Spectrophotometric characterization of plasticizer migration in poly(vinyl chloride)-based artificial leather

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HIGHLIGHTS

- Plasticized PVC is a remarkable alternative to genuine leather.
- Choosing the correct plasticizer is crucial to get the desired artificial leathers.
- A new spectrophotometric method for the determination of plasticizer migration.
- Chemical structure is the prominent determinant for the migration of plasticizers.

GRAPHICAL ABSTRACT
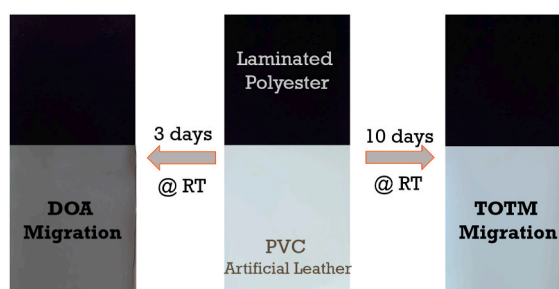
ABSTRACT

Plasticized polyvinyl chloride (PVC) is one of the most commonly used material in the manufacture of artificial leather because of its flexibility, high durability and low cost. While hundreds of plasticizers have been produced to obtain PVC films and artificial leathers, it is important to choose the correct plasticizer to produce the desired products. Therefore, here five non-phthalate type plasticizers with three levels (40 phr, 60 phr and 80 phr); trioctyl trimelliate (TOTM), tributyl trimelliate (TBTM), dioctyl terephthalate (DOTP), dioctyl adipate (DOA) and dioctyl succinate (BIO) were used to prepare plasticized PVC films. They were studied in terms of their compabilities with PVC polymer chains, and their effects on mechanical properties of PVC films. Although, linear plasticizers e.g. BIO and DOA have higher compabilities with PVC, a branched plasticizer e.g. TOTM showed higher mechanical properties. Moreover, a new spectrophotometric method for determination of plasticizer migration from PVC polymer matrix to the surface of artifical leather was developed. According to lightness change on the surface of PVC artifical leather before and after heat treatment at 70 °C, the migration rates of used plasticizers increase in this order: TOTM < TBTM < DOTP < BIO < DOA.

1. Introduction

Artificial leather has similar appearance and durability with real leather at lower cost. Its production is being less labor-intensive and also protects animal welfare. These practical and ethical considerations give importance to production of artificial leathers which are used in wide area such as handbag, shoes, upholstery, garment, automotive covering, medical and marine equipments. Polyvinyl chloride (PVC) is one of the most employed thermoplastic material to produce artificial leather [1, 2]. Since pure PVC has relatively rigid and brittle features, plasticizers

are added to PVC to obtain the desired durability and flexibility [3]. The PVC artificial leather, which is called "vinyl coatings", is widely preferred material because of its low cost, high durability and easy to clean compared to other fabrics and real leathers. Moreover, easy colorization, designation and embossment makes PVC leathers a "must-have product".

The presence of chlorine (Cl) in the monomer of a PVC polymer $-[CH_2-CHCl]_n-$ increases the interchain attraction via dipole-dipole forces which make PVC rigid with large values of hardness and stiffness (poor thermal stability) [4–6]. However, absorption of plasticizer molecules inside PVC chains increases its flexibility and workability. As a result, plasticizers are used to make PVC applicable in different areas. Plasticizers are generally high boiling point organic liquids that reduce the melting and glass transition temperatures of polymers [7,8]. Therefore, addition of plasticizers reduces tensile modulus and tensile strength, and also increases elongation at break point [9,10].

The widely used plasticizers are generally low molecular weight or monomeric plasticizers, mostly derived from phthalic acids, and the others are phosphates, trimelliates, adipates, citrates, etc. [11]. Most plasticizers are usually prepared via esterification reactions between corresponding acids/anhydrides and alcohols in the presence of acidic catalysts [12,13]. Since plasticizers do not bind chemically to the PVC, they tend to migrate from PVC into other material [14]. This leads to some problems, for example food contaminations, toxicity, deformation of material due to losing its flexibility, etc. [15]. The migration of plasticizers depends on the type of plasticizer, nature of contact material, and also temperature [15,16]. Furthermore, several phthalate esters are suspected to being responsible of cancer propagation in mice and rats. Therefore, many of the phthalate esters using in the skin contact material were restricted in the world after they were listed in the SVCH (Substances of Very High Concern) by ECHA (European Chemicals Agency) [17,18]. Nowadays, there is an increasing interest in the use of phthalate free plasticizers those are characterized by low toxicity, low migration, and good compatibility with several plastics, resins, rubbers and elastomers in substitution of conventional plasticizers [19–24]. In this work, different than the restricted plasticizers; trimelliate, adipate, succinate and terephthalate types of plasticizers were used.

