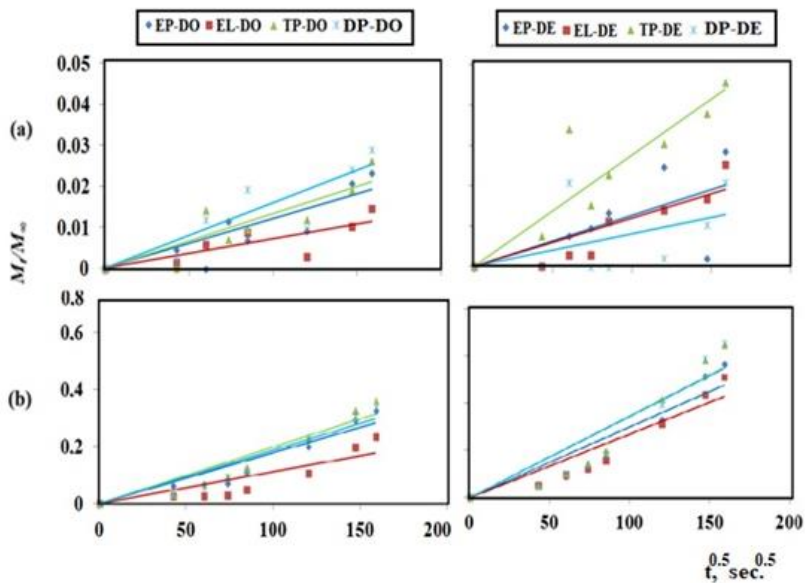


Fig. 12 Fractional loss of the films at (a) 100°C (b)150°C

Table 7. Diffusion coefficients of P-PVC films

T, °C	100		150	
Film Codes	De*10 <sup>16</sup> , m <sup>2</sup> /s	R <sup>2</sup>	De*10 <sup>16</sup> , m <sup>2</sup> /s	R <sup>2</sup>
EP-DO	0.7	0.8	141.1	0.9
EL-DO	0.2	0.7	55.1	0.8
TP-DO	0.8	0.8	174.3	0.9
DP-DO	1.1	0.8	154.5	0.9
EP-DE	1.3	0.9	399.7	0.9
EL-DE	0.6	0.8	322.1	0.9
TP-DE	3.4	0.8	535.0	0.9
DP-DE	0.3	0.6	525.2	0.9

#### 4. Conclusion

PVC is difficult to process due to its relatively high processing conditions and low thermal stability. The use of plasticizers and thermal stabilizers solves this problem. Epoxidized vegetable oils are known to be co-stabilizers for PVC resins, environmentally friendly, and good nominees for PVC secondary stabilizers. However, they are problematic and tend to deteriorate as they cause the polymer to become brittle and discolored at high temperatures. Also, unreacted double bonds in epoxidized vegetable oils reduce compatibility between PVC and plasticizer. This may cause more plasticizer to migrate from the PVC matrix to the surrounding environment. This study focuses on the thermal stabilization efficiency of phosphite and urea derivative-based stabilizers that are non-

toxic against epoxy-based stabilizers on the thermal degradation of p-PVC films. As a result, phosphite and urea derivative-based stabilizers generally provided better long term thermal stability than epoxidized vegetable oils stabilizers. Diphenyl urea, relative to all other thermal stabilizers, showed higher long-term stability than the other stabilizers in terms of the number of polyenes, concentration of polyenes, and yellowness index. Diphenyl urea has a variety of functional groups that can interact with the evolved HCl gas obtained from degraded PVC. It is recommended to use e-PVC in 0.3-0.5 part [25]. In this study, diphenyl urea was used in 3 parts for 100 parts of e-PVC. It performed better than other stabilizers, even 10 times over the specified amount. Therefore, it will be economically beneficial if it is used in lower amounts. In addition, it is also advantageous that it represents a class of compounds with a wide variety of biological properties, such as bactericidal, fungicidal and anticancer activities. However, epoxidized vegetable oil stabilizers generally more affected by the prevention of plasticizer migration than phosphite and urea derivative-based stabilizers.

The findings of this study and the publication of these results will contribute to studies on improving the thermal stability of PVC with different stabilizers, solving the structural degradation problem of PVC, PVC stabilization and plasticizer diffusion.

### Acknowledgement

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