Uşak Üniversitesi Fen ve Doğa Bilimleri Dergisi
Usak University Journal of Science and Natural Sciences

http://dergipark.gov.tr/usufedbid
https://doi.org/10.47137/usufedbid.1522771

Research Article (Araştırma Makalesi)

Effect of surface modification of hydrotalcite on plasticizer diffusion from hydrotalcite/PVC/chitosan composite films into air

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Geliş: 26 Temmuz 2024 *Revizyon: 4 Aralık 2024* *Kabul: 16 Aralık 2024*
Received: 26 July 2024 *Revised: 4 December 2024* *Accepted: 16 December 2024*

Abstract

In this study, the effect of surface modification of the filler was investigated to reduce plasticizer migration from polyvinyl chloride (PVC) films. Therefore, the surface of the inorganic filler was coated with crosslinked chitosan. The effect of the addition of inorganic filler (hydrotalcite), modification of the filler with chitosan, the addition of crosslinking and crosslinker type (glutaraldehyde (GA) and 1-(3-dimethyl aminopropyl)-3-ethyl-carbodimide (EDC)) on the plasticizer diffusion of the films was examined. Diffusion of plasticizer and oxidation were analyzed by FT-IR spectroscopy. The diffusion coefficient and activation energies for the migration of plasticizers were calculated by mass loss. The results show that adding inorganic filler to PVC, modifying the filler with chitosan, and cross-linking of the filler generally reduced the diffusivity. The effective diffusion coefficients are 0.27-2.54 10-16m2/sec, 3.98-4.81 10-16 m2/sec, and 11-74.7 10-16m2/sec at 100, 130 and 150oC, respectively. The highest and lowest effective diffusivity values at high temperatures were observed in films without filler and cross-linked modified filler with EDC, respectively.

Keywords: *PVC, hydrotalcite, chitosan, surface modification, plasticizer diffusion*

Hidrotalsit/PVC/kitosan kompozit filmlerden havaya plastikleştirici difüzyonu üzerinde hidrotalsitin yüzey modifikasyonunun etkisi

Özet

Bu çalışmada, polivinil klorür (PVC) filmlerden plastikleştirici göçünü azaltmak için dolgu maddesine yüzey modifikasyonunun etkisi araştırılmıştır. Bunun için, inorganik dolgu maddesinin yüzeyi çapraz bağlı kitosan ile kaplanmıştır. İnorganik dolgu maddesi (hidrotalsit) ilavesinin, dolgu maddesinin kitosan ile modifikasyonunun, çapraz bağlanma ve çapraz bağlayıcı tipinin (glutaraldehit (GA) ve 1-(3-dimetilaminopropil)-3-etil-karbodimid (EDC)) filmlerden plastikleştirici difüzyonuna etkisi incelenmiştir. Plastikleştiricinin difüzyonu ve oksidasyon indeksi değerleri, FT-IR spektroskopisi ile analiz edilmiştir. Plastikleştiricilerin göçü için difüzyon katsayısı ve aktivasyon enerjileri kütle kaybı ile hesaplanmıştır. Sonuçlar PVC'ye inorganik dolgu maddesinin eklenmesinin, dolgu maddesinin kitosan ile modifiye edilmesinin ve dolgu maddesinin çapraz bağlanmasının genel olarak difüzyon kabiliyetini azalttığını göstermektedir. Etkin difüzyon katsayıları seviyeleri sırasıyla 100, 130 ve 150oC'de 0,27-2,54 10-16m2/sn, 3,98-4,81 10-16 m2/sn ve 11-74,7 10-16m2/sn'dir. Yüksek sıcaklıkta en yüksek ve en düşük etkin difüzyon değerleri sırasıyla dolgusuz ve EDC'li çapraz bağlı modifiye dolgu içeren filmlerde gözlenmiştir.