The aim of this study is to obtain and characterize PVC films which are used in artificial leather production using different kinds of plasticizers, and to develop a new method to study plasticizer migration. Here, five types phthalate free plasticizers; trioctyl trimelliate (TOTM), tributyl trimelliate (TBTM), dioctyl terephthalate (DOTP), dioctyl adipate (DOA) and dioctyl succinate (BIO) were used to obtain PVC films and artificial leathers including three different plasticizers compositions, 40 phr, 60 phr and 80 phr. Fig. 1 shows chemical structures and molecular weights of the used plasticizers. The degree of conjugation
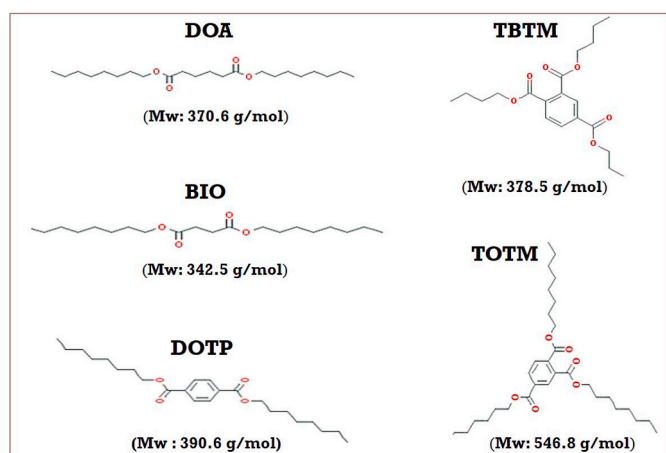
between plasticizers and PVC was studied with FTIR spectroscopy. Mechanical properties of plasticized PVC films in terms of tensile strength, maximum elongation at break point, tear strength and cold flexibility were studied. Thus, this study could be a guide to obtaining a desired product in optimum formulation according to area of usage. Moreover, an easy spectrophotometric method was developed to study migration of plasticizers. Briefly, one side of the PVC artificial leather was laminated with polyester fabric included disperse black dye. Movement of the black disperse dye with plasticizers from the laminated polyester fabric to the other side of PVC artificial leather was monitored using a spectrophotometer within 24 h' time period.

2. Experimental

2.1. Materials and methods

Trioctyl trimellitate (TOTM), tributyl trimellitate (TBTM), dioctyl terephthalate (DOTP), dioctyl adipate (DOA) and dioctyl succinate (BIO) were supplied by Plastifay Kimya Company. Polyvinyl chloride (PVC 682) was supplied by INOVYN. Three sets of each plastisol were prepared containing 40, 60 and 80 phr of plasticizers with 100 g of PVC resin. For every plastisol, to improve heat and light stabilization 2 g of liquid Ca–Zn stabilizer (NT-1) and epoxy soybean oil (Plasteks) were added. Also, to avoid presence of extra air bubbles in final test samples, BYK 3155 air release additive was used (1% of plastisol w/w). All these materials were mixed in laboratory mixer until dispersion of PVC resin homogeneously. The plastisols were hold for release their air content for at least 10 min before they were used for transfer coating. Transfer coating was used to obtain PVC films. 705 ultramat plain from Arjo Wiggins was used as transfer paper, which has flat surface to obtain homogenous thickness in all part of coating. First, the transfer paper was heated to 190 °C to avoid any surface defect on it. 0.35 mm coating was managed by using jolly pilot on to transfer paper, then it was put in the oven at 190 °C for 2 min for gelification. After that, 0.35 mm s layer coating thickness was arranged by Jolly Pilot, followed by heating at 190 °C for 2 min again.

2.2. Characterization

Fourier transform infrared spectra (FTIR) of plasticizers, PVC and plastisols were taken by Bruker Alpha II FTIR with the attenuated total reflectance (ATR) accessory. PVC was measured as pressed solid. For liquid samples, plasticizers and plastisols, a drop of samples was put on the crystal and measured.

Tensile strength and elongation measurements of specimens with 50 mm × 150 × 0.7 mm in dimensions were performed by Devotrans tensile tester at a constant speed of 100 mm/min. The pre-load of test was about 0.1–0.5 N to obtain accurate value of elongation. The tensile strength was determined as the maximum force at break point divided by the initial cross-sectional area of the specimen. The elongation at break was given as a percentage of the original length of the specimen.

