

**OBTAINING AND CHARACTERIZATION OF
ARTIFICIAL LEATHER USING DIFFERENT
TYPES OF PLASTICIZERS**

**A Thesis Submitted to
the Graduate School of Engineering and Sciences of
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MASTER OF SCIENCE

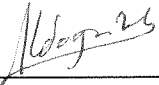
in Materials Science and Engineering

**by
İffet AKKUŞ ALTINDAĞ**

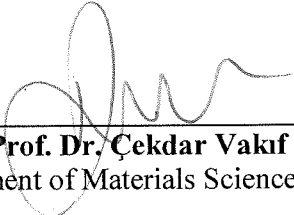
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ABSTRACT

OBTAINING AND CHARACTERIZATION OF ARTIFICIAL LEATHER USING DIFFERENT TYPES OF PLASTICIZERS

Artificial leather is the material which has wide range of use in life from fashion garment, upholstery to technical applications such as defense industries. PVC artificial leather is preferred material by manufacturers because of its low cost and modification can be done easily by using true plasticizers which are fitting for purpose.

In this study, number of six different plasticizers which are non-phthalate plasticizers; trioctyl trimellitate (TOTM), tributyl trimellitate (TBTM), dioctyl terephthalate (DOTP), tributyl citrate (TBC), dioctyl adipate (DOA) and dioctyl succinate (Plast BIO) were used for obtaining artificial leather. To characterize the properties of different kinds of plasticizer in artificial leather, mechanical tests including tensile and tear strengths, elongation at break, cold flexibility and effects of migrability tests were applied. Materials were formulated at three degrees of plasticizers ratios. Also, chemical changes during plasticization were observed using FTIR spectroscopy with ATR accessory, according to types and used levels of plasticizers. In conclusion, plasticizers showed different properties, i.e. material with TOTM plasticized had maximum tear and tensile strengths, while DOA and TBC including materials showed maximum elongation under same load. Considering cold flexibility of six plasticizers, DOA, BIO and TBC have more resistance to cold were obtained, respectively. In addition, migration studies showed that plasticizers including TOTM and TBTM have the least migration properties.

ÖZET

FARKLI PLASTİFİYANLAR KULLANILARAK YAPILAN SUNİ DERİ ELDESİ VE KARAKTERİZASYONU

Suni deri, moda giyim, döşeme ve savunma sanayi gibi hayatın bir çok alanında kullanılan bir malzemedir. PVC suni deriler, ucuz olması ve amaca uygun doğru plastifiyanlar ile kolayca modifiye edilmesi sebebiyle üreticiler tarafından çok tercih edilir.

Bu çalışmada, 6 farklı fitalat içermeyen plastifiyanlardan trioktil trimellitat (TOTM), tribütil trimellitat (TBTM), dioktil tereftalat (DOTP), tribütil sitrat (TBC), dioktil adipat (DOA) ve dioktil suksinat (BIO) suni deri eldesi için kullanılmıştır. Üç farklı oranda hazırlanan plastifiyan çeşitlerinin karakterizasyonu için kopma, yırtılma, uzama, soğuk esnekliği gibi mekanik testler ve migrasyon testi yapılmıştır. Aynı zamanda, plastifiyanların çeşitlerine ve kullanım oranlarına göre plastikleşme sırasındaki kimyasal değişiklikleri ATR aksesuarı kullanılarak incelenmiştir. Sonuç olarak karakterizasyon deneylerinde, plastifiyanlar farklı özellikler göstermiştir. Örneğin TOTM ile hazırlanan ürün en yüksek kopma ve yırtılma dayanımına sahipken, aynı yük altında en yüksek uzama DOA ve TBC kullanımında görülmüştür. Kullanılan altı plastifiyanın soğuk esnekliği dayanımı ele alınacak olursa, sırasıyla DOA, BIO ve TBC en yüksek dayanıma sahip olduğu gözlemlenmiştir. Plastifiyanlar migrasyon özelliğine göre değerlendirilecek olursa, en az migrasyon TOTM ve daha sonra TBTM içeren malzemelerde gözlemlenmiştir.

Dedicated to my husband and my family...

TABLE OF CONTENTS

LIST OF FIGURES	ix
LIST OF TABLES.....	xii
CHAPTER 1. INTRODUCTION	1
1.1. Artificial Leather, History and Area of Usage	1
1.2. General Information About Plasticizers	1
1.3. Theory and Mechanism of Plasticizer Action	3
1.4. Structure of Plasticizers Used in This Study	5
1.5. Aim of the Study	6
CHAPTER 2. EXPERIMENTAL	7
2.1. Materials and Methods	7
2.2. Preparation of Plastisols	7
2.3. Transfer Coatings of Plastisols.....	8
2.4. Fourier Transform Infrared Spectroscopy During Plasticization	8
2.5. Tensile Strength Test.....	8
2.6. Tear Strength Test	9
2.7. Migration Test	9
2.8. Cold Flexibility Test.....	10
2.9. Characterization Tools.....	10
2.9.1. Fourier Transform Infrared Spectroscopy	10
2.9.2. Tensile Tester	11
2.9.3. Flexometer	12
2.9.4. Spectrophotometer.....	12

CHAPTER 3. RESULTS AND DISCUSSION	14
3.1. Infrared Spectral Changes of Plastisols and Plasticized Plastisols	14
3.2. Tensile Strength and Elongation at Break	21
3.3. Tear Strength	24
3.4. Migrability	27
3.5. Cold Flexibility	31
3.6. Summary of Results	32
CHAPTER 4. CONCLUSION	34
REFERENCES	34

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
Figure 1.1. Mapping of three main plasticizer theories (Source: [7]).....	3
Figure 1.2. Schematic representation of plasticizer interaction with PVC resin.	4
Figure 1.3. Chemical structures of used plasticizers.	5
Figure 2.1. Transfer coating using Jolly Pilot on transfer paper.....	7
Figure 2.2. Test specimen look trouser method for tear resistance (Source: [14]).....	9
Figure 2.3. Fourier transform infrared spectroscopy with ATR instrument.....	11
Figure 2.4. Tensile tester.....	12
Figure 2.5. Flexometer.....	12
Figure 2.6. The visualization of CIELAB three dimensional color space (Source:[32]).	13
Figure 2.7. Typical portable spectrophotometer	13
Figure 3.1. Infrared spectra of used plasticizers and PVC 682.....	14
Figure 3.2. FT-IR spectra of PVC, 60 DOTP phr plastisol and pure plasticizer, DOTP.	15
Figure 3.3. FT-IR spectra of PVC, 60 DOA phr plastisol and pure plasticizer, DOA. ..	16
Figure 3.4. FT-IR spectra of plastisols and PVC at 617 cm^{-1} and 637 cm^{-1}	17
Figure 3.5. Compability difference of plastisols based on the ratio of intensity at 637 cm^{-1} and 617 cm^{-1}	18
Figure 3.6. FT-IR spectra of 60 phr DOA plastisols after heat treatment steps	18
Figure 3.7. FT-IR spectra of 60 phr DOTP plastisols after heat treatment steps.....	19
Figure 3.8. Shifting of C=O band of DOA plastisol spectra after heating steps	19
Figure 3.9. Shifting of C=O band of DOTP plastisol spectra after heating steps.....	20
Figure 3.10. C=O bands of TBC plastisols after heating steps.....	20

<u>Figure</u>	<u>Page</u>
Figure 3.11. C=O bands of TBTM plastisols after heating steps	21
Figure 3.12. Load vs. Elongation graphs of plasticized PVC a) at 40 phr plasticizer b) at 60 phr plasticizer c) at 80 phr plasticizer level	22
Figure 3.13. Change in tensile strength and elongation based on plasticizer level a)TOTM, b) TBTM, c) DOTP, d) TBC, e) DOA, f) BIO.....	24
Figure 3.14. Tear Strength of PVC plasticized with a) 40 phr b) 60 phr c) 80 phr of 6 different plasticizers	25
Figure 3.15. Change in tear strength based on plasticizer level	26
Figure 3.16. Color changes of artificial leathers obtained by using TOTM, TBTM, DOTP after 70 °C heat treatment a) initial b) after 24 hours.....	27
Figure 3.17. Color changes of artificial leathers obtained by using TBC, DOA, BIO after 70 °C heat treatment a) initial b) after 24 hours	27
Figure 3.18. Lightness decrease of 40 phr plasticizer level by the migration	28
Figure 3.19. Lightness decrease of 60 phr plasticizer level by the migration	29
Figure 3.20. Lightness decrease of 80 phr plasticizer level by the migration	29
Figure 3.21. Lightness change based on plasticizer kind and level.....	30

