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Research Article

Evaluation of the effect of boron waste sludge and clay on the diffusion of plasticizer to different environments from PVC composite films

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Abstract

Poly (vinyl chloride) (PVC) is a rigid polymer that can also be used in flexible applications by the addition of plasticizers. When plasticized PVC (p-PVC) film is heated, plasticizer evaporates from the surface of the film and it degrades by the loss of hydrogen chloride (HCl) gas. Plasticizers are not chemically bound to the polymers, easily diffuse to the contact media during its life-time and contaminate the environments which are in contact. The aim of this study is to reduce the diffusion of plasticizer by means of boron waste sludge (BWS) and clay filler (CF, kaolinite) to assess the effects of BWS and CF on the diffusion of plasticizer.

Plastisols were prepared by mixing of plasticizer, heat stabilizer, BWS and CF into PVC resin and were cured in plastigel films. Thus obtained plastigel films were subjected to heat treatment in an oven at 100, 130 and 150°C. During heat treatment diffusion of plasticizers from p-PVC films into air was studied. In addition, migration of plasticizers into hexane was compared with the migration of plasticizers into air during the heat treatment. For this purpose, the effects of BWS and CF on the migration of the plasticizer to different environments were examined. Diffusion coefficient of plasticizer was evaluated according to the Fick's law and to determine related activation energies according to the Arrhenius relation. Oxidation index (OI) values were determined by using FTIR spectroscopy. The addition of boron waste was reduced the diffusion of the plasticizer into air and increased the activation energy value. Its determined that, the mass loss of the films decreased with increasing amount of BWS and CF

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1. Introduction

Among the polymers PVC has a wide application area, due to its high versatility and low production costs and excellent properties [1-4]. However, oxygen, UV radiation, temperature and humidity in the atmosphere are the main factors causing the polymer to age [5]. Additives are added to PVC to achieve the desired material properties [6].

In order to decrease the processing temperature and to obtain desirable properties such as processability, flexibility or extensibility, plasticizer needs to be added into PVC [7, 8]. Among these commercial plasticizers, phthalate esters especially bis(2-ethylhexyl) phthalate (DEHP) known as di-octyl phthalate, (DOP, as well) play an important role owing to their excellent performance, its unique properties [2, 4, 7, 9]. Nowadays, phthalates based plasticizers are criticized. Because they are not chemically bonded to polymers and allowing them to easily migrated from materials and diffuse to the surrounding media, resulting in adverse effects of human exposure through inhalation, ingestion, and skin contact as a potential carcinogenic agents and detrimental environmental problems [1, 2,

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8]. Among the group of new general purpose plasticizers are also terephthalates, especially dioctyl terephthalate (DOTP), also known as di- (2-ethylhexyl) terephthalate (DEHTP), has the same molecular weight as DEHP. However, the linear structure of DOTP provides better compatibility with PVC, resulting in low migration than that of DEHP [1]. In addition, DOTP has no carcinogenic, genotoxic or developmental effects [1, 10]. There are several studies in literature about migration of plastic products from PVC products to the environments where they are in contact. Royaux et al. 2018, investigated the degradation kinetics of ancient and model plasticized PVC films containing phthalate to emphasize the role of contact material in aging of plasticized PVC. They reported that silk paper reduces the migration of plasticizers and PVC degradation rate and had a protective effect during the storage of PVC objects [11]. Münch et al. 2018, reported that phospholipids used as anti-coagulation increased the migration of plasticizers from PVC tubing into blood [12].

Plastisols are prepared by mixing plasticizer, heat stabilizer and other additives in PVC resin and then heated up to 180-200°C to obtain plastigel forms [1, 13]. When a plasticized PVC (p-PVC) film is heated, plasticizer evaporates from the surface of the film and PVC degrades by the loss of hydrogen chloride (HCl) gas (dehydrochlorination). PVC could be stabilized with heat stabilizers to prevent dehydrochlorination. Hydrotalcite (HT) is a non-toxic, environmentally friendly compound and is a layered double hydroxide (LDH) inorganic complex having HCl absorption capacity to be used as PVC thermal stabilizers [14, 15]. Boron is rarely found in nature. It can be combined with oxygen and other elements, called borates. [16]. Borates and their products are important issues of industrial development in the world. However, their wastes are the most abundant inorganic waste in Turkey that has 67% of the world's boron reserves are in Turkey. Therefore, the evaluation of such wastes is very important [17, 18].

In literature, Alva et al., 2018, reported that the composite with boron nitride showed the best improvement in thermal conductivity of polyvinyl butyral [19]. Fang et al, 2013, investigated the thermal decomposition and fire retardancy of wood-flour (WF) and zinc borate (ZB)-polyvinyl chloride composites. The results showed that the addition of WF and ZB significantly influenced the thermal degradation behavior of PVC and PVC composite [20]. Cui et al., 2015, reported the effect of boron nitride with graphene nanosheets on the improvement of thermal properties of polymeric composites [21]. However, in the literature, there is no study examining the effect of boron waste sludge to reduce the migration of plasticizers from flexible PVC products.