Anahtar Kelimeler: *PVC, hidrotalsit, kitosan, yüzey modifikasyonu, plastikleştirici difüzyonu*

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1. Introduction

Poly(vinyl chloride) (PVC), is used in various fields, due to its superior mechanical, physical, and chemical properties [1]. The addition of plasticizers, resulted in the flexibility of the PVC chain [2, 3]. Plasticizers can easily diffuse into the contact environment. Because they do not chemically bond to PVC [4]. Plasticizers are toxic substances released into the environment and cause harmful effects on human health [5]. Additionally, the performance of the products decreases [2]. This study focused on the effect of modification of filler added to films to reduce plasticizer diffusion from flexible films. Inorganic fillers, prevent unwanted migration of plasticizers. The structure of layered double-layer hydroxides (LDHs), is based on positively charged sheets and, capture anions [6, 7]. However, due to the low compatibility between fillers and polymers, the adhesion problem at the interfaces creates difficulties in some applications of composites [8]. When fillers are modified with organic substances, their surface energy decreases and better adhesion to the polymer matrix is achieved. Organic cations strengthen the inner surface bonds between the polymer and silicate [9]. A good interfacial bond can be achieved by the inclusion of some natural modifiers containing amino groups in their molecular chains [10]. Chitosan is a deacetylated derivative of the natural biopolymer chitin, is abundant in nature, derived from crustacean shells, and is used in many sectors such as materials science [11, 12]. Due to the abundant hydroxyl groups of chitosan, which have strong interaction with PVC, chitosan can easily spread on the filler surface and bind tightly to the filler after the cross-linking reaction[13]. There are many compounds used as crosslinking agents [14, 15]. In this study, the surface of the inorganic filler was coated with cross-linked chitosan. The effect of filler (Hydrotalcite (H)) addition, modification of the filler with chitosan, crosslinking, and type of crosslinker on the plasticizer diffusion of the films were examined. For this purpose, plastisol pastes (without filler, with filler, with modified filler, with cross-linked modified filler) were prepared from the formulations given in the method. Firstly, the surface of the inorganic filler coated with crosslinked chitosan was prepared to reduce plasticizer migration from PVC films. After modification of filler, plastisols were obtained. Taking a small amount of the plastisols from which air bubbles were removed, 150μm thick films were obtained. These films were exposed to thermal aging for certain periods. Diffusion of plasticizer and oxidation were analyzed by FT-IR spectroscopy. Calculations were made regarding the diffusion kinetics of plasticizers. It is of importance to use appropriate additives to reduce plasticizer diffusion from PVC composites.

2. Materials and Methods

To prepare composite films, PVC resin (emulsion type, K# 71-75; Mw 97300-110643 g/mol), plasticizer (DOTP), thermal stabilizer mixture (CaSt2-ZnSt2), secondary thermal stabilizer (epoxidized soybean oil). (ESBO)), hydrotalcite and medium molecular weight chitosan ((190000-310000 Da), supplied from Sigma-Aldrich)were mixed. Glutaraldehyde (GA) and 1-(3-dimethylaminopropyl)-3-ethyl-karbodimide (EDC) were supplied from Merck. Materials and their manufacturers are given in Table 1.

2.1. Method

2.1.1. Preparation of Solutions

To prepare a 2% chitosan solution (w/v), 2 g of chitosan was added with 100 ml of 1% acetic acid solution and mixed for about 2 hours [16].To prepare 0.5% glutaraldehyde solution (v/v), 2 ml of 25% glutaraldehyde solution diluted with acetic acid. To prepare a 0.5% EDC solution (w/v), 0.5 g of EDC was diluted with 100 ml of pure water [17].

2.1.2. Filler Modification

Hydrotalcite was dried for 24 h, then soaked in chitosan solution for 1 h, and then dried to removed water. To cross-link chitosan to the surface of hydrotalcite, it was kept in hydrotalcite cross-linker solutions with stirring for 45 min and then dried [10].

2.1.3. Preparation of PVC Plastisols

To prepare plastisol, with the 100 parts by weight PVC resin, 60 parts of DOTP, 3 parts of Ca-Zn stearate mixture, 5 parts of epoxidized soybean oil (EPSO), 2 parts of hydrotalcite/ hydrotalcite modified with chitosan/ hydrotalcite modified with crosslinked chitosan were mixed. Film codes and their contents are given in Table 1.