LIST OF TABLES

<u>Table</u>	<u>Page</u>
Table 1.1. Chemical formulas and molecular weights of used plasticizers.....	5
Table 3.1. Spectrophotometric lightness change of artificial leathers after 70 °C heat treatment at 40 phr plasticizer level.....	28
Table 3.2. Spectrophotometric lightness change of artificial leather after 70 °C heat treatment at 60 phr plasticizer level.....	28
Table 3.3. Spectrophotometric lightness change of artificial leather after 70 °C heat treatment at 80 phr plasticizer level.....	28
Table 3.4. Summary lightness change of artificial leather based on spectrophotometric measurements.....	30
Table 3.5. Maximum load, elongation and migration order at 40 phr plasticizers.....	31
Table 3.6. Maximum load, elongation and migration order at 60 phr plasticizers.....	32
Table 3.7. Maximum load, elongation and migration order at 80 phr plasticizers.....	32
Table 3.8. Maximum tear force at three plasticizer levels.....	32

CHAPTER 1

INTRODUCTION

1.1. Artificial Leather, History and Area of Usage

The first artificial leathers were developed in the 19th century as Nitrocellulose and then collodion (proxylin) [1]. Collodion was used as protective coating and it was later applied to fabrics which called “Fabricoid”, created and patented by DuPont in 1915. It was used in some area such as upholstery, book bindings, linings and automobile coverings [1, 2]. Since 1960s, fabric coated with PU (polyurethane) and PVC (poly vinyl chloride) became preferred types of artificial leather, because of its look and durability like real leather [3].

Artificial leather has many advantages over real leather which are approximate appearance and durability of real leather at lower cost, its production’s being less labor-intensive, and animal rights. These practical and ethical considerations give importance to artificial leather which is used in wide area from handbag, shoes, upholstery, garment, automotive covering, and medical field to marine applications.

There are two main types of artificial leather. One of them PU leather, which is based on coating a fabric with flexible polyurethane. The other one is PVC artificial leather which is done by adding dye and plasticizer to PVC where plasticizer gives flexibility to the PVC [4].

The PVC artificial leather, which is called “vinyl coatings”, is widely preferred material in life space because of its low cost, high durability and easy to clean compared to other stuffs like fabrics and real leather. On the other hand, it’s easily being colored, designed, embossed and relevant character makes vinyl leathers a “must-have product”.

1.2. General Information About Plasticizers

PVC (polyvinyl chloride) is one of the most used polymers because of its low cost, easy processing and formability especially with plasticizers. In 1951, definition of

plasticizer was developed by IUPAC, which accepted universally as “a substance or material incorporated in a material (a plastic or an elastomer) to increase its flexibility, workability, or distensibility [5, 6]”. The general role of plasticizers is to improve flexibility and make easy to process of polymers because of their decreasing glass transition temperature (T_g) effect on the material [7, 8]. They reduce hardness, elastic modulus of a polymer while they increase fracture and impact resistance [7, 9].

They are classified based on several categories, one of them is their being external or internal plasticizers [8, 10]. Internal plasticizer are attached to the polymer chains by primary bonds chemically based on copolymerization or reaction with the initial polymer, while external plasticizers which are in general low volatile substance and are not attached to polymer chains chemically or by the primary interactions, their interactions are only secondary [7, 11]. The use of external plasticizers is very common because this kind of plasticizers allow wide range of formulations to develop different kinds of products.

The used amount of plasticizers varies depending on the effect wanted in final product. PVC without any plasticizers can be a window profile, pipes, siding but with plasticizers, cables, PVC floorings, automotive trims can be formed even the products can be wearable like garment, shoes or useable in home like upholstery, tablecloth or curtains. The choice of PVC plasticizers for the properties of material is the most important decision to have desired final product. The two structural characteristic acts on plasticizer performance which are mainly depend on chain length or molecular weight and linearity. Generally, solvation power, efficiency, volatility, compability decrease while low temperature flex resistance and brittleness are improving as the ester chain length increases [11].

The widely used plasticizers are generally low molecular weight or monomeric plasticizers, mostly derived from phthalic acids and the others which are used as phosphates, trimellitates, adipates, citrates, etc. [12, 13]. Most plasticizers are usually prepared via esterification reactions between corresponding acids/anhydrides and alcohols in the presence of acidic catalysts [9, 14]. Because of this kind of low molecular weight plasticizers do not bind chemically to the PVC, plasticizer tend to migrate from PVC into other material which movement depends on plasticizer, nature of contact material, and temperature [5, 15]. This migration behavior could lead to some problems, for example food contaminations, health effect, deformation of material due to lose its flexibility, etc. [5]. Several phthalate esters are suspected to being responsible of cancer

propagation in mice and rats, many of the phthalate ester using in the skin contact material was restricted in the world after they were listed in the SVCH (Substances of Very High Concern) by ECHA (European Chemicals Agency) [12, 15-17]. Nowadays, there is an increasing interest in the use of phthalate free plasticizers that are characterized by low toxicity, low migration, and good compatibility with several plastics, resins, rubbers and elastomers in substitution of conventional plasticizers [12, 13, 18-21]. In this work, none of the restricted plasticizers were used, trimellitates, adipates, succinates and terephthalate were processed, which don't have any carcinogenic, genotoxic or developmental effects [12, 13].

1.3. Theory and Mechanism of Plasticizer Action

There are three main theories about plasticizer action, proposed to explain external plasticization to which consider polymer- plasticizer interaction in a parallel way [7, 22] (Figure 1.1).

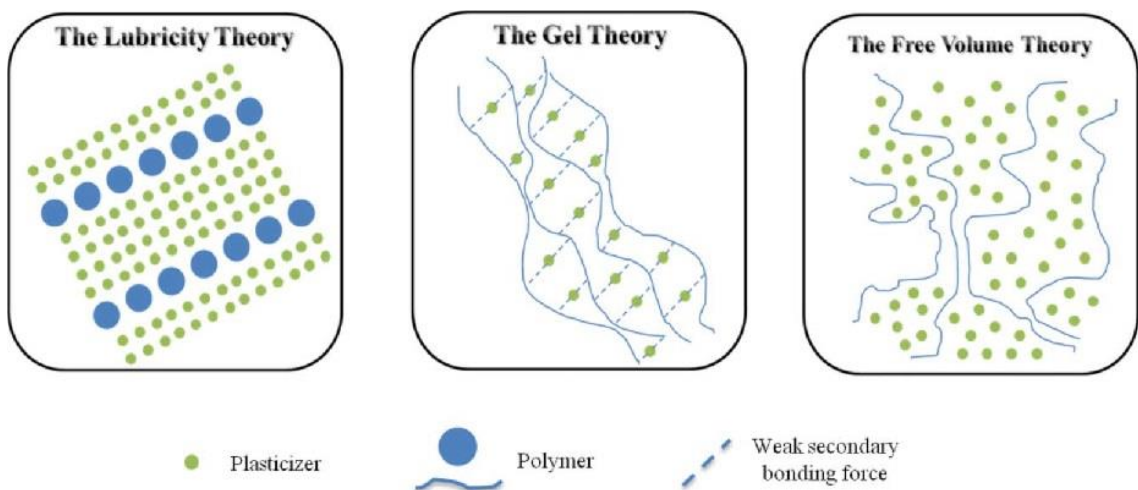


Figure 1.1. Mapping of three main plasticizer theories (Source: [7]).

First, the lubricity theory, it is based on diffusing and inserting of plasticizers into the polymer chains and decreasing the intermolecular frictions [7, 11]. The plasticizer reduces polymer internal resistance to slide and hinders the reformation of the rigid matrix. In view of this theory, plasticized polymer is defined as parallel alternating layers of polymers and plasticizers. On the other hand, the gel theory assumes that the plasticized polymer is a three-dimensional network with plasticizer molecules which interact with

the resin chains by weak secondary forces [7, 11]. The plasticizer breaks the polymer-polymer bonds and interactions, masking these centers of attachment from each other and prevents their reformation [7, 22, 23]. The free volume of a polymer is defined as the internal space available within a polymer. A rigid polymer has very little free volume, when plasticizer added into a polymer, free volume and the motion of the molecule increases and the polymer becomes softer and rubberier. This theory is more comprehensive than other two theories because it is giving more precise explanation about plasticizing which based on relationship between physical and chemical properties and variables of polymers [7, 11, 22, 23].

On the other hand, there is another theory which is thermodynamic and mechanistic theory, is based on migration of plasticizer from plasticized polymer which explains that the plasticizer molecules are not bound to polymer permanently, but there is dynamic equilibrium exist between solvation and desolvation of polymer by plasticizer. The theory claims that in one word, different plasticizers family are attracted to the polymer in different magnitude but the attraction is not permanent [11].