Kaoline is one of the abundant minerals found naturally in the earth's crust and has a layered silicate structure (LDH) [22]. It is widely used to production of polymeric composites [23]. Kaolin refers to a family of kaolinitic clays that consist of a 1:1-type clay mineral with one tetrahedral sheet and one octahedral sheet, depending on the geological and weathering conditions [23]. It is used in the ceramic industry, paper, plastics, paints, production of portland cement as filler [22]. The recent increase in research on polymer-clay composites is due to the fact that they offer more fire, mechanical and thermal properties than polymer composites containing conventional fillers [24]. Kaolin has smaller spacings of layers compared to montmorillonite, due to strong internal hydrogen bonds between layers. PVC-LDH composite has better thermal stability than PVC because the hydroxides can absorb the HCl as it is evolved [24].

Two main processes are considered in the migration of plasticizers. The first is the diffusion through the polymer matrix to the surface of the material and the second is to the surrounding environment through the polymer boundary. Both processes should be considered when analyzing the migration rate [25]. The migration rate is determined by the diffusion coefficient. The activation energy is the kinetic component of the temperature dependence of permeation and is mainly determined by penetrant size and shape of a

polymer. Generally, it can be defined as the energy required to separate the polymer chains for a diffusional splash [26]. Diffusion coefficient of the plasticizers can be calculated from the corresponding mass loss data when the other evaporating or decomposing components are negligible [1].

The process of diffusion of additives to the surface from the bulk of polymer is described by Fick's law of diffusion. Crank has shown that, the solution of Fick's law for the layer geometry is as given in Eq. (1) [25].

$$\frac{M_t}{M_\infty} = (4/l) \times (D t/\pi)^{0.5} \quad (1)$$

Where; D is the diffusion coefficient, M_t and M_∞ are the mass of diffusing substance from a distance of l at time t , and, at equilibrium of sorption attained theoretically after infinite time, respectively. Hence; D can be calculated from the slope of initial portion of M_t/M_∞ versus square root of time plots.

Activation energy of plasticizers for diffusion is expected to be inversely proportional to the diffusivity values. Diffusion coefficient can be expressed in the Arrhenius form in Eq. (2)

$$D_e = D_o \times e^{\frac{-E_A}{RT}} \quad (2)$$

Where; D_e is the effective diffusion coefficient (m^2s^{-1}), D_o is a constant defined as preexponential factor which is the theoretically maximum diffusion coefficient at infinitely high temperature, E_A ($Jmol^{-1}$) is the activation energy for diffusion, R is the universal gas constant and T is the temperature studied. The activation energy values can be calculated from the slope of Arrhenius plots of the present data as $\ln D_e$ versus T^{-1} . The universal gas constant R is taken as $8.314 Jmol^{-1}K^{-1}$.

IR spectroscopy is useful for the characterization of additives in polymer. It is also a useful tool to monitor polymer degradation. Plasticizer migration, oxidative degradation during processing and oven aging are determined using IR spectroscopy. During the degradation oxygen diffuses into the polymer, reacts with free radicals inside and causes more oxidation. This process results in thickening of the oxidized surface layer and higher Oxidation Index (OI) as the degradation increases [1]. Absorption bands appeared in the IR spectra at around $1720 cm^{-1}$, can be attributed to carbonyl (C=O) groups between two methylene groups (-CH₂COCH₂-). The formation of oxidative substances are associated with α and β chloro carboxylic acids ($1716 cm^{-1}$) and α and β chloroketones ($1730-1770 cm^{-1}$) [27]. OI is calculated considering the absorbance of carbonyl band and the absorbance of a reference group of -CH₂- at $1363 cm^{-1}$, $1420 cm^{-1}$ or $2920 cm^{-1}$ band [1] as shown in Eq. (3).

$$OI = \frac{A_{C=O}}{A_{ref}} = \frac{A_{[1722.cm^{-1}]}}{A_{[2920.cm^{-1}]}} \times 100 \quad (3)$$

The present study compares the effect of a BWS and CF additives on the diffusivity of the plasticizers migrated to different contact media (air and hexane) from the p-PVC films. The plastisols were prepared mixing of plasticizer (di-octyl tere ftalat) (DOTP), secondary stabilizer (epoxidized soy bean oil) (ESBO), heat stabilizer (hydrotalcite) (HT), BWS and CF into 100 parts of PVC resin. Films in $150 \mu m$ thickness on glass plates were cured for 15 minutes at $160^\circ C$. The p-PVC films were subjected to heat treatment to follow the mass loss to find out diffusivity of and to determine activation energies.

2. Materials and Methods

2.1. Materials

A typical commercial emulsion PVC resin (paste type, $<63\mu\text{m}$, K# 71-75; Mw 97300-110643 gmol^{-1} , Petkim Co, Turkey), was used throughout the study. Dioctyl terephthalate (DOTP) is used as plasticizer, while epoxidized soy bean oil (ESBO) and hydrotalcite (HT) are used as heat stabilizers, BWS and kaolinitic type clay mineral (CF) are used as auxiliary materials as filler.

The plasticizer (DOTP; $\geq 99.5\%$ purity, CAS: 117-81-7) and the heat stabilizers (epoxidized soybean oil (ESBO) and HT (SC-491880) were supplied by the producer, Sigma Aldrich. Boron waste sludge was supplied by ETİ Maden, Turkey. CF with about 46% SiO_2 content having average particle diameter of $6\mu\text{m}$ was provided from Uşak shelves, Turkey.

2.1. Methods

2.1.1 Plastisol Preparation

The plastisols were prepared mixing with 60 phr (per hundred resin) of DOTP, 5 phr of ESBO and 3 phr of HT, 0, 1, 3 phr of BWS and 0, 1, 3 phr of CF into PVC resin, on the mass basis. A homogeneous mixture was obtained mixing dried PVC resin with firstly solid and then liquid ingredients by using a steel mixer (8011 EB, SS 610).