2.1.4. Preparation of Plastigel Composite Films

Plastisols were spread homogeneously on the glass plate. With the help of a film applicator (Shen), small amounts of plastisols were applied on a glass plate in the form of films of thicknesses 150μm [2]. Then, the polymer films were cured in an oven [2].

Table.1 Contents of p-PVC films and their codes (hydrotalcite (H), PVC (P), Chitosan (C), Gluteraldehyde (G), EDC (E)

Sample code	Inorganic filler	Modifier for filler	Crosslinker
P	-	-	-
PH	H	-	-
PHC	H	C	-
PHCG	H	C	G
PHCE	H	C	E

2.1.5. Thermal Aging Studies

Film pieces cut in 4x4 cm^2 size were thermally aged in an air circulation oven at 110, 130 and 150^{o}C up to 300 minutes.

2.1.6. Structural Analysis:

The films were analyzed using a Perkin Elmer FT-IR spectrometer(Spectra 100) by doing 64 scans at a resolution of 4 cm^{-1}.

3. Results and Discussions

3.1. Determination of plasticizer diffusion and oxidation index by FT-IR Spectroscopy

Thermal degradation, oxidation index (OI), and plasticizer diffusion are detected using a Fourier Transform Infrared (FT-IR) spectrophotometer.

With heat treatment, oxygen enters the polymer and causes oxidation with free radicals, and in the meantime, the oxidized surface thickens. OI is calculated by dividing the absorbance (A) value of the carbonyl band at approximately 1720 cm^{-1} by the A value of -CH2- reference group in the band of 1363 cm^{-1}, 1420 cm^{-1} or 2920 cm^{-1}in the FT-IR spectrum (Eq. 1) [18].

$$OI = \frac{A_{C=O}}{A_{ref}} = \frac{A_{[1717\ cm^{-1}]}}{A_{[2920\ cm^{-1}]}} \times 100 \qquad (1)$$

FT-IR analyses were performed to confirm the plasticizer migration from the films, and the oxidation of the films. The diffusion of the plasticizer and the degradation of PVC are monitored by the FT-IR spectrum in the 1800-1600 cm^{-1} band (carbonyl group). Figure 1 shows the FT-IR spectra of the films. Since zinc and calcium stabilizers were consumed after heat treatment, the 1570 and 1530 cm^{-1} bands attributed to these stabilizers showed a similar decreasing behavior in all films, since the amount of stabilizer was constant in all films [19, 20]. The height of the carbonyl peak at 1720 cm^{-1} increased with increasing temperature. Diffüsion of easily evaporatable plasticizers coincides with the early stage of oxidation. As plasticizer migration increases as a result of heat treatment, the ester peak at 1720 cm^{-1} also shortens. Plasticizer migration and carbonyl formation are competing processes. This increase and decrease in peak height results from two processes competing in opposite directions.

The oxidation observed in p-PVC films during degradation was monitored by evaluating the OI via FT-IR spectroscopy. While films are degraded by heat treatment, oxygen causes oxidation. Meanwhile, the oxidized surface layer thickness, and the OI increases. This eliminates the change in film thickness, and gives better results than the 1720cm^{-1} peak evaluation. The change in OI values for films with heat treatment is given in Table 2. OI values generally increased with increasing temperature. The highest and lowest OI increment (%) values at high temperature were obtained in films containing without filler (%10) and cross-linked modified filler with gluteraldehyde (there was no increment), respectively. The OI method has a weakness in distinguishing plasticizer migration and oxidation due to degradation in the presence of ester peaks in the same band. It can be said that the increase resulting from oxidation is dominant in long heat treatment processes.