By the combination of these four theories, the plasticization can be divided into five stages which are;

1. Adsorption step, where plasticizer mixed with PVC resin
2. Adhesion step, plasticizer diffuses and swells the resin particles
3. Absorption step, polar groups in the PVC resin are liberated from each other
4. Intermolecular plasticizing step, the polar groups of plasticizer molecules interact with polar group on the resin (Figure 1.2).
5. Intramolecular plasticizing step, the structure of resin is established by full retention of plasticizer [11].

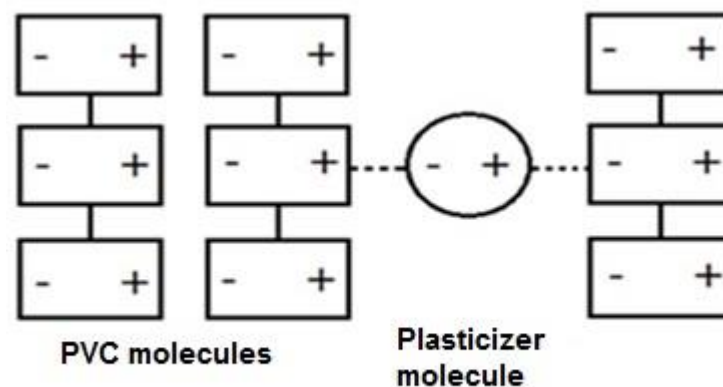


Figure 1.2. Schematic representation of plasticizer interaction with PVC resin.

1.4. Structure of Plasticizers Used in This Study

In this study, phthalate free plasticizers were used because of phthalate plasticizers being restricted in use for artificial leather. Six types of plasticizers were used; trioctyl trimelliate (TOTM), tributyl trimelliate (TBTM), dioctyl terephthalate (DOTP), tributyl citrate (TBC), dioctyl adipate (DOA) and dioctyl succinate (plast BIO). Figure 1.3 shows chemical structures and Table 1.1 shows chemical formulas and molecular weights of used plasticizers.

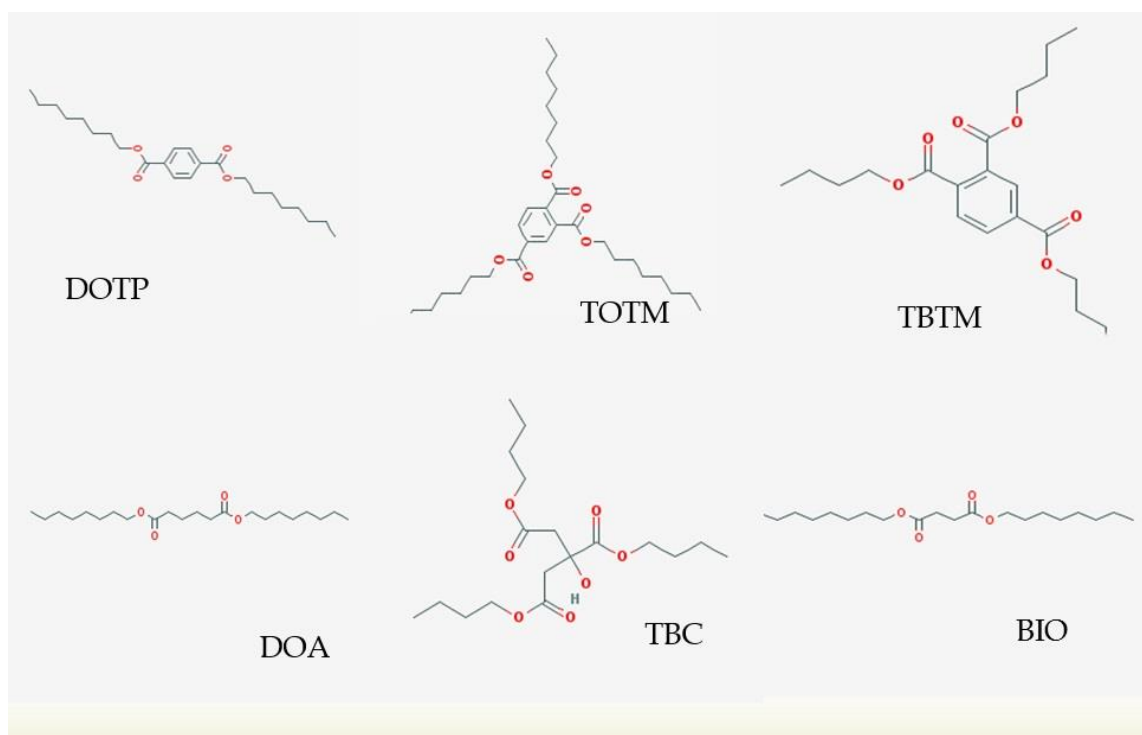


Figure 1.3. Chemical structures of used plasticizers.

Table 1.1. Chemical formulas and molecular weights of used plasticizers

Plasticizer	Chemical Formula	Molecular Weight
DOTP	$C_{24}H_{38}O_4$	390.564 g/mol
TOTM	$C_{33}H_{54}O_6$	546.789 g/mol
TBTM	$C_{21}H_{30}O_6$	378.465 g/mol
DOA	$C_{22}H_{42}O_4$	370.574 g/mol
TBC	$C_{18}H_{32}O_7$	360.447 g/mol
BIO	$C_{20}H_{38}O_4$	342.520 g/mol

1.5. Aim of the Study

The aim of this study is to obtain and characterize artificial leathers using different kind of plasticizers. In order to obtain flexible or stiff artificial leathers, different plasticizers with different ratios were used. They were prepared using specific compositions in order to achieve their desired mechanical properties like elongation, strength, flexibility and migration. In this study, the mechanical and chemical properties of PVC plasticizers for artificial leathers were studied, that could be a guide to obtaining a desired product in optimum formulation according to area of usage. The choose of plasticizer kind and level is one of the most important stage in development of a flexible plasticized PVC material such as artificial leather. So, in this work, the connection between chemical and physical performances of plasticizers for PVC are studied for understanding the interactions and the effects on final products of plasticizers with PVC.

CHAPTER 2

EXPERIMENTAL

2.1. Materials and Methods

For the obtaining of PVC films and artificial leather, transfer coating was used, which process is based on spread the plastisol on to release paper, then heating it in the oven to form a film, by using Jolly Pilot equipment that helps to adjust wanted thickness or grammage of coating (Figure 2.1). 705 ultramat plain from Arjo Wiggings was used as transfer paper, which has flat surface to obtain homogenous thickness in all part of coating. Trioctyl trimellitate (TOTM), tributyl trimelitate (TBTM), dioctyl terephthalate (DOTP), Tributyl citrate (TBC), dioctyl adipate (DOA) and dioctyl succinate (trade name is plast BIO) were supplied by Plastifay Kimya Endüstrisi A.Ş. which plasticizers were used in this work. In all concentration level of plasticizers, PVC 682 was used, supplied by INOVYN. For the migration test, disperse dyed polyester fabric was used.

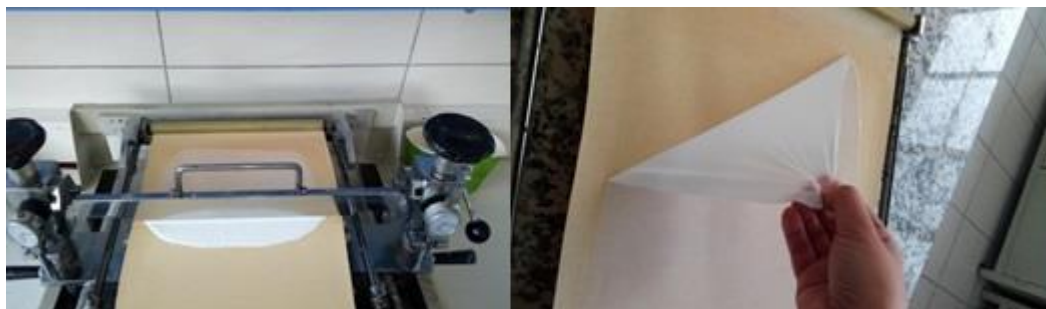


Figure 2.1. Transfer coating using Jolly Pilot on transfer paper

2.2. Preparation of Plastisols

Three sets of plastisols were prepared using six types of plasticizers, as 40, 60 and 80 phr for 100 g of PVC resin. For every plastisol, to improve heat and light stabilization 2.0 grams of liquid Ca-Zn stabilizer (NT-1) and epoxy soybean oil (Plasteks) were added.