For tear strength, trouser tear method was applied. It is based on making split on test specimen (50 mm × 200 mm X 0.7 mm) and measuring its tear strength (Force/thickness) by using tensile strength tester. For cold flexibility tests, the PVC films were plasticized with 80 phr of the plasticizers and cut in 45 mm × 70 mm dimensions. The flexometer is equipped with a flex counter and a freezing compartment in order to obtain the tests in a cold condition (at −20 °C). The test specimen was held between clamps, and almost 40 flexes were done in 1 min. Experiments were performed in triplicate.

2.3. Migration test

For the migration test, disperse black dye included polyester fabric was laminated on the one face of the PVC films. This method gives quick results for the migration of plasticizers. Because of clear observation of

Fig. 1. Chemical structures and molecular weights of the plasticizers: DOA, BIO, DOTP, TBTM and TOTM.

color change, 3% TiO$_2$ powder was added in to the plastisols which gives bright white color. After preparation of TiO$_2$ containing plastisols, two times transfer coatings were applied just as mentioned above. On the top of the two layers of films, third layer was applied for the lamination of polyester fabric at 190 °C for 2 min. After that, the artificial leathers were put in the oven at 70 °C for 24 h or they were kept at RT for 10 days. The lightness changes of artificial leather which was bright at initial, were measured using a spectrophotometer (Konica Minolta CM-2500d) at different times.

The migration of plasticizers from PVC artificial films was also evaluated in terms of the weight loss percentages. PVC films (3.5 g), which are used in artificial leathers, including 60 phr of different plasticizers were soaked in 400 mL water or isobutanol solutions. After 48 h, the samples were wiped up and dried in oven at 40 °C for 2 h. Drying the samples in oven more than 2 h did not change the results. After that, the samples were weighed and the plasticizer loss was calculated with Eq. (1).

$$Weight\ loss(\%) = \left[(W1 - W2)/_{W1} \right] \times 100 \qquad (1)$$

where W1 is the initial weight of PVC sample and W2 is the final weight of PVC sample [25].

3. Results and discussion

3.1. The degree of conjugation between plasticizers and PVC polymer chains

Fourier transform infrared spectroscopy (FTIR) is a widely used technique for studying chemical changes in the PVC plasticization. FTIR with the attenuated total reflectance (ATR) accessory (ATR-FTIR) allows obtaining spectrum of liquid or solid materials without any sampling method (i.e. pellet preparation). Fig. 2 shows ATR-FTIR spectra of PVC resin and plasticizers which were used in this work.

The strength of interactions between PVC and plasticizers could be analyzed through the changes of C–Cl and C=O IR bands in the regions of 600–700 cm^{-1} and 1680-1780 cm^{-1}, respectively. The C–Cl vibration energies depend on the conformational structure of the polymer and on the atoms surrounding the C–Cl bonds [26]. In addition, the dipole-dipole interactions between C=O in plasticizers and C–Cl in PVC shifts the C=O band to lower wavenumbers (red shift) [27]. In order to study the interaction between the PVC and plasticizers, the C–Cl and

C=O stretching vibrations were analyzed before and after plasticization. The degree of conjugation between plasticizers and PVC is called compability. A plasticizer showing high compability with PVC induces higher spectral changes in the FTIR spectra of the plasticizer and PVC [28]. Fig. 3 (A) shows the normalized C–Cl stretching vibrations bands of PVC and obtained different plastisols centered at 615 and 635 cm^{-1}. The used plasticizer levels are 40, 60 and 80 phr. The two bands at 615 and 635 cm^{-1} are assigned to the C–Cl stretching vibrations found in the noncrystalline (atactic) and crystalline (tactic) regions of PVC chains, respectively [28]. After plasticization, C–Cl stretching vibrations found in the noncrystalline (atactic) region shifts to higher wavenumbers.

while the C–Cl stretching vibrations found in the crystalline (tactic) region do not shift. This supports the idea that amorphous (not ordered) regions of PVC are more prone to interact with plasticizers compared to the ordered regions of PVC.

Furthermore, in the normalized spectra, variations in the intensity ratio of two bands, I_{615}/I_{635}, were observed for PVC and different plastisols. A plasticizer showing higher compability with PVC changes the ratio of I_{615}/I_{635} more. Since plasticizers interact with amorphous regions of PVC more, the I_{615}/I_{635} ratio decreases more upon plasticization with more compatible plasticizers. The I_{615}/I_{635} ratios in the spectra of PVC and plastisols containing different plasticizers with 40, 60 and 80 phr contents are in these orders:

PVC ≈ TBTM-PVC > TOTM-PVC ≈ DOA-PVC ≈ BIO-PVC > DOTP-PVC for 40 phr, PVC > TBTM-PVC > TOTM-PVC > BIO-PVC ≈ DOA-PVC ≈ DOTP-PVC for 60 phr, and.