2.2.2. Preparation of Plastigel Films

Plastisols were applied on a glass plate as 150μ thick films with the help of a four sided film applicator (Sheen Ins., UK; 1107/60/2). The films after curing (gelling to produce plastigel) for 15 minutes in oven at 160°C were cooled down to room temperature and stripped off the glass plates. The codes of p-PVC films and their filler contents were given in Table 1.

Table 1 The codes of p-PVC films and their filler contents

Film Codes	Filler, phr	
	BWS	CF
BOC0	-	-
B1	1	-
B3	3	-
C1	-	1
C3	-	3

2.2.3 Kinetic Study of Plasticizer Diffusion in Air

The films were cut into small pieces about $10 \times 20\text{mm}$ and placed in the oven set at 100, 130 and 150°C . The films were weighed from the beginning up to 420 minutes during the heat treatment at certain time intervals, by using a digital balance (Denver Instrument; SI:234, max:230 g, d:0,1 mg).

2.2.4. Kinetic Study of Plasticizer Diffusion in Hexane

The films cut into small pieces about $10 \times 20\text{mm}$ were put in hexane. The films were weighed from the beginning up to 420 minutes at certain time intervals during the immersion in hexane.

2.2.5. Spectroscopic study on p-PVC films

FTIR spectroscopy was used as a complementary technique to follow of functional groups and to determine the oxidation after degradation.

Fourier transform infrared (FTIR) spectra of untreated, heat treated and hexane treated films were obtained on a Perkin Elmer (Spectra 100) FTIR spectrometer, at a resolution of 4 cm^{-1} . The FTIR spectra were recorded in transmittance units within the $4000\text{--}400\text{-cm}^{-1}$ range. The intensity of the carbonyl bands ($1500\text{--}2000\text{ cm}^{-1}$) was used to estimate degradation.

3. Results and Discussion

3.1 Determination of Mass Loss

The nature and amount of the plasticizer, heat stabilizer and other additives, surrounding media, environmental conditions effect the migration of plasticizer [1, 26, 28]. When the plasticized PVC film is exposed to heat treatment, mass loss occurs by evaporating the plasticizer from the surface. The mass loss of p-PVC films into air containing BWS and CF during the heat treatment at 100, 130 and 150°C are given in Figure 1 (a), (b) and (c) respectively.

Since the stabilizers used herein have very high molar mass (603.973 g/mole and 975.5 g/mole for HT and ESBO, respectively), they hardly evaporate and their contributions at the applied temperature to mass loss is considered negligible [20].

The mass loss of the films increased with temperature and thermal processing time. While the mass loss for B0C0, B1, B3, C1, C3 having films at 420 minutes at 100°C are 0.1, 0.7, 0.6, 0.21, $0.16 \times 10^{-2}\%$, those at 150°C are 0.87, 0.46, 0.24, 0.85, $0.46 \times 10^{-2}\%$ respectively.

BWS and CF (filler)-free film showed the highest mass loss compared to other films whereas the films having boron waste sludge were lower mass loss. In general, the mass loss of the films decreased with increasing amount of boron.

The mass loss of p-PVC films containing BWS and CF into hexane at ambient temperature are given in Figure 2. The mass loss in CF films exposed to the hexane medium was higher than that of BWS films.

In the filler free film, the mass loss after hexane immersion was about 220-times higher than in the 100°C heat treatment, which was approximately 25-times higher than in the 150°C heat treatment. In the film containing 1 part of boron, the mass loss observed in the hexane medium was observed to be about 110 and 22 times higher than that of 100 and 150°C heat treatment, respectively. However, in the film containing 1 part of CF, the mass loss observed in the hexane medium was observed to be about 240 and 67 times higher than that of 100 and 150°C heat treatment, respectively.