To avoid presence of extra air bubbles in final test samples, BYK 3155 air release additive was used as 1% of plastisol total weight. All these materials were mixed in laboratory mixer until dispersion of PVC resin managed homogeneously. The plastisols were hold for release their air content for at least 10 minutes before they were used for transfer coating.

2.3. Transfer Coatings of Plastisols

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 minutes to gelification. After first layer was gelificated, 0.35 mm second layer coating thickness was arranged by Jolly Pilot, and at the same condition it was gelificated.

2.4. Fourier Transform Infrared Spectroscopy During Plasticization

FTIR spectra of plasticizers, PVC, plastisols and their coatings were taken which were set in to oven for 30, 60, 90 and 120 seconds. All spectra were taken by Bruker Alpha II FT-IR ATR accessory, PVC and coatings were taken by pressing them on it because of their being solid, plastisols's and plasticizers's spectrum were taken by directly putting them on ATR diamond. The transfer coating of plastisols for FT-IR spectral change were done by applied them side by side during spreading on to release paper, for the purpose of obtaining their gelification at the same time and temperature.

2.5. Tensile Strength Test

The three samples for each formulation were cut 50 mm x 150 mm in dimension. The samples are placed in to clamping jaws where the samples are hold by two jaws in 25 mm. There must be 100 mm free sample except the jaws hold, because of easy determination of elongation in percentage. The tests were performed in 100 mm/min velocity which is general chosen speed in this kind of tests [24-26], by using Devotrans

tensile tester. The pre-load of tests were about 0.1 - 0.5 N to obtain accurate value of elongation. Data were collected and load - elongation graphs were plotted.

2.6. Tear Strength Test

For this work, Trouser tear method for tear strength was used which is based on making split on test specimen and measuring its tear strength by using tensile strength tester. Figure 2.2 shows the test specimen look during tear test.

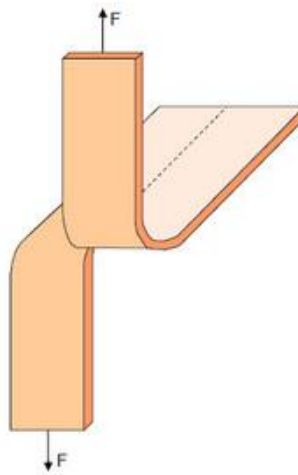


Figure 2.2. Test specimen look trouser method for tear resistance (Source: [14]).

The tearing test data were collected and their tear force - elongation graphs were plotted.

2.7. Migration Test

For the migration test, migrability of polyester fabric dye in different plasticizer was used which gives quick results for the migration of plasticizers. Because of clear observation of color change, 3% TiO_2 powder is added in to plastisols which are mentioned above "2.2. Preparation of Plastisols". The plastisols that are used for migration were prepared separately because of adding extra material on them. After preparing TiO_2 content plastisols, transfer coating was applied. At the end of 2 layers of transfer coating, third layer was applied for the lamination of dispersed polyester fabric

(which is not yarn dyed). Because of the migration property of different kind of plastisols, movement of the fabric dye to surface was observed. When they were put in the oven at 70 °C, the color change could be observed earlier, despite of the fact that. After 3, 6 and 24 hours, color changes of artificial leather which were light and almost have same color at initial, were measured using spectrophotometer within time period.

2.8. Cold Flexibility Test

At room temperature most plastics show their usual properties such as flexibility. Many of plastics become brittle and lose their flexibilities when the temperature decreases [27]. To obtain most cold flexibility of plasticizers, Devotrans leather and artificial leather flexometer was used. The samples were chosen from 80 phr level plasticizers and cut in 45 mm x 70 mm dimension to clump test device. The flexometer is in the cabinet where the temperature can be controlled. After the conformation of test sample, the flexometer which is counting and saving every flex started at -20°C. The test was going on until there is any deformation of test samples. The non-deformed samples were proceeded until their deformation was observed, and their flex scores were recorded.

2.9. Characterization Tools

2.9.1. Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy measure the reflectance and transmittance of a species to identify its chemical structure. It can give both qualitatively and quantitatively information by bombardment of infrared beam to the surface of the sample. Solid or liquid samples can be measured. To get more intense signals, the attenuated total reflectance (ATR) apparatus can be used, with ZnSe, diamond, Ge or Si [28]. Figure 2.3 shows a typical FT-IR spectrometer with ATR aparatus.



Figure 2.3. Fourier transform infrared spectroscopy with ATR instrument.

2.9.2. Tensile Tester

Tensile tests are used for determination of ultimate tensile strength of the material. The amount of force and elongation (ΔL) against this force are measured. The velocity of testing can be arranged for different test types or needs. Material properties are often expressed in terms of load (force) or stress (force per unit area, σ) and elongation (mm) or strain (percent change in length, ϵ). To obtain stress, the force measurements are divided by the sample's cross sectional area ($\sigma = F/A$). Strain measurements are obtained by dividing the change in length by the initial length of the sample ($\epsilon = \Delta L/L$). These values are then presented on an XY plot called where X is elongation or strain, Y is load or stress. Testing methods changes according to material or its intended application [29]. Figure 2.4 shows a tensile tester with two jaws.



Figure 2.4. Tensile tester

2.9.3. Flexometer

Flexometer is used for determination of the flexing endurance of leather or any flexible material. For artificial leathers used especially in shoes, garments or lever caps in outomobiles, this flexibility test is very important because of material being always in motion. This flexometer machine is equipped with flex counter and freezing compartment in order to obtain the tests in cold condition (min. -30°C) if needed. The test specimen is held between clamps like shoe wearing, and almost 40 flex are done in one minute. Figure 2.5 shows a typical flexometer with a freezing compartment.



Figure 2.5. Flexometer

2.9.4. Spectrophotometer

Spectrophotometers are color measurement devices used to capture and evaluate color [30]. The $L^*a^*b^*$ color space was established by the International Lighting Commission (CIE, referred to as CIELAB) [31] is presently one of the most popular spaces for measuring object color and is widely used in virtually all fields. In this space, L^* represents lightness and a^* and b^* are the chromaticity coordinates [32]. The visualization of CIELAB three dimensional color space is shown in Figure 2.6. Figure 2.7 shows the typical portable spectrophotometer which makes color measurements in a few seconds using it directly on the specimen in parallel position easily.

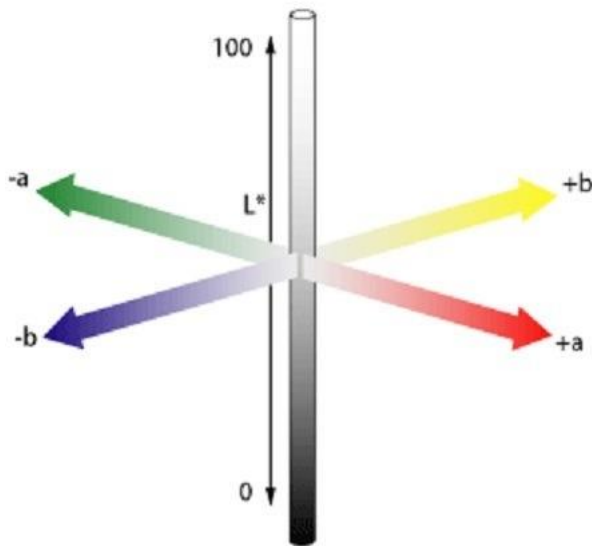


Figure 2.6. The visualization of CIELAB three dimensional color space (Source: [32])



Figure 2.7. Typical portable spectrophotometer

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Infrared Spectral Changes of Plasticsols and Plasticized Plasticsols

Infrared spectroscopy is a widely used technique for studying chemical changes in many applications. Fourier transform infrared spectroscopy with ATR allows obtaining spectrum of liquid or solid materials without any sampling method (i.e. pellet preparation). Liquid samples were directly put on ATR apparatus's diamond part and their spectra were taken in seconds. Solid samples were also put on diamond part and they were compressed by helping of the pressing part of the ATR apparatus. Figure 3.1 shows FTIR spectra of pure plasticizers and PVC resin which were used in this work by using ATR technique.