PVC > TBTM-PVC ≈ TOTM-PVC ≈ DOA-PVC > BIO-PVC > DOTP-PVC for 80 phr.

These show that BIO, DOA and DOTP have stronger interaction with PVC therefore they have higher compability with PVC. The common features of these plasticizers are having linear conformation and similar molecular weights. On the other hand, branched-chain trimellitate plasticizers, TBTM and TOTM, have less compability with PVC. Furthermore, the compability between the PVC and trimellitate plasticizers increases with increasing the molecular weight. Therefore, compability between TOTM (Mw: 546.8 g/mol) and PVC polymer chains is higher than the compability between TBTM (Mw: 378.5 g/mol) and PVC.

Similarly, the C=O bond in plasticizers is affected as a consequence of the interaction with PVC. The C=O stretching vibration band of the plasticizer shifts to lower wavenumbers after PVC plasticization. Fig. 4 shows C=O IR bands of the pure plasticizers and PVC plastisols containing 40, 60 and 80 phr plasticizers in the region of 1680–1780 cm^{-1}. A significant red shift of C=O band was observed when DOA or BIO were used after PVC plasticization. Also, a comparable red shift of C=O band was observed when another linear plasticizer DOTP with a ring substitution was used for the PVC plasticization. But, there were not any observable red shifts when branched-chain trimellitate plasticizers TBTM and TOTM were used for the PVC plasticization. According to the shift extent of C=O band, the order of compability is TBTM ≈ TOTM < DOTP ≈ BIO ≈ DOA for the plasticizers with 40, 60 and 80 phr contents. The analysis of both bands, C–Cl and C=O stretching bands, collectively revealed that DOTP, DOA and BIO have higher compabilities with PVC.

3.2. The mechanical properties of plasticized PVC films prepared with different plasticizers

In order to compare the mechanical properties of plasticized PVC films prepared with different plasticizers, tensile strength, elongation at break, tear strength and cold flexibility were studied. Increasing the level of plasticizers decreased the tensile and tear strengths, while the elongation at break increased gradually. Solvation of plasticizers in the PVC matrix weakens the intramolecular bindings of the PVC chains, and increases the distance between polymer chains which causes higher mobility of molecular chains. Fig. 5 (A) shows the tensile strength values of PVC films plasticized with 40, 60 and 80 phr of different plasticizers.
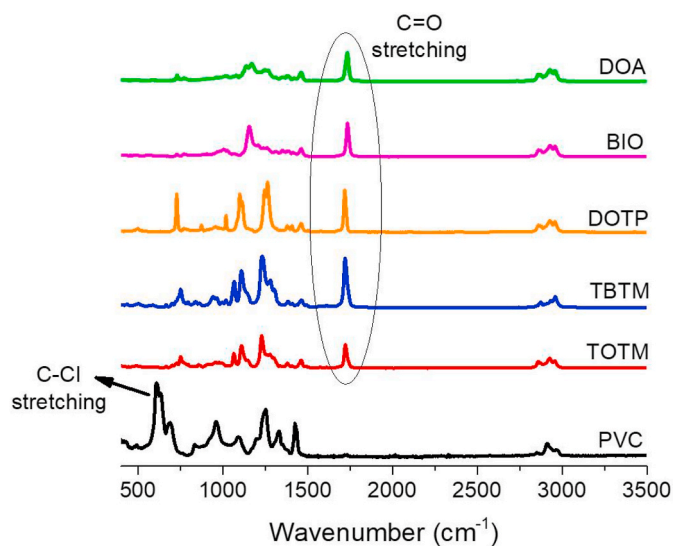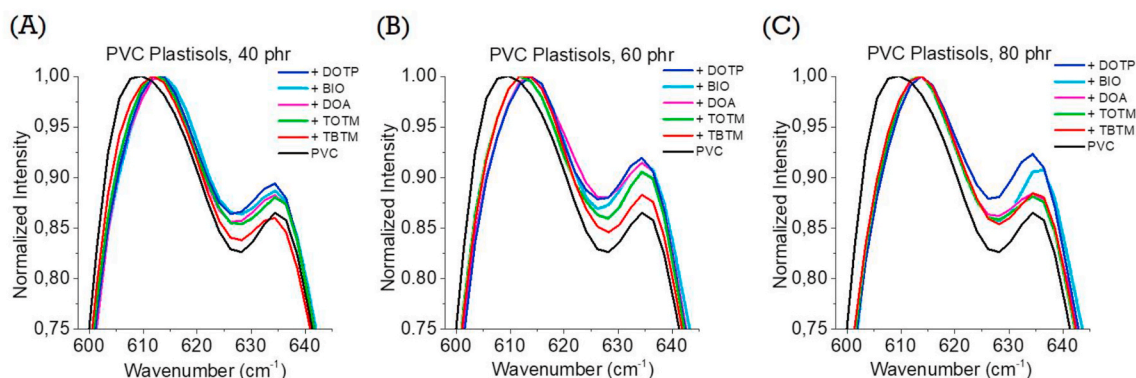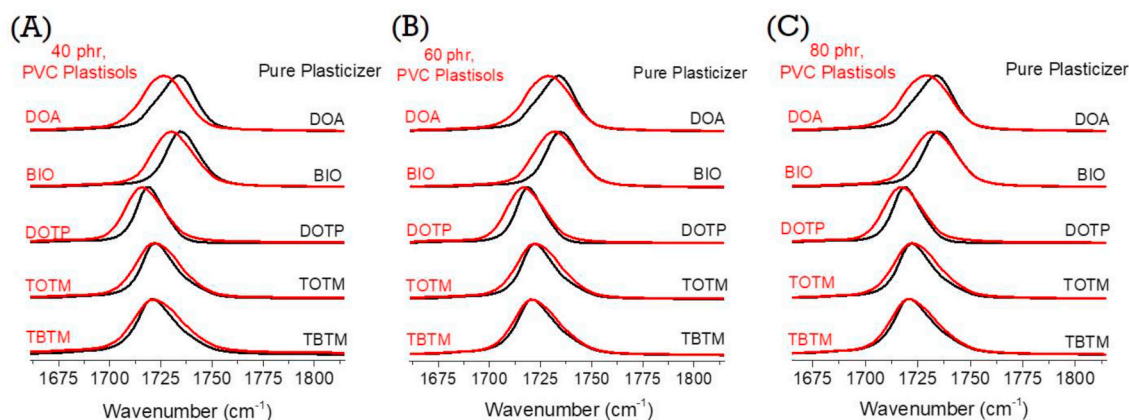