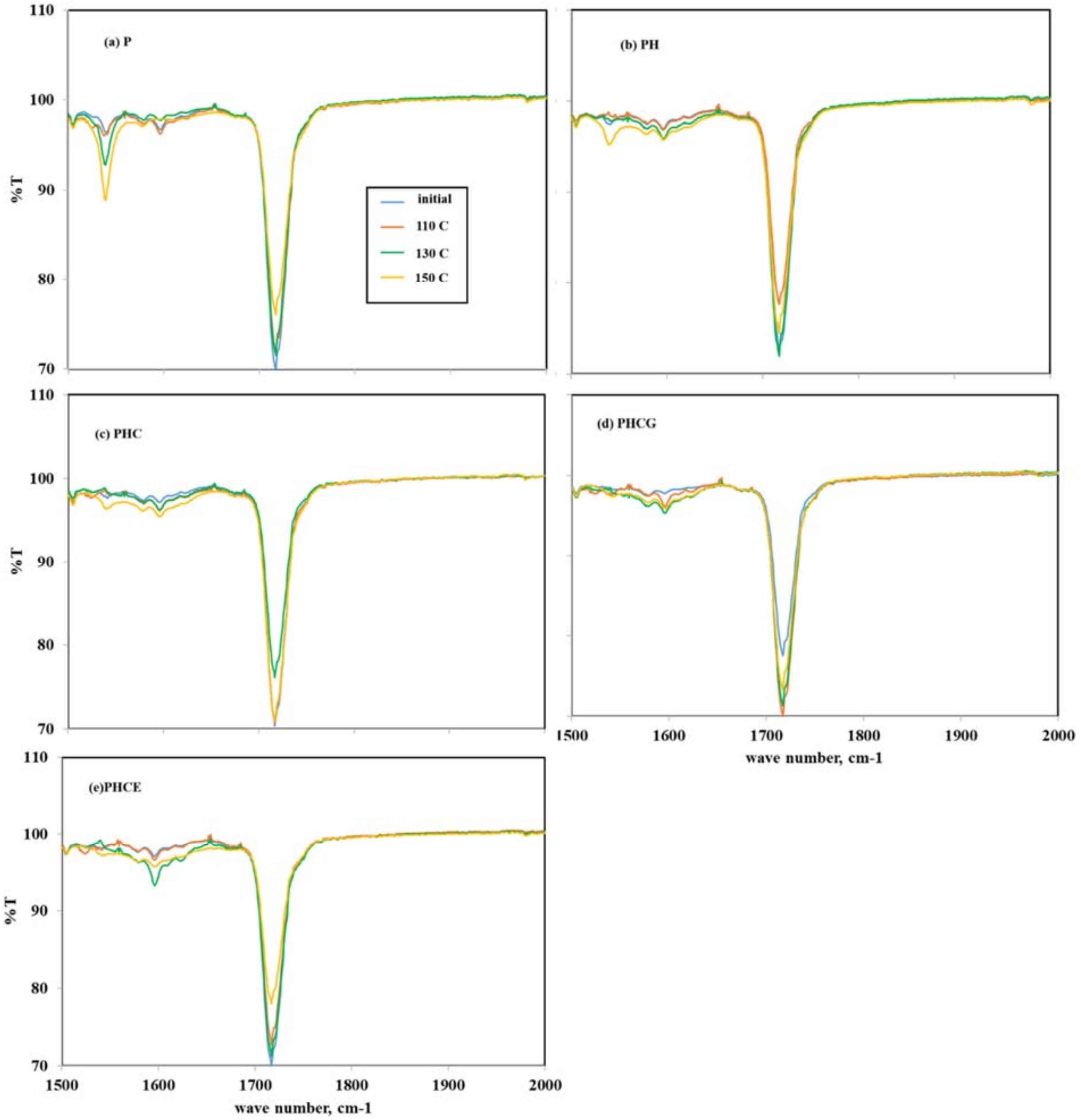

Figure 1. FT-IR spectra of films having (a) unfilled, (b) filler (hydrotalcite), (c) filler modified with chitosan, (d) cross-linked modified filler with gluteraldehyde, (e) cross-linked modified filler with EDC

Table 2. Oxidation index of the films after treatment

Sample code	Before heat treatment	After heat treatment			OI increment %
		100^{o}C	130^{o}C	150^{o}C	
P	83	86	85	91	10
PH	84	89	85	88	5
PHC	82	85	89	85	4
PHCG	87	85	86	87	0
PHCE	83	87	87	90	8

3.2. Determination of Mass Loss and Diffusion Coefficient

When the films are heated, the weight decreases due to the plasticizer evaporating from the surface of the film. Mass losses of the films after heat treatment are given in Figure 2. It was observed that the mass loss increased with increasing temperature. The diffusion of plasticizers from films into the environment complies with Fick's Law (Eq. 2).