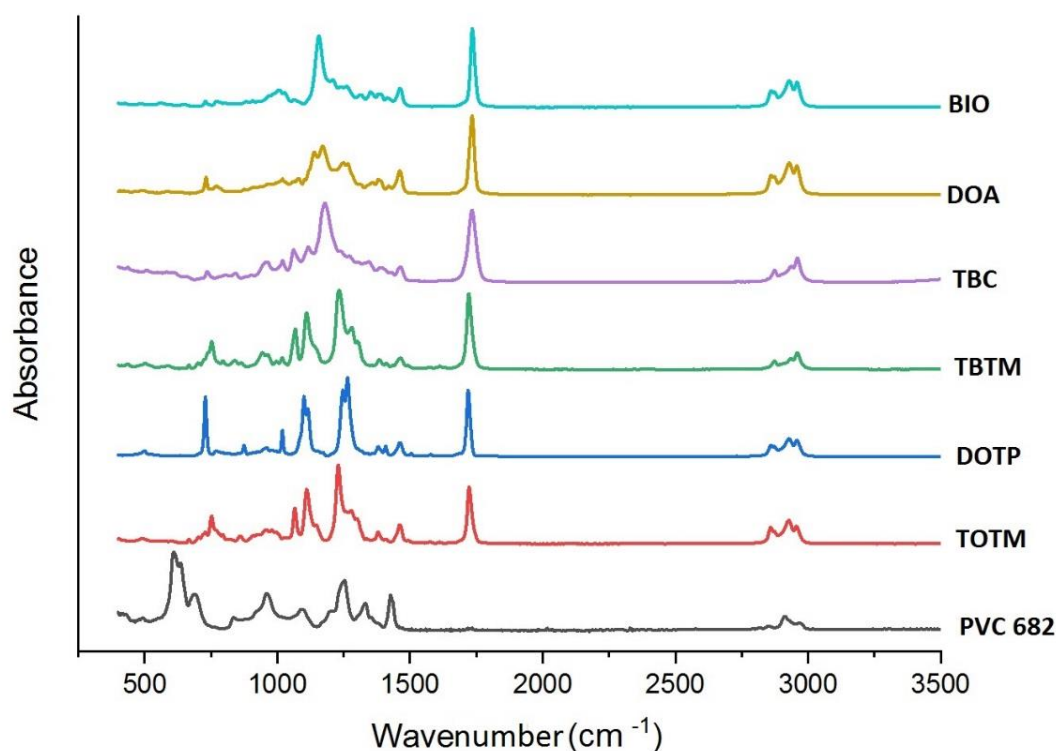


Figure 3.1. Infrared spectra of used plasticizers and PVC 682.

Considering spectrum of PVC 682 in Figure 3.1, in the region of 600-700 cm^{-1} , the bands are more characteristic of the spectrum of the PVC which are corresponding to C-Cl stretching vibrations, and the rest bands correspond to different C-C and C-H vibrations. On the other hand, the spectra of plasticizers have bands at $\sim 1740 \text{ cm}^{-1}$ that belong to C=O stretching. Figures 3.2 and 3.3 show the spectra of PVC, 60 phr plastisol and pure plasticizers, which belong to DOTP and DOA, respectively that are mostly used in artificial leather production.

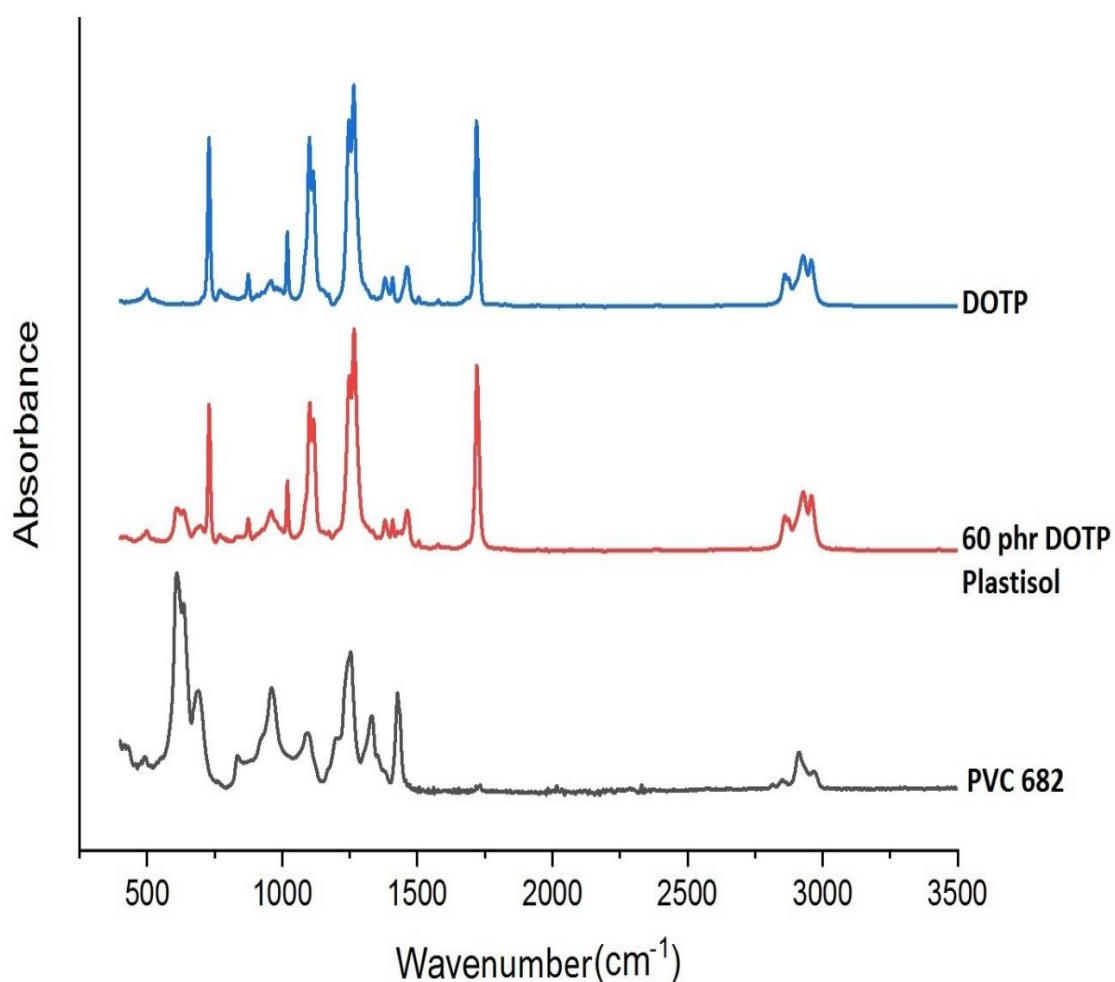


Figure 3.2. FT-IR spectra of PVC, 60 DOTP phr plastisol and pure plasticizer, DOTP.