Fig. 2. ATR-FTIR spectra of PVC resin and plasticizers which were used in this work.

Fig. 3. C–Cl stretching vibrations bands of PVC resin and PVC plastisols prepared with five different plasticizers: DOTP, BIO, DOA, TOTM or TBTM with three different levels; (A) 40 phr, (B) 60 phr and (C) 80 phr.

Fig. 4. C═O stretching vibrations bands of pure plasticizers (black) and PVC plastisols (red) prepared with five different plasticizers: DOTP, BIO, DOA, TOTM or TBTM with three different levels; (A) 40 phr, (B) 60 phr and (C) 80 phr. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
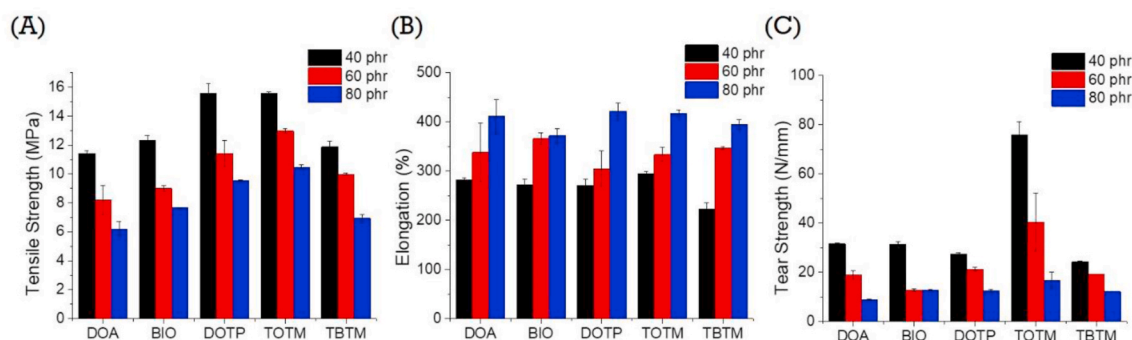
Fig. 5. (A) Tensile strengths, (B) maximum elongation percentages at breaking point and (C) tear strengths of the plasticized PVC with DOA, BIO, DOTP, TOTM or TBTM with three different levels; 40 phr (black), 60 phr (red) and 80 phr (blue). Experiments were performed in triplicate. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Upon the increasing plasticizer content, tensile strengths of PVC films decreased. The tensile strengths of PVC films containing DOTP or TOTM are higher than those of PVC films containing other plasticizers at all three levels. The maximum tensile strengths of 16 ± 0.6 MPa and 16 ± 0.06 MPa were obtained with DOTP or TOTM at 40 phr. Also, the maximum tensile strengths of 13 ± 0.17 MPa and 10 ± 0.15 MPa were obtained with TOTM at 60 phr and 80 phr contents, respectively. On the other hand, elongation at break values increased with plasticizers content and also they are similar when different plasticizers were used. (Fig. 5 (B)). At 40 phr, 60 phr and 80 phr levels, the elongation at break

values were around 250%, 350% and 400%, respectively.