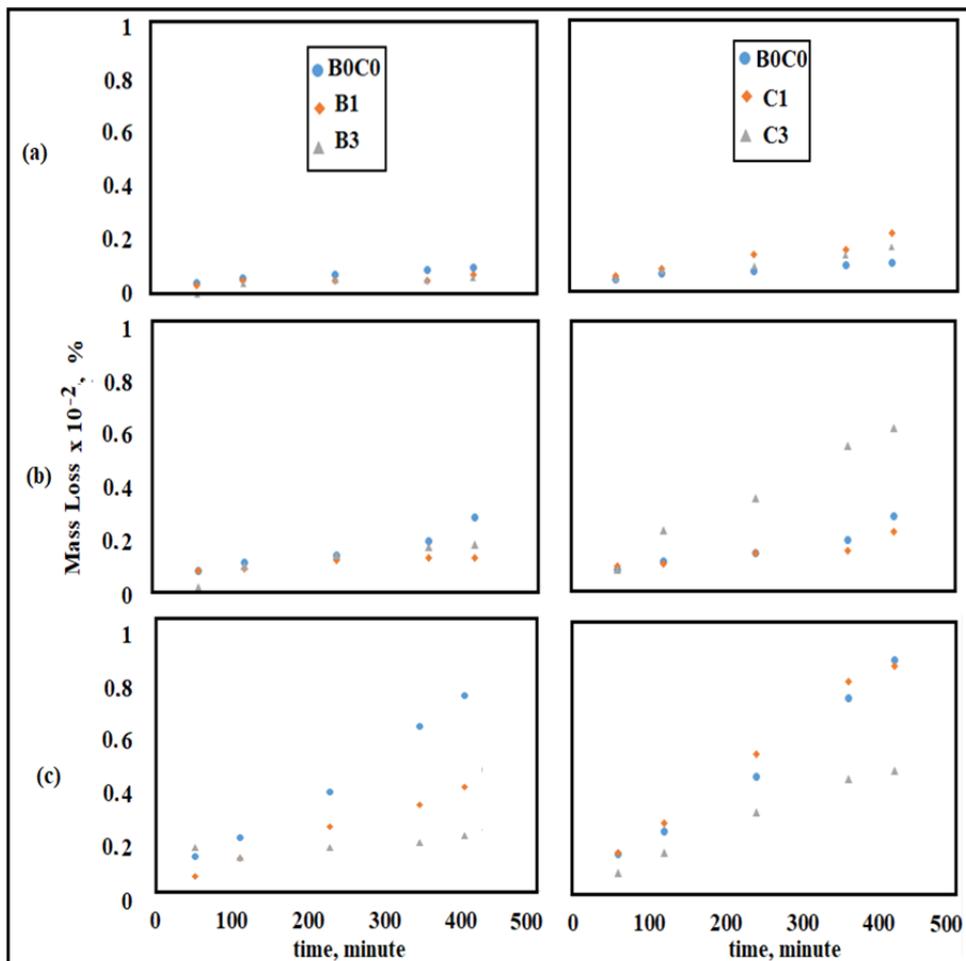


Fig. 1 Mass loss of p-PVC films containing BWS and CF after heat treatment in air at (a) 100°C (b) 130°C (c) 150°C

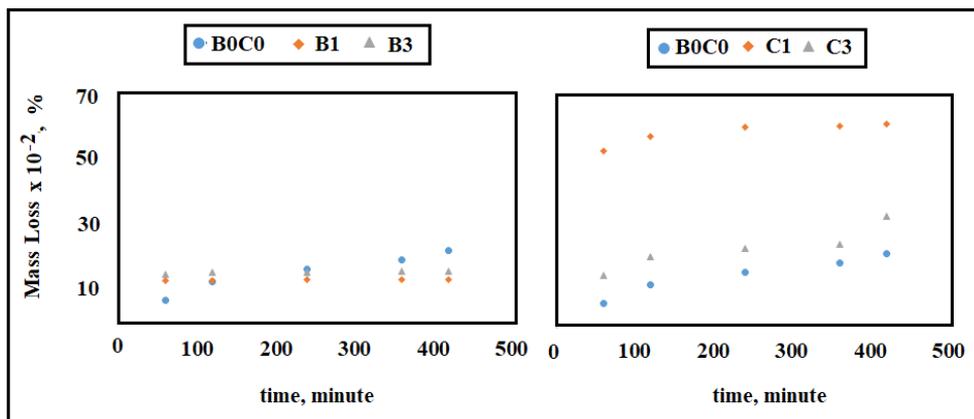


Fig. 2 Mass loss of p-PVC films in the course of hexane immersion

Since BWS addition reduces plasticizer migration out of such plastic objects to the environment in which it contacts, BSW utilization in such an application has two way benefit: Decreasing environmental contamination in terms of plasticizer migration and piles of BSW.

3.2 Calculation of Diffusion Coefficient for Determination of Plasticizer Migration

Diffusion coefficient of the migrating molecule out of a polymer film was estimated from the slope of the linear portion of the graph of fractional loss versus $t^{0.5}$ by using Eq. (1). The data as the mass loss of the films during the heat treatment were evaluated to calculate fractional loss (M_t/M_∞). The M_∞ is the mass at equilibrium, which is considered herein as the maximum amount of evaporable plasticizer and corresponds in this study to 0.357 g plasticizer/g film, for filler free film. The linearity of M_t/M_∞ versus $t^{0.5}$ plots in the region of $M_t/M_\infty < 0.5$ confirms that the model is valid (Figure 3). Fractional mass losses of BWS and CF films into hexane are given in Figure 4.

The plots revealed a good fit to the Fickian diffusion kinetics which is confirmed by the correlation coefficient for diffusion, R^2 , as reported in Table 2 together with the diffusion coefficients, D , for the migration of plasticizers out of p-PVC films into air and hexane. The diffusion coefficients of films increased with temperature as expected. The addition of boron waste sludge has reduced the diffusion of the plasticizer from the films into air.