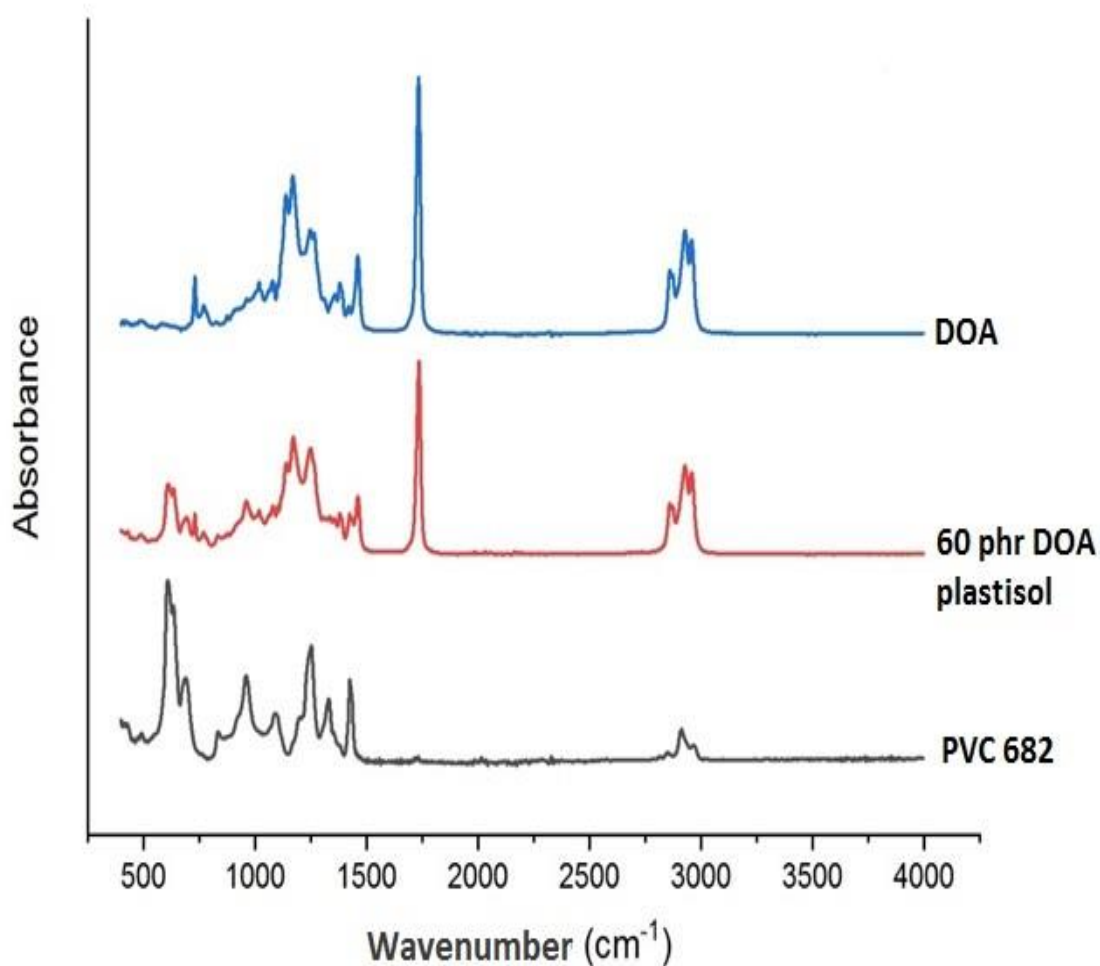


Figure 3.3. FT-IR spectra of PVC, 60 DOA phr plastisol and pure plasticizer, DOA.

In the first part, to understand compability of six plasticizers, the PVC, and 60 phr of six different plasticizer containing plastisols were compared to each other based on their spectral changes. According to previous works [33-35], the more variations in signals at 617 and 637 cm^{-1} bands were assigned to the better compability of the plasticizer. In this work, both signals' intensities decreased and the different intensity ratios of the bands at 617 cm^{-1} and 637 cm^{-1} were clearly observed when different kind of plasticizers were used (Figure 3.4).

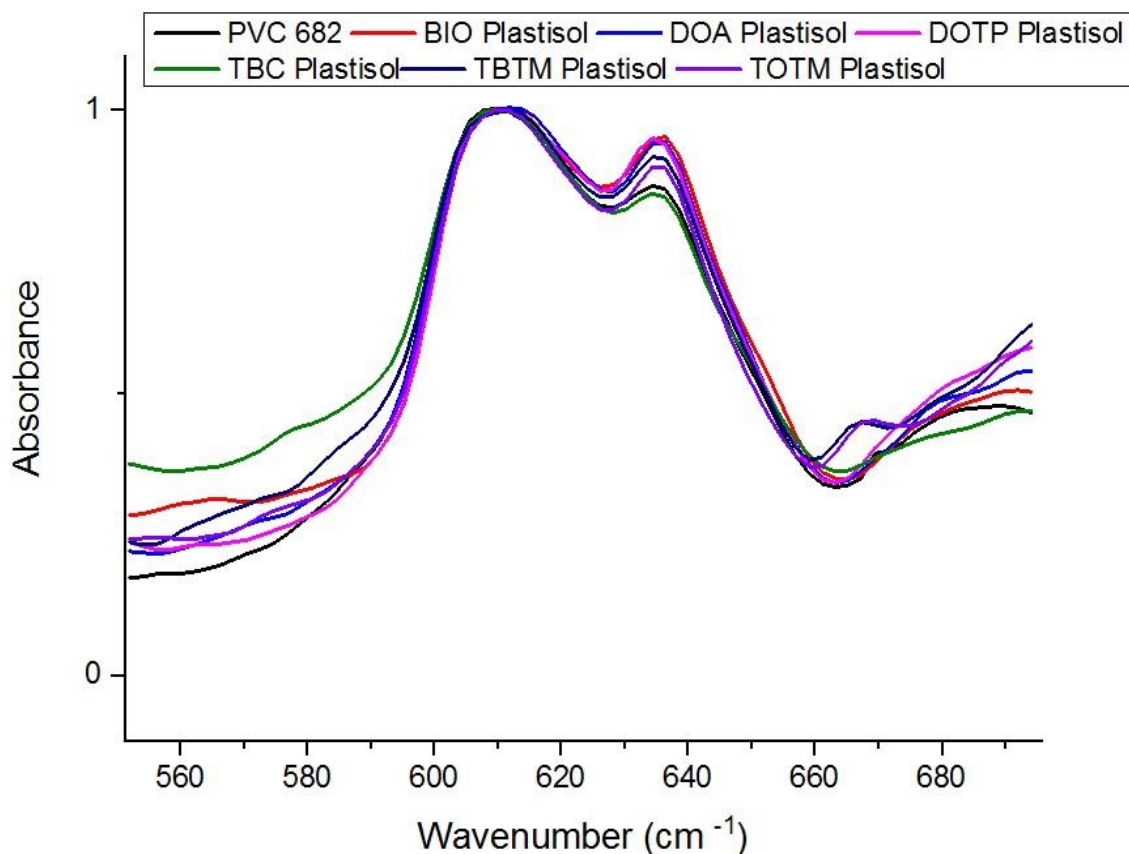


Figure 3.4. FT-IR spectra of plastisols and PVC at 617 cm⁻¹ and 637 cm⁻¹.

Among the six plasticizers, TBC and TBTM plasticizers have less compatibility than other plasticizers when considering the spectral changes, their absorbance bands at 617 cm⁻¹ and 637 cm⁻¹ were not affected as others. In sample preparation part, these plastisols which were prepared as 40 phr, lost their rheology by increasing their viscosity in minutes, which is an undesirable situation for coating processes, whereas other four plasticizers have more stable viscosity. This rheology change also can be correlated with the compatibility of plasticizers with PVC. According to the ratio change of the bands at 617 cm⁻¹ and 637 cm⁻¹, the same result was observed for putting in order plasticizers, where BIO, DOTP and DOA have higher compatibility than others. TBC shows minimum compatibility and TOTM and TBTM follow it in increasing order respectively. Figure 3.5 shows the compatibility order of plasticizers based on the intensity ratio of the bands at 637 cm⁻¹ and 617 cm⁻¹.

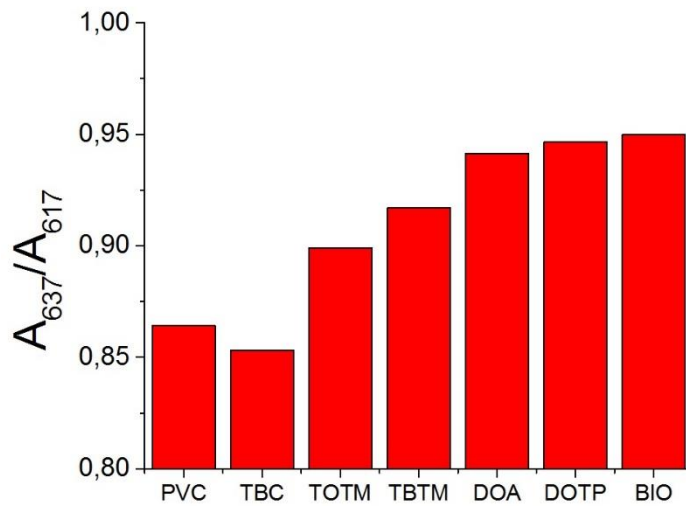


Figure 3.5. Compatibility difference of plastisols based on the ratio of intensity at 637 cm^{-1} and 617 cm^{-1} .

In the second part, infrared spectral changes of plasticized PVC using six different plasticizers which were in 40, 60, and 80 phr levels were observed. Spectra of mixtures of plastisols were taken after 30, 60, 90 and 120 seconds heating process. As an example, 60 phr DOA and DOTP spectra are given in Figure 3.6 and 3.7.