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial^2 x} \qquad (2)$$

where *De* is the effective diffusivity, *C* is the plasticizer concentration, *t* is time, and *x* is the layer thickness. The short-time solution is given by Eq.3.

$$\frac{M_t}{M_\infty} = \left(\frac{4}{l}\right)\left(\frac{D_e t}{\pi}\right)^{0.5} \qquad (3)$$

Here; M_t *and* M_∞ represent the amount of mass emitted from the film of thickness *l* at times *t* and t_∞, respectively. It was assumed that the molecules diffusing from the polymeric film were the only plasticizers in the formulation, and the diffusion of other molecules was neglected.

The diffusion coefficient of the plasticizer migrating from the polymer film during the heat treatment was calculated from the fractional loss (M_t/M_∞) values due to the mass loss of the films (Eq.3). M_∞ is the maximum amount of plasticizer that can evaporate from a film and its value in infinite time is equal to the amount of plasticizer in that film. $M_t/M_\infty < 0.5$ region is the linear where the model is valid (Figure 3). The graphs revealed a good fit, which was confirmed by the R^2. The temperature-dependent diffusion coefficients are given in Table 3. Diffusivities increased with increasing temperature.

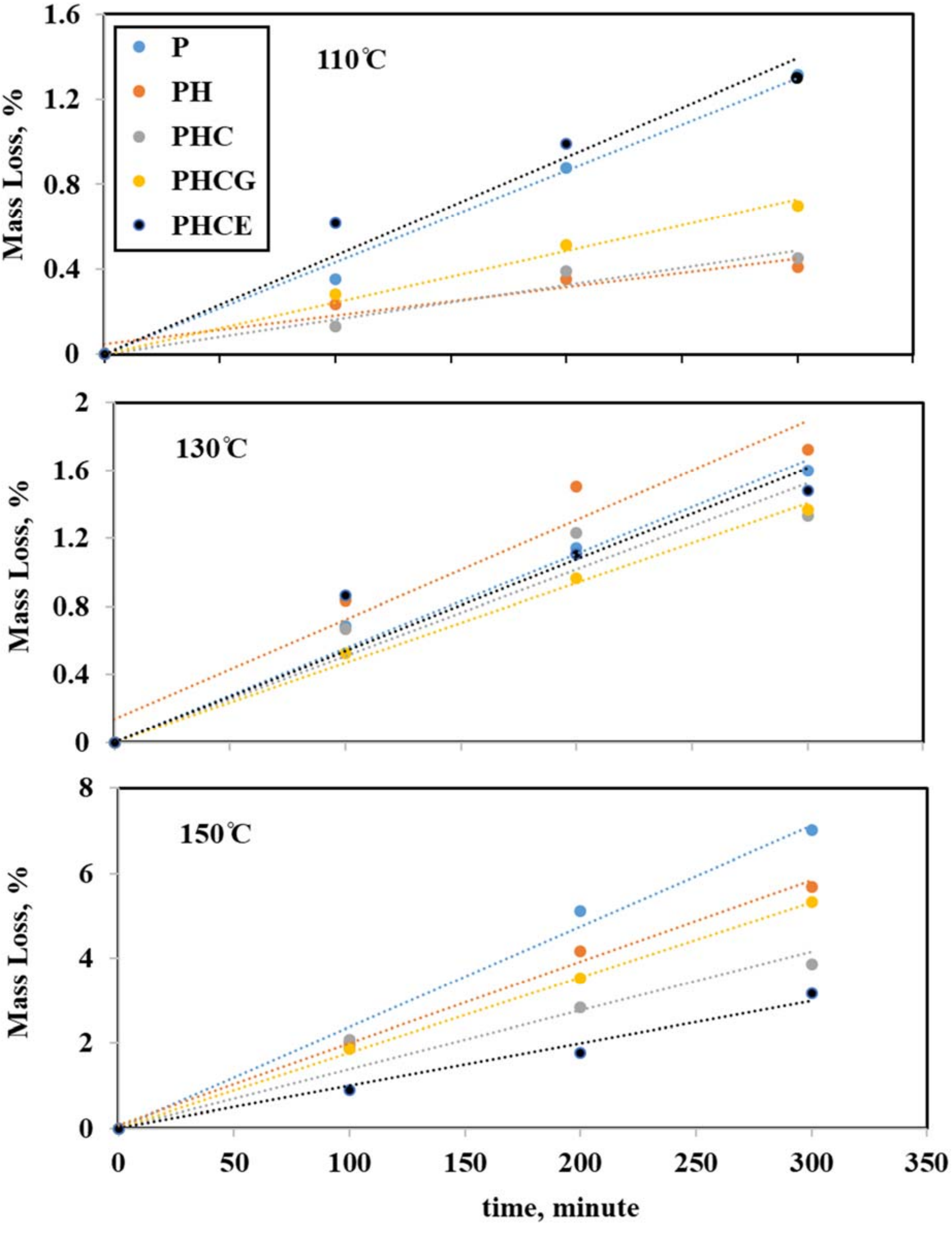

Figure 2. Mass loss of the films during heat treatment

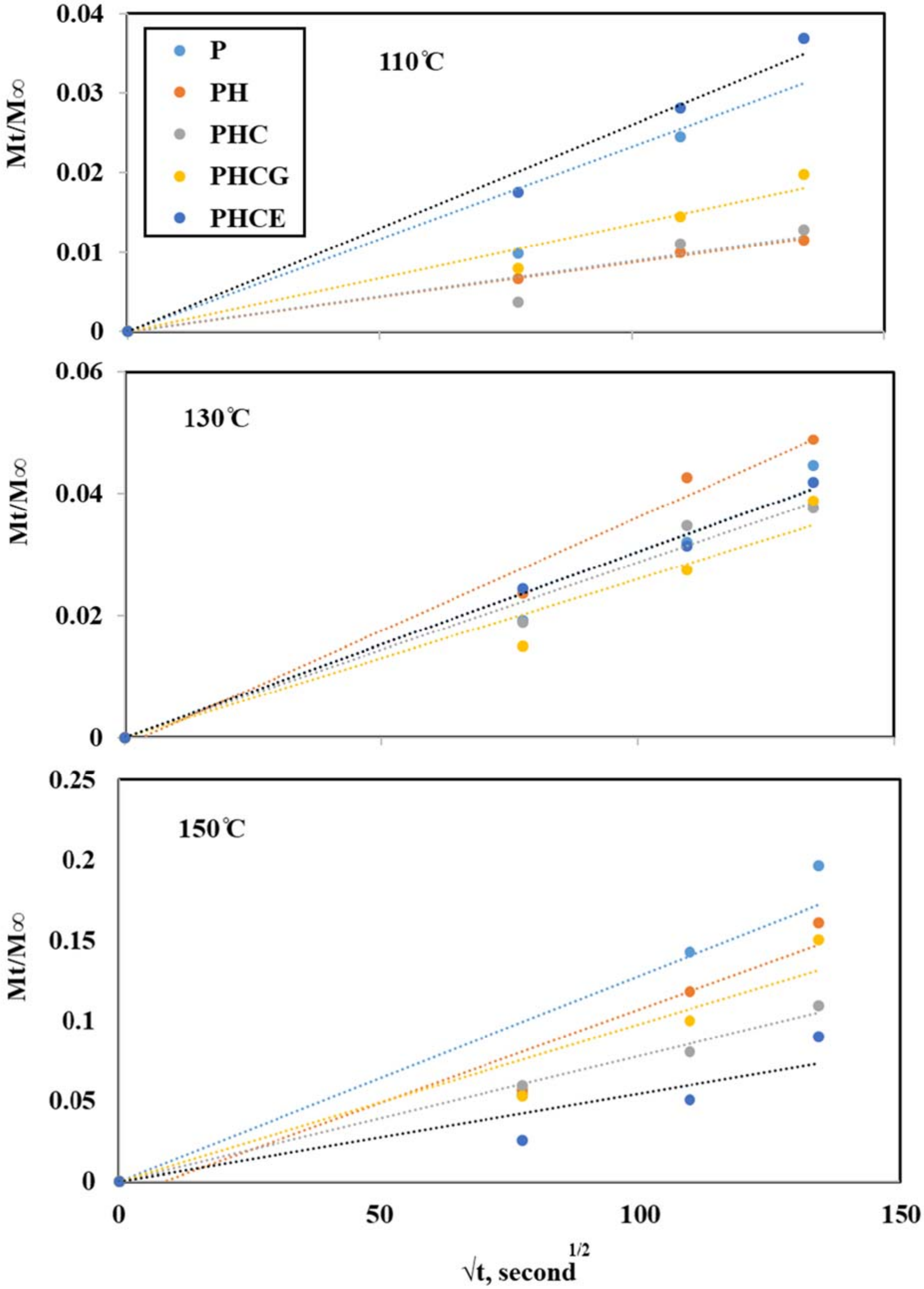

Figure 3. Fractional loss from the films during heat treatment.

Table 3. Diffusion coefficients of plasticizer during heat treatment

Sample Code	100°C		130°C		150°C	
	D_e*10^{16}, (m^2/sec)	R^2_{diff}	D_e*10^{16}, (m^2/sec)	R^2_{diff}	D_e*10^{16}, (m^2/sec)	R^2_{diff}
P	1.77	0.87	4.81	0.97	74.7	0.88
PH	0.36	1	4.37	0.98	53.5	0.93
PHC	0.27	0.88	3.98	0.97	28.3	0.99
PHCG	0.44	0.96	3.98	0.95	44.2	0.92
PHCE	2.54	0.99	3.98	0.99	11	0.85

Diffusion coefficients of plasticizer from the films increased with increasing temperature. (Table 2). The effective diffusion coefficients are0.27-2.54 $10^{-16}m^2$/sec, 3.98-4.81 $10^{-16}m^2$/sec, and 11-74.7 $10^{-16}m^2$/sec at 100, 130 and 150°C, respectively. The order of diffusivities was determined as P>PH>PHCG>PHC>PHCE, at 150°C. The highest and lowest effective diffusivity values were observed in films containing without filler and cross-linked modified filler with EDC, respectively.

It has been reported in the literature that polymers filled with inorganic components, prevent the migration of components [21]. In this study, the finding that adding inorganic filler to PVC, and modifying and cross-linking the filler with chitosan generally reduced the migration of plasticizers to air.

To determine the effect of temperature on diffusion, high-temperature data are extrapolated to lower temperatures [22, 23]. Thus, the relationship of the D_e with temperature can be given in Arrhenius form (Eq. 4).

$$D_e = D_o\exp(-E_D / (RT)) \qquad (4)$$

In this equation; D_e is the effective diffusion coefficient (m^2/ sec), D_o is the pre-exponential factor (m^2/ sec), E_D is the diffusion activation energy (J/mol), R is the universal gas constant (J/molK) and T is the temperature (K).

The E_D values for diffusion of plasticizers are inversely proportional to the D_e values [22, 24].