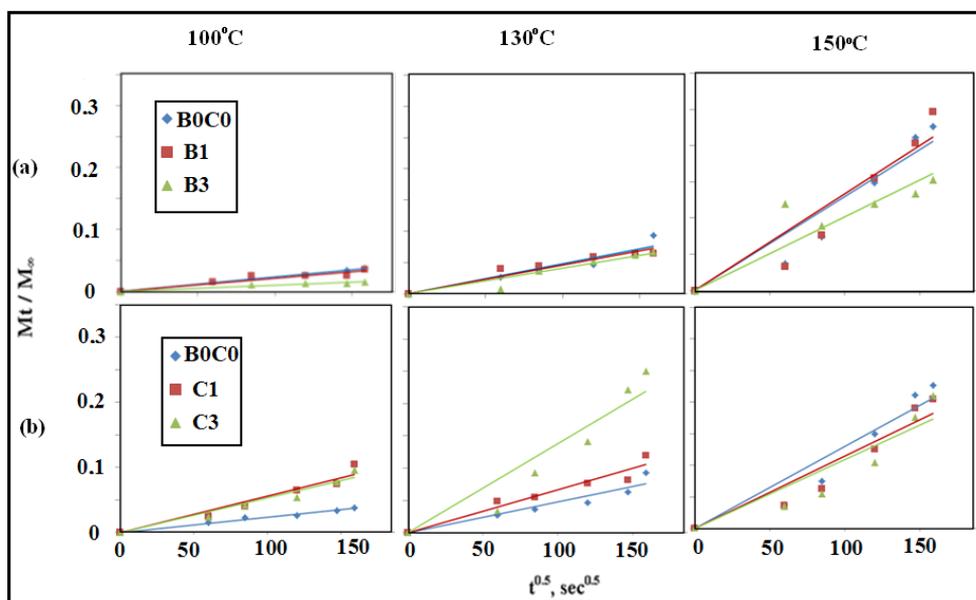


Fig. 3 Uptake ratio of p-PVC films during heat treatment in air for films containing (a) BWS (b) CF

In our previous study [1], the diffusion coefficient of DOTP from films into air was found to be $7.1 \times 10^{-15} \text{ m}^2/\text{sec}$ at 160°C heat treatment. In this study, for boron waste sludge and CF free film, this value was found to be so close as $7.5 \times 10^{-15} \text{ m}^2/\text{sec}$ into air at 150°C heat treatment. This value was decreased approximately 41% by 3 phr boron waste sludge addition. The addition of boron waste sludge is more effective than that of CF.

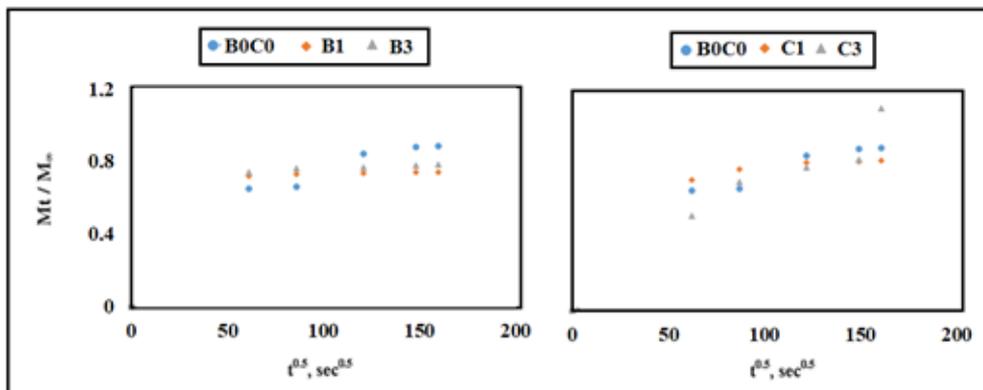


Fig. 4 Uptake ratio of p-PVC films after treatment in hexane

The diffusion coefficient of the plasticizers into the hexane was found to be 37 to 104% times higher than that of into air at 150°C heat treatment, as expected.

Table 2 Diffusion coefficients ($D \times 10^{16} \text{ m}^2/\text{sec}$) of plasticizer from the p-PVC films into air and into hexane

Temperature, °C	into air						into hexane	
	100		130		150			
P-PVC Films and Codes	$D \times 10^{16}, \text{m}^2\text{sec}^{-1}$	R^2						
B0C0	2.44	0.99	11.0	0.93	74.7	0.91	3500	0.92
B1	1.97	0.87	9.15	0.91	78.3	0.90	4240	0.92
B3	0.43	0.95	7.07	0.92	44.2	0.74	4600	0.93
C1	13.8	0.94	19.4	0.93	58.5	0.90	4510	0.95
C3	12.4	0.95	83.5	0.90	53.5	0.87	1990	0.92

3.3 Temperature Effect on Diffusion Related Activation Energies

Product lifetime is controlled mainly by the plasticizer migration. 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 [1]. The relations of diffusion coefficients with temperature were associated with the Arrhenius equation (Eq. (2)). Activation energies for the diffusion of plasticizers were calculated for the p-PVC films heat treated at 100, 130 and 150°C up to 420 minutes. While the activation energy is 40.62 kJ/mol for the film without BWS and CF, these values are found to be 41.26, 52.28, 36.35 and 41.01 kJ/mol B1, B3, C1 and C3 respectively. Activation energies for the diffusion of plasticizers from p-PVC films into air were given in Table 3.

Table 3 Activation energies for the diffusion of plasticizers from p-PVC films into air

P-PVC FILMS	B0C0	B1	B3	C1	C3
$D_0 \times 10^{10}$	3.36	7.10	214	1.62	4.92
E_A, KJmol^{-1}	40.62	41.26	52.28	36.35	41.01

3.4 Determination of Oxidation Index (OI) and Functional Group Changes by using FTIR Spectroscopy

Information concerning the functional group changes of p-PVC films is obtained by means of spectroscopic methods. IR study was used herein to characterise the migration of plasticizer and the oxidation following the carbonyl group formation in the films upon heat treatment in air and upon hexane treatment. IR spectra of p-PVC present some characteristic bands at around 2950 and 1720 cm^{-1} correspond to ester bands which come from plasticizer.