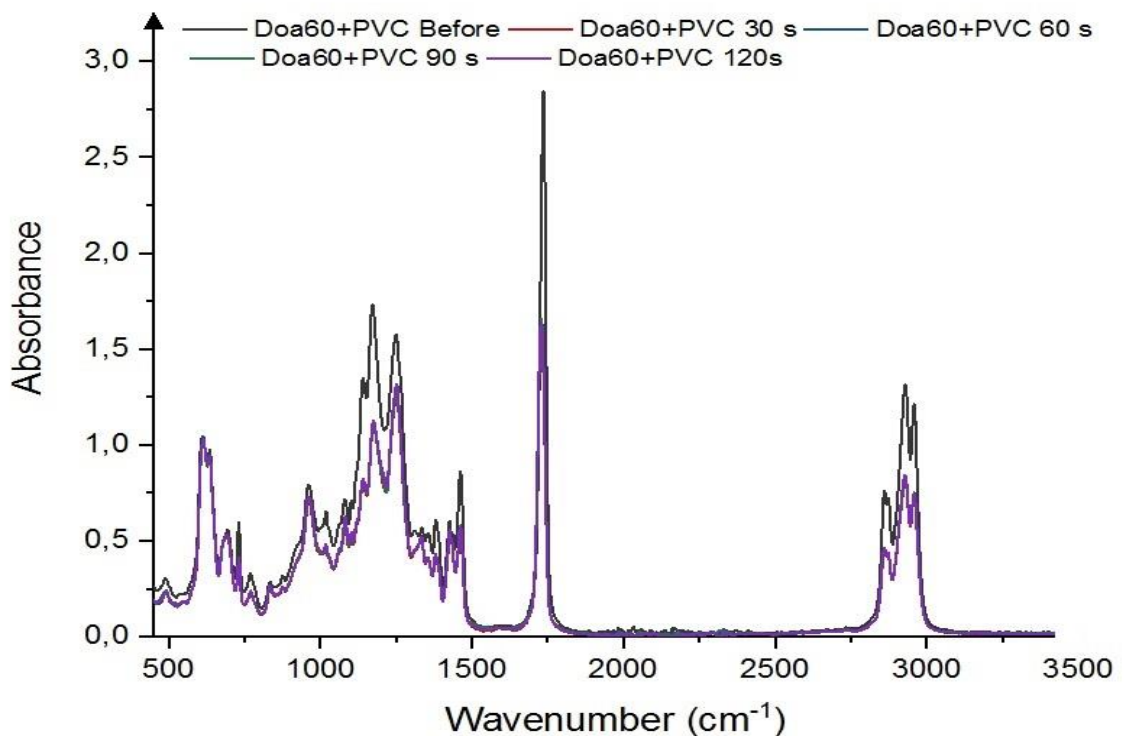


Figure 3.6. FT-IR spectra of 60 phr DOA plastisols after heat treatment steps

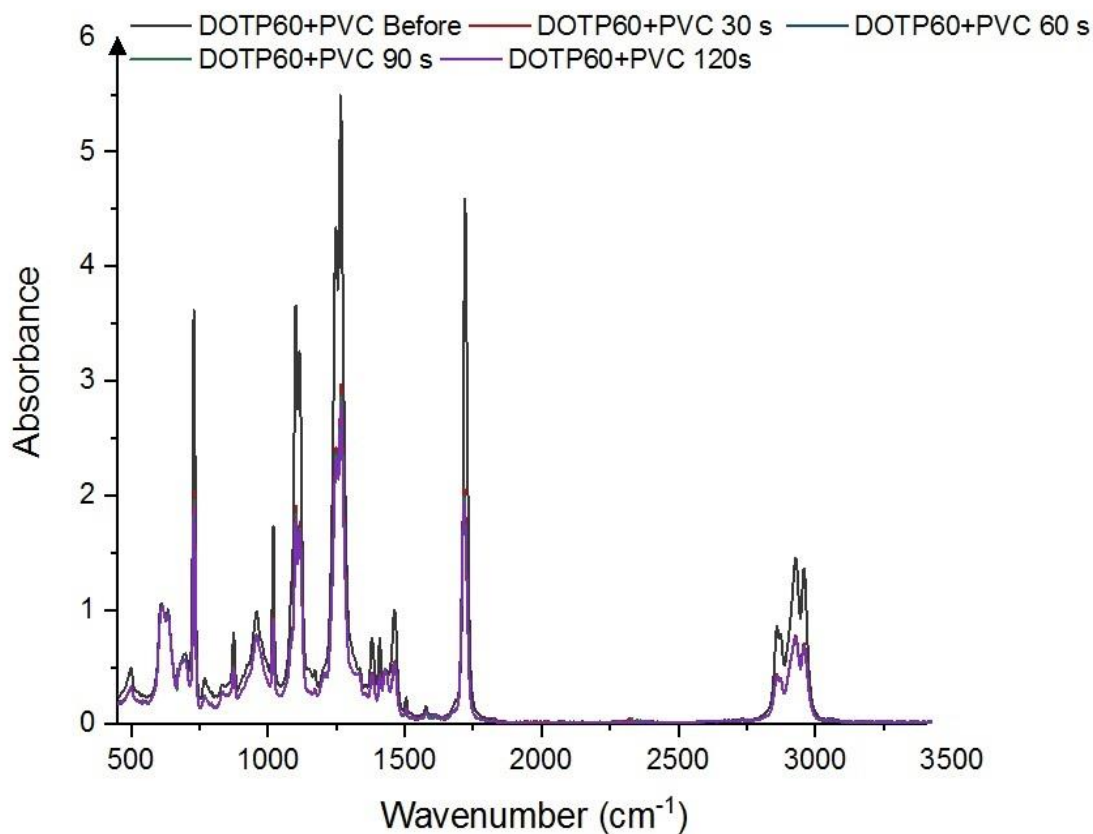


Figure 3.7. FT-IR spectra of 60 phr DOTP plastisols after heat treatment steps

There is a significant decrease at C=O band ($\sim 1740\text{ cm}^{-1}$) which shows the absorption of plasticizer molecules by PVC resin. By the same way, an increase of C-Cl stretching band absorbance ($\sim 736\text{ cm}^{-1}$) can be observed. As the plastisols were heated, the carbonyl band of plasticizers goes an irreversible shifting to lower wavenumbers and this shifting quantity depends on plasticizer types. Figure 3.8 and 3.9 show these shifting at 1740 cm^{-1} band of DOA and DOTP plastisols after heat treatment at given times.

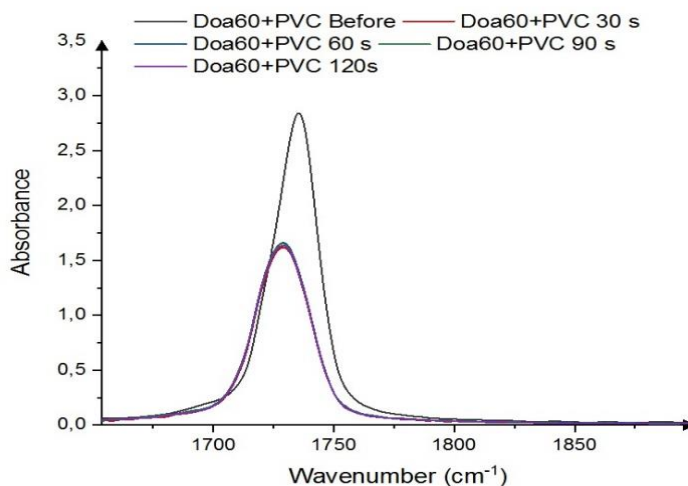


Figure 3.8. Shifting of C=O band of DOA plastisol spectra after heating steps.

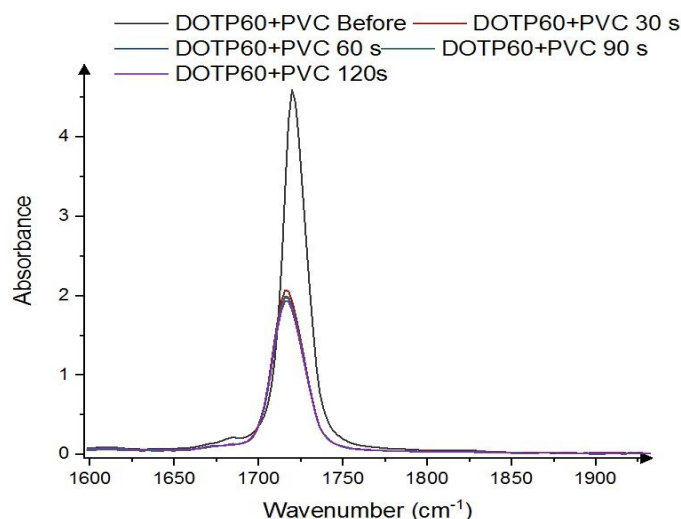


Figure 3.9. Shifting of C=O band of DOTP plastisol spectra after heating steps.

There are some differences of spectral changes of plastisols during heating, based on plasticizer types which results from different gelification rate, compatibility and durability of plasticizers. According to compatibility comment of plasticizers in the first part of spectral changes, TBC plastisol shows at least shifting, which means there is less interaction with PVC resin at the same condition with the other plasticizers, that explains compatibility by the same way again. For 60 phr TBC and TBTM plastisols, a smaller shifting from 1740 cm^{-1} were observed (Figure 3.10 and 3.11). This showed less compatibility of TBC and TBTM at the same heat treatment time with others.