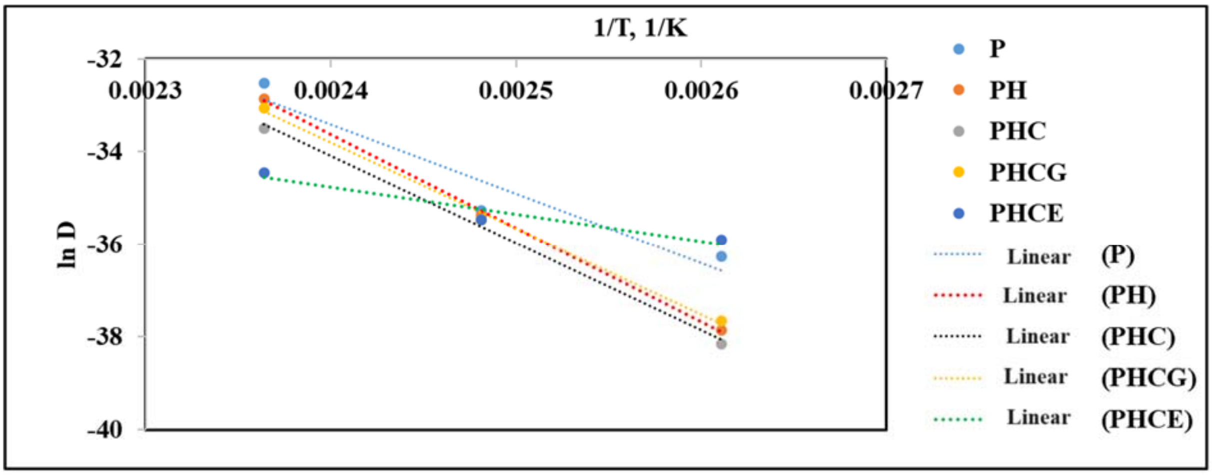

Figure 4. $\ln D_e$ versus 1/T(K^{-1}) graphs for diffusion of plasticizer

$E_D$values(kJ/mol) (Table 4) were calculated from the slope of Arrheniusplots as $\ln D_e$ versus 1/T as K^{-1}(Figure 4).

Table 4 Activation energy for the diffusion of plasticizers

Film Code	Activation Energy for diffusion, E_D (kJ/mol)	R^2
P	125.0	0.92
PH	168.5	1.0
PHC	157.1	1.0
PHCG	154.8	1.0
PHCE	490.0	0.94

E_D values are different as a result of the different mobility of the plasticizer in the matrix and different diffusion rates. While the activation energy for diffusion was lowest in the film containing no filler, the addition of filler increased the activation energy, and the highest value was observed in the film containing chitosan-modified filler cross-linked with EDC.

4. Conclusion

Plasticizers used to make PVC soft and flexible are toxic substances that are released into the environment because they are physically bonded, causing harmful effects on human health and meanwhile, the performance of the products decreases. This study focuses on the effect of modification of the filler in reducing plasticizer diffusion. FTIR results show that the OI values of each film generally increased with increasing heat treatment. The highest and lowest OI values were observed in films without filler and cross-linked modified filler with gluteraldehyde, respectively. At high heat treatment temperatures, the highest weight loss was observed in the film containing no filler, while the lowest was observed in the film containing hydrotalcite modified with chitosan cross-linked with EDC. The order of effective diffusivity of the plasticizer is determined as P>PH>PHCG>PHC>PHCE, at 150°C. The highest and lowest effective diffusivity values were observed in films containing without filler and cross-linked modified filler with EDC, respectively. The addition of inorganic components reduced the migration of plasticizers. Reducing migration also reduces toxicological emissions and prevents premature brittleness of plastics. Due to the limited internal compatibility between filler and polymer, when the filler was modified with organic substances (chitosan), their surface energy decreased and provided better adhesion to the polymer matrix, preventing the plasticizer from separating from the polymer surface, further reducing migration. Because organic cations strengthen the inner surface bonds between the polymer and silicate. Cross-linking of chitosan increased the interaction with the inorganic filler and was effective in reducing migration. Limitations regarding the use of GA relate to its high cytotoxicity. EDC activates carboxylic groups by reacting with amine groups and forming amide bonds. It does not form toxic aldehydes as a result of this cross-linking, and studies have shown that it is more biocompatible than glutaraldehyde. In the results of this study, it was observed that the composite film with the least weight loss and migration was the film containing modified hydrotalcite with chitosan cross-linked with EDC. The addition of inorganic filler to PVC, modification of the filler with chitosan, and cross-linking of the filler generally reduced the migration of plasticizers into the air and increased the activation energy for diffusion. It is thought that with the modification of the filler, plasticizer migration decreased as a result of the increased interaction between the inorganic filler and the organic polymer.

Funding

The financial support of the Uşak University Research Fund (Project No: UBAP 01/ 2024/MF004) is gratefully acknowledged.

Conflict of Interest

Since the article is single-authored, there is no conflict of interest.

Ethics Consent

Ethics committee approval is not required for this study.

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