Fig. 5 (C) shows the effect of plasticizers on tear strength of PVC films. Similar to the tensile strength, the tear strength decreases with increasing plasticizer level. The tear strengths of PVC films plasticized with TOTM at 40 phr and 60 phr levels were 76 ± 5 and 40 ± 11 N/mm, respectively, which are much higher than the tear strengths of PVC films plasticized with other plasticizers, probably due to the branched structure with a higher molecular weight. However, all the PVC films with 80 phr plasticizers have similar tear strengths. Yet, the maximum tear strength of 17 ± 3 N/mm was obtained with TOTM at 80 phr.

In addition, the flexible PVC films used to prepare artificial leathers must have a resistance to cold weather. They must be still wearable and useable for a long time in cold seasons or in cold areas. The cold flexibility performances of PVC films plasticized with 80 phr of TOTM, TBTM, DOTP, BIO or DOA were studied at −20 °C. The highest cold flexible feature of PVC was obtained when linear plasticizers DOA and BIO were used. After about 550.000 and 450.000 flex cycles, DOA and BIO plasticized PVC films were cracked, respectively. Other PVC films plasticized with TOTM and DOTP were cracked after about 300.000 flex cycles. On the other hand, TBTM plasticized PVC film was cracked only after 100.000 flex cycles. The cold flexibility results were in accordance with the compability results and elongation results. FTIR results showed that DOA and BIO have higher compatibilities with PVC polymer chains. As a result, PVC films obtained using these plasticizers have higher resistance to break at cold conditions. On the other hand, PVC plasticized with TBTM which has the lowest compability with PVC has lower resistance to break at cold conditions.

3.3. Determination of plasticizer migration spectrometrically

Plasticizers can be removed from PVC artificial leathers because they usually are not chemically bound to PVC [8]. This can lead to unwanted results e.g. reducing flexibility, becoming more brittle and shortening physical life. This behavior of plasticizers also results in environmental pollution and health effect, i.e. skin contact with migrated plasticizers and their penetration into body [29]. Here, migration rates of plasticizers were evaluated using a lightness change method. In order to observe a better lightness change, TiO_2 was added into the plastisols which gives a bright white color. Fig. 6(A) and (B) show the pictures of the produced PVC artificial leathers, one side is laminated with polyester fabric included disperse black dye. Fig. 6 (B) shows the pictures of artificial leathers obtained by using 60 phr of TOTM, TBTM, DOTP, DOA or BIO before (top) and after 70 °C heat treatment within 24 h (bottom). The surfaces of prepared artificial PVC leathers which were whitish at

the beginning became darker with time at 70 °C. Movement of the disperse black dye from laminated polyester to the PVC surface was correlated with the migration rate of plasticizers. Therefore, the surface darkness characterized spectrophotometrically is related with the migration rate of plasticizers (Fig. 6 (C)). At first 6 h, the migration rates of BIO and DOA from PVC are much higher than those of others. The lightness decreased from 94% to 66% and to 62% when BIO or DOA was used, respectively (Fig. 6 (C)). Instead, the lightness decreased from 94% to 83% when DOTP was used, and decreased from 94% to only 89% when TOTM or TBTM was used. After 24 h, the lightness decreased only from 66% to 57% and from 62% to 56% when 60 phr BIO or DOA was used, respectively, compared to the 6 h' results. For BIO and DOA, the lightness decrease ceased after 6 h. On the other hand, the lightness decrease sustained till 24 h when 60 phr of TOTM, TBTM and DOTP were used. The lightness decreased from 89% to 69% and to 66% when TOTM or TBTM was used, and also from 83% to 61% when DOTP was used. The migration rates of plasticizers were also studied at room temperature. For DOA, the decrease of lightness ceased after three days, lightness decreased to 62%, however the decrease of lightness pursued when TOTM was used even after eleven days (with 92% of lightness).

Decreasing lightness of artificial leather with time was also observed when other concentrations of plasticizers, at 40 phr and 80 phr, were used (Fig. 7 (A) and (B)). At 40 phr plasticizer loading, migrations of TOTM, TBTM and DOTP were very limited and much less than those of BIO and DOA after 24 h. However, at 80 phr plasticizer content, migrations of all plasticizers except TOTM have similar migration results after 24 h. Fig. 7 (C) shows the lightness change of the PVC artificial leather surface versus plasticizer level after 70 °C heat treatment within 24 h. Since BIO and DOA have higher migration rates, they changed the.

lightness of PVC similarly at all levels. But, lightness change depends on the plasticizer content for other plasticizers. The migration rates of TOTM were found to be lower at all plasticizer levels.