Thermal decomposition can also be observed on the 1720 cm^{-1} band attributed to the C=O vibrations, becoming deeper because of the carboxylic acids forming by the evolved HCl out of PVC [29]. The peaks in the region of 1444-1414 cm^{-1} are attributed to the C-H bonds of PVC and, peaks at 1464 cm^{-1} are attributed to the methyl (-CH₃) groups of the plasticizer [30]. The peak at 2920 cm^{-1} corresponds to -CH₂- and -CH- stretching groups [29]. The higher the applied temperature of heat treatment is, the higher the amount of carboxylic acids and hydroperoxydes are, as implied by the band intensities on IR spectra [30]. Since the plasticizers are easy evaporating species, mainly the early stage of oxidation overlaps with the plasticizer migration.

As the heat treatment gets severer in terms of temperature 1720 cm^{-1} peak, which is the ester peak, gets shorter due to the plasticizer migration (Figure5). The highest change of 1720 cm^{-1} peak i.e., the highest plasticizer migration was observed in filler free films. As the boron amount increased, the reduction in the peak height was less. As seen in the Figure5, the peak height decreased with increasing heat treatment time for filler free film. OI evaluation gives better results than those obtained from 1720 cm^{-1} peak evaluation since it is expressed as the peak height ratio in the formulation and thus the change in sample thickness during the heat treatment is eliminated.

During the aging and degradation oxygen diffuses into the polymer, reacts with free radicals trapped inside and eventually causes more oxidation. This process results in thickening of the oxidized surface layer and higher oxidation index (OI) as the ageing time gets longer. The oxidation suffered by the p-PVC films during the degradation was monitored by the evaluation of the oxidation index (OI) by means of FTIR spectroscopy. The OI values were obtained by using the absorbances of carbonyl band (C=O) around 1720 cm^{-1} and of a reference group of -CH₂- at 2920 cm^{-1} band (Eq.(3)). Changes of OI values for each film in the experiments were given in Figure6. P-PVC does not show important oxidation within these temperature range, as deduced from Figure7. The highest value obtained is about the same for all. Even with small increments in OI values, it can be said that the oxidation rate gets higher with increasing temperature. Oxidation index values of each film generally increased with longer treatment time and increasing temperature. The lowest OI values were observed on the films having boron waste sludge.

OI method has a weakness to distinguish between plasticizer migration and oxidation due to degradation in case of the presence of ester peaks in the same band.

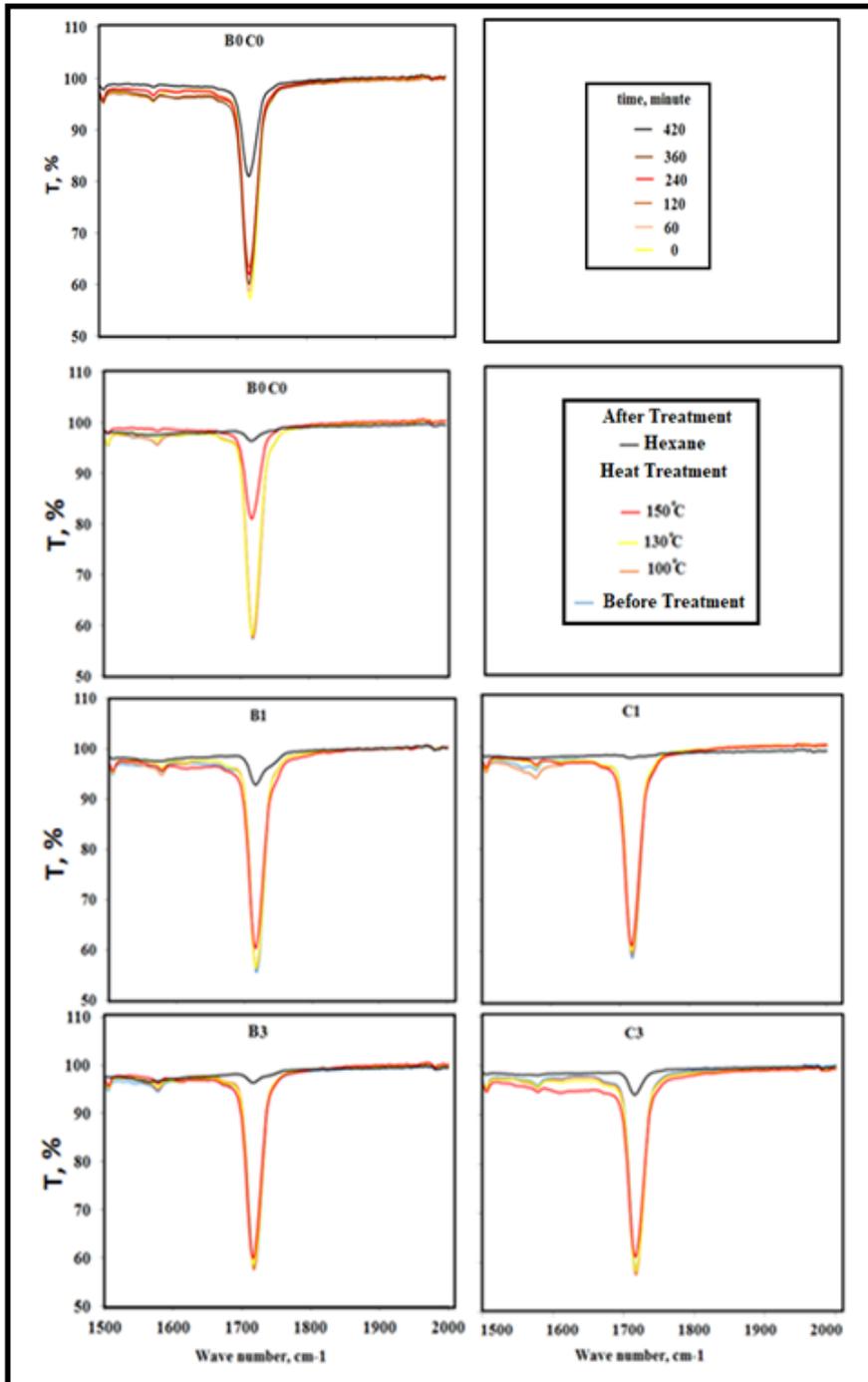


Fig. 5 FTIR spectra of the p-PVC films at 1720 cm-1 (rankings; from top to bottom)

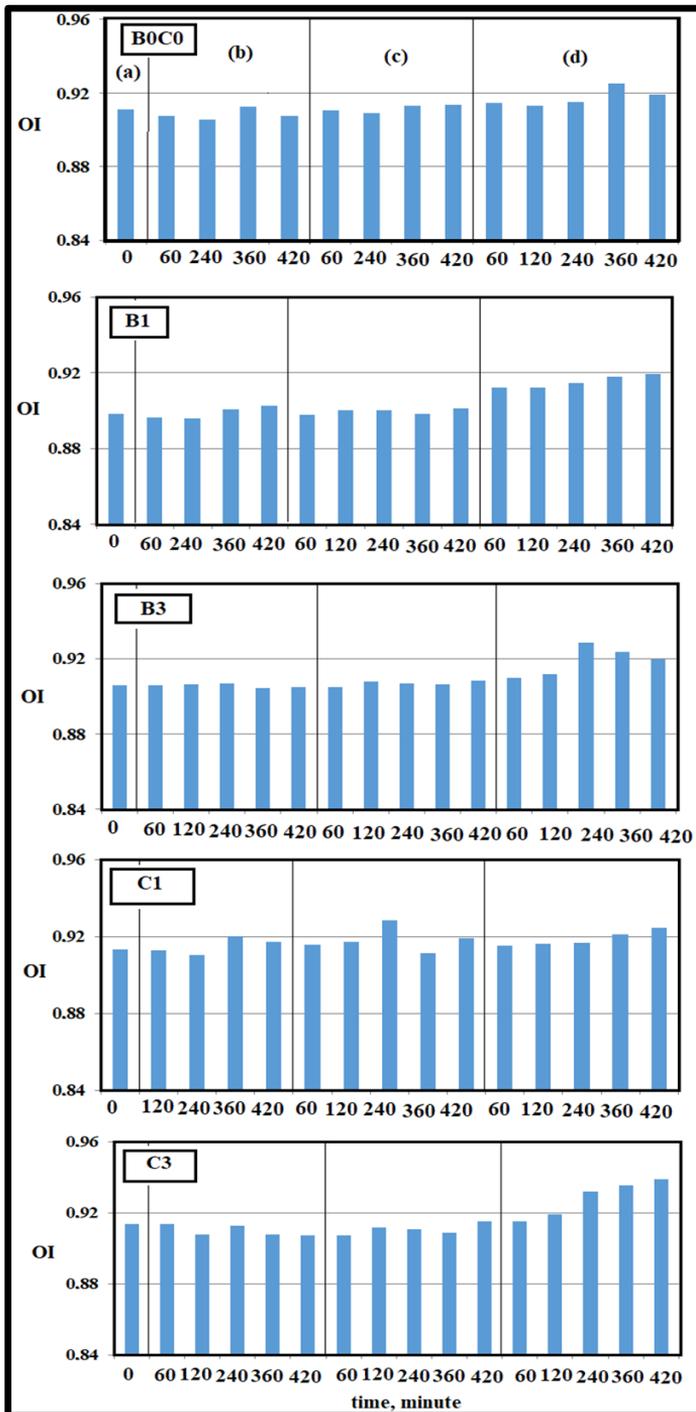


Fig. 6 Change of oxidation index values for p-PVC films according to the time and temperature (before heat treatment (a), after heat treatment (b) 100°C, (c) 130°C and (d) 150°C)

3.5 Discoloration of The Films upon The Treatments

PVC has low thermal stability and the HCl is released as a result of degradation, which is followed by the coloration of the resin [31]. Effect of environmental conditions on the colors of the films were evaluated with bare eyes. The photographs of the films with respect to heat treatment period, temperature and different environment have been depicted in Figure 7. discoloration was observed only when the heat treatment period was long enough thanks to the used efficient stabilizer system. Yellowing of the films proves that dehydrochlorination occurs through conjugated double bond formation [32]. The colors of the films prepared by using CF became the darkest at the long heat treatment period. After consumption of stabilizers, the formation of polyenes reinitiated in turn unzipping process to yield free HCl. The translucent films were still translucent or light yellow at 130°C. This suggests that the stabilization system utilized was not consumed up during processing and therefore, these films can be used under these conditions, without degradation. It was observed that the color of boron waste sludge containing films had less yellowing. It can be said that polyene formation was less in these films. Supporting this result by UV spectroscopic analysis will be the subject of a future study. The amount of additive has shown only a slight difference.