The migration rate of plasticizers depends on their structure, molecular weight, number of polar groups, compability and their
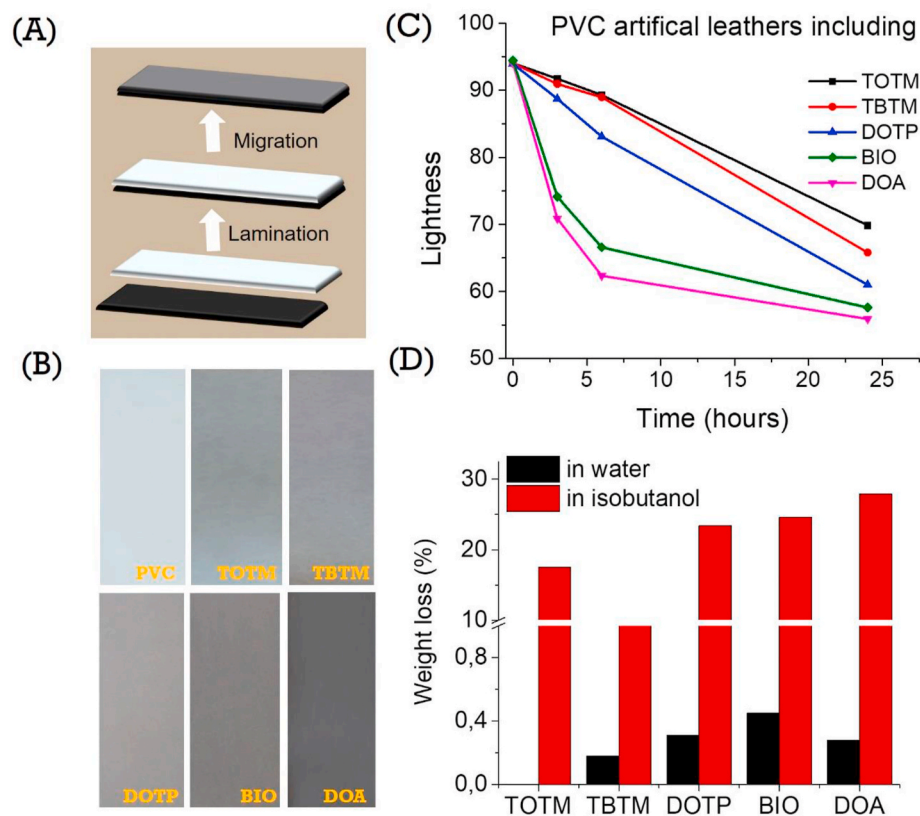

Fig. 6. (A) Pictures of the produced PVC artificial leather, one side is laminated with polyester fabric included disperse black dye, and plasticizer diffusion with black dye. (B) Pictures of PVC artificial leathers prepared using 60 phr of TOTM, TBTM, DOTP, BIO or DOA: initial (upper-left) and after 24 h heat treatment at 70 °C. (C) Lightness values of the PVC artificial leathers shown in (B) before and after 3 h, 6 h and 24 h heat treatment. (C) Weight loss of PVC films prepared using 60 phr of TOTM, TBTM, DOTP, BIO or DOA after soaked in water (black) or isobutanol (red) 48 h. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
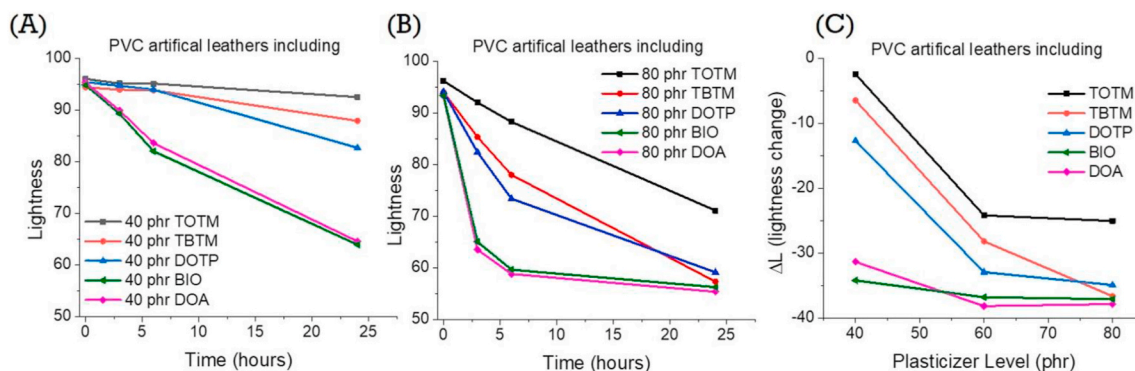
Fig. 7. Lightness values of the PVC artificial leathers prepared using (A) 40 phr and (B) 80 phr of TOTM, TBTM, DOTP, BIO or DOA before and after 3 h, 6 h and 24 h heat treatment at 70 °C. (C) Effects of plasticizer level (phr) on the lightness changes of the PVC artificial leathers.

concentration in the PVC resin [7,30]. Having linear structures and relatively lower molecular weights, BIO and DOA showed higher migration rates compared to other plasticizers. Although, FTIR results showed that BIO and DOA have higher compability with PVC, migration rates of them are still higher than others. This showed that chemical structure is the prominent determinant for the migration of plasticizers. The migration rate of another linear plasticizer of DOTP with an aromatic group is less than that of BIO and DOA, but it is higher than that of branched plasticizers TOTM and TBTM. The effect of molecular weight of plasticizer on the migration behavior can be analyzed within branched plasticizers, TOTM and TBTM, which have very different molecular weights. At the end of 24 h, TOTM with a higher molecular weight (M_w: 546.79 g/mol) has a lower migration rate compared to that of TBTM (M_w: 378.5 g/mol) at all plasticizer's levels. Other used plasticizers have very similar molecular weights which hinders the studying effect of molecular weights on the migration rate.

Plasticizer migration from PVC films can be also studied by the leaching test using two different solvents, water and isobutanol [31,32]. The prepared PVC test samples including 60 phr of different plasticizers were soaked in the solvents for 48 h. After drying the samples completely, samples were weighed to measure the weight loss. While the weight loss is very low in water which is less than 1%, it is much higher in isobutanol which is in the range of 10–25%. Fig. 6 (D) showed that plasticizers migrate from the PVC films to water in this order BIO > DOTP ≈ DOA > TBTM. But TOTM migration from the PVC film was not observed. These results are in accordance with the spectrophotometric results which showed this migration rate order: BIO > DOA > DOTP > TBTM > TOTM (Fig. 6 (B)). Since the PVC artificial leather samples were treated at 70 °C, the migration of TOTM was detected from the lightness experiments. Fig. 6 (C) also showed the migration of plasticizers from the PVC films to isobutanol. Different than water, an organic solvent of isobutanol can diffuse into PVC and helps plasticizers to migrate out. Therefore, the weight loss of PVC films much higher in isobutanol than that of PVC films in water. Similarly, DOA, BIO and DOTP have higher migration abilities when isobutanol was used as a medium, but also TBTM and TOTM migrated significantly from PVC films to isobutanol medium. Since used plasticizers are also organic solvents, they interact with isobutanol more than water which favors migration. The rates of weight loss for PVC films performed in the isobutanol medium are also correlated with the results obtained from the spectrophotometric method. Therefore, the developed method based on the spectrophotometer can be used to monitor the plasticizer migration.

4. Conclusion

In this work, different PVC films and artificial leathers were prepared using five types of phthalate free plasticizers (TOTM, TBTM, DOTP, BIO, DOA) at different levels (e.g. 40 phr, 60 phr and 80 phr). The products were characterized in terms of the interaction between PVC polymer and

plasticizers using FTIR spectroscopy. Analyses of C–Cl and C=O stretching bands revealed that linear plasticizers DOTP, BIO and DOA have greater interactions with PVC polymer chains. Mechanical properties of the prepared plasticized PVC films were also found different from each other with respect to tensile strength, elongation at break point, tear strength and cold flexibility. When TOTM was used as a plasticizer, PVC films gained a much higher tear strength. In addition, TOTM or DOTP including plasticized PVC films have relatively higher tensile strengths than that of other produced PVC films. Cold flexibility test results are also in accordance with the compability results. DOA and BIO plasticized PVC films have a higher resistance to break at −20 °C, but TBTM plasticized PVC films have a lower resistance to break. Differently, migrations of plasticizers were determined by a developed spectrophotometric method. Movement of the black disperse dye with plasticizers at 70 °C within 24 h was monitored using a spectrophotometer. The lightness change on the surface of PVC artificial leather was correlated with the migration behaviors of the used plasticizers. BIO and DOA which have linear structures showed fast migration rate compared to others. On the other hand, TOTM with a branched structure and relatively higher molecular weight migrated very slowly. For comparison, migration behaviors of the plasticizer were studied with the leaching method. Obtaining the similar migration trends of plasticizers with both methods showed that migration of plasticizers from artificial leathers can be studied easily and quickly with the developed spectrometrical method.

CRediT authorship contribution statement

Iffet Akkus Altindag: Conceptualization, Investigation, Methodology. **Yasar Akdogan:** Conceptualization, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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