4. Conclusion

Filler-free film showed the highest mass loss compared to other films whereas the films having BWS were lower mass loss. The mass loss in CF films exposed to the hexane medium was higher than that of BWS films. As a result, the BWS added to the films reduces plasticizer migration to the environment in which it contacts. The diffusion coefficients of films increased with temperature as expected. The addition of BWS has reduced the diffusion of the plasticizer from the films into air.

The highest change of 1720 cm^{-1} peak i.e., the highest plasticizer migration was observed in filler free films. As the boron amount increased, the reduction in the peak height was less. The peak height decreased with increasing heat treatment time for filler free film. Oxidation index values of each film generally increased with longer treatment time and increasing temperature. The lowest OI values were observed on the films having BWS.

The colors of the films prepared by using CF became the darkest at the long heat treatment period. It was observed that the color of BWS containing films had less yellowing. It can be said that polyene formation was less in these films.

The addition of boron waste sludge has reduced the diffusion of the plasticizer from the films into air. The addition of boron waste sludge and the increase in the amount of boron waste slurry increased the activation energy value for diffusion of plasticizer. In general, the mass loss of the films decreased with increasing amount of BWS and CF. As a result, the boron waste sludge added to the films contributes to the economy of the country by using waste sludge and reduces the hazard effects by decreasing to plasticizer migration to the environment in which it contacts.

For PVC based films, it can be said that the plasticizers in the films quickly migrated to the oil-like hexane. Therefore, for the films used in food packaging, especially in contact with fatty foods, precautions should be taken or their use should be restricted.

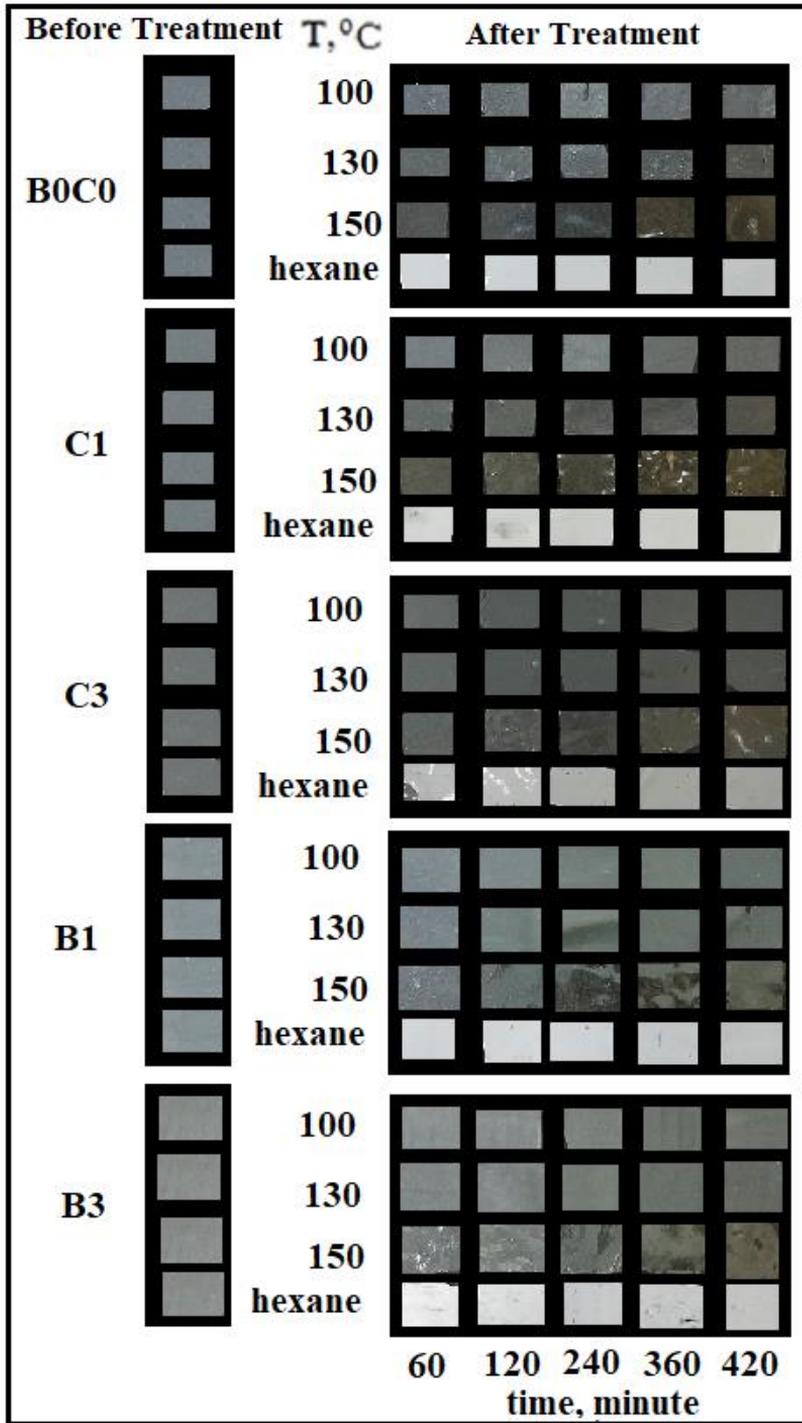


Fig. 7 The color images of the p-PVC films in the course of treatments

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