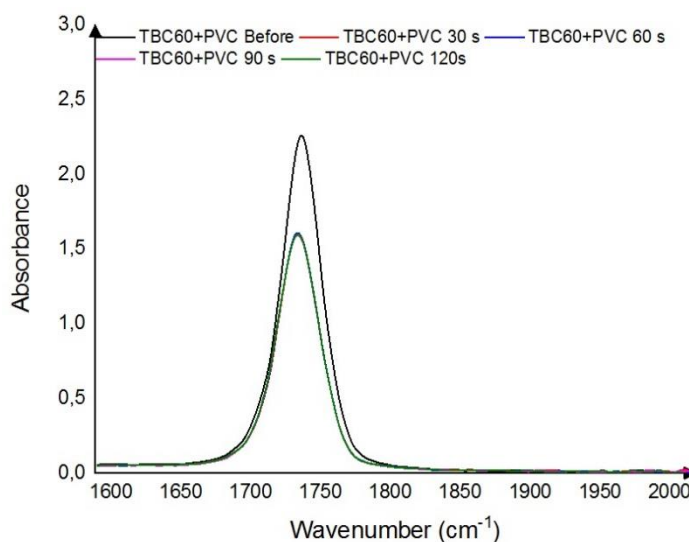


Figure 3.10. C=O bands of TBC plastisols after heating steps.

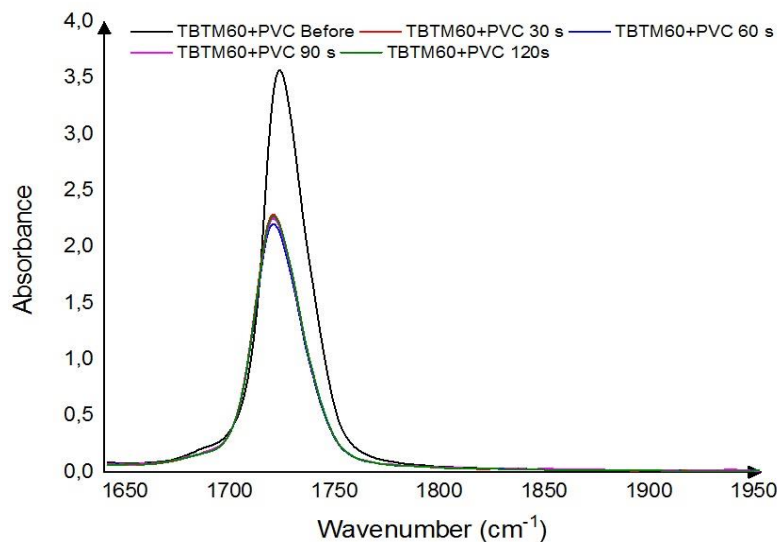


Figure 3.11. C=O bands of TBTM plastisols after heating steps.

Additionally, plasticizer BIO showed nearly same spectral changes with DOA and DOTP at carbonyl band after heat treatment which means they have the similar compatibility with PVC.

3.2 Tensile Strength and Elongation at Break

At low level of plasticizers, TOTM and DOTP have nearly same strain – stress quality. Although DOA, BIO, TBC have lower tensile strengths than TOTM and DOTP, their elongation values are nearly same at break. At low level of TBTM and TBC, it is too hard to control viscosity of plastisol due to butyl structure of materials, viscosity was getting higher so fast by the time which is a big problem for transfer coating. 40 phr TBTM PVC film's showing lowest elongation but close tensile strength with DOA, TBC and BIO. It can be explained by its bad rheology during coating, which leads to a low mechanical strength (Figure 3.12a).

At 60 phr level of plasticizers, significant differences start to be appear, DOA has highest elongation value with the lowest tensile strength. DOTP and TOTM show close behavior under the same load, but TOTM has more tensile strength than DOTP. BIO, TBC, TBTM are in the middle of TOTM and DOA when we consider strain and stress property of them (Figure 3.12b).

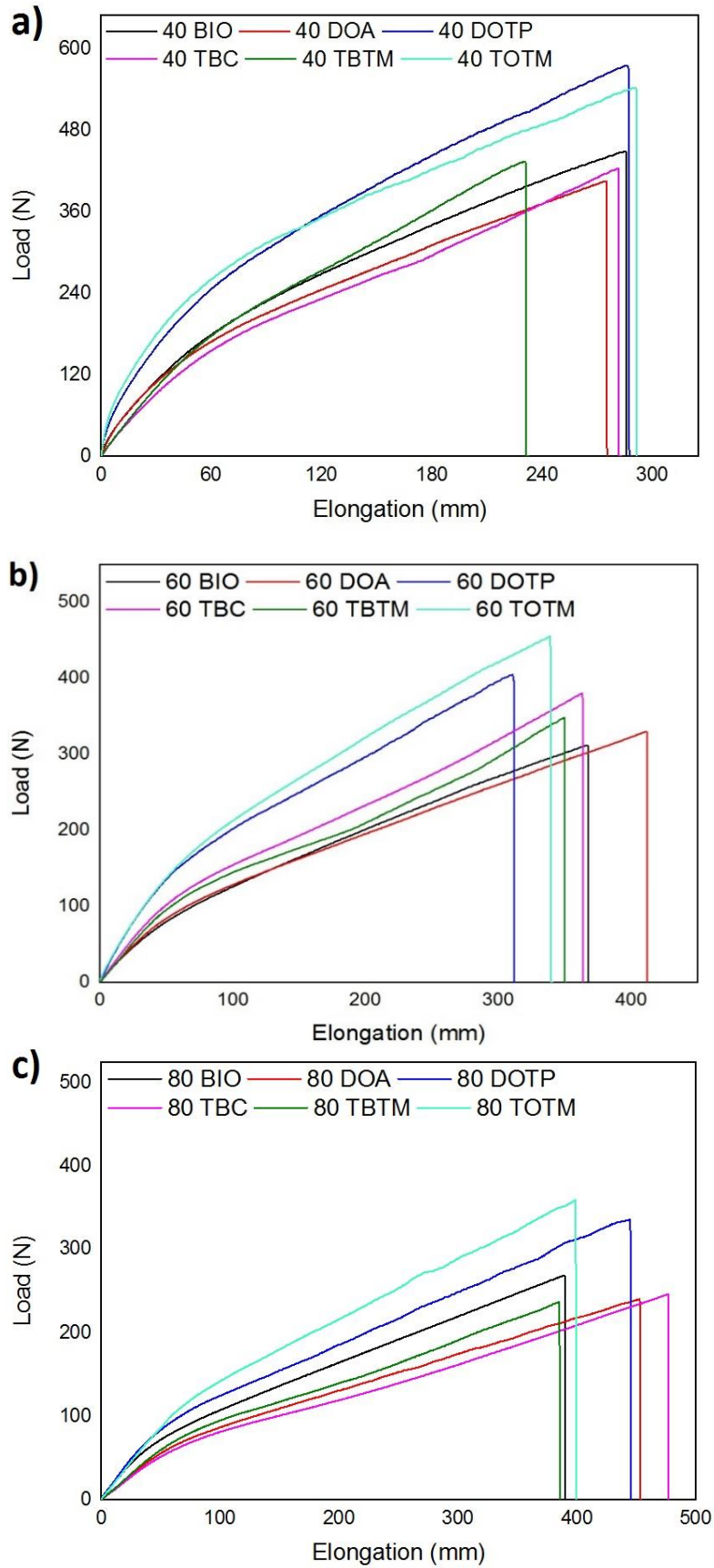


Figure 3.12. Load vs. Elongation graphs of plasticized PVC a) at 40 phr plasticizer b) at 60 phr plasticizer c) at 80 phr plasticizer level

At 80 phr level of plasticizer, TBC and DOA have competition about flexibility and strength. On the other hand, DOTP and TOTM show same behavior where DOTP is higher elongation but lower tensile strength. BIO and TBTM have nearly same slope with DOTP, but their strengths are less (Figure 3.12c).

For all kind of plasticizers, when plasticizer amount increases, the elongation increases, while tensile strength decreases. It means material is getting more flexible and softer by increasing plasticizer level. Figures 3.13 a-f show the change in tensile strength and elongation based on plasticizer level.

3.3. Tear Strength

As the tensile strength decreasing with increasing plasticizer level, tear strength of materials is affected by the same way about maximum force, but not elongation. When material comes to be more flexible by increasing plasticizer, tearing of it is getting to be easy. In tear strength, elongation does not depend on flexibility, because tear may not be occurred in a plain way, this test is manually stopped after tearing the specimen about 75 mm. So, for evaluation this type of resistance, the maximum or average force is recorded for tearing [36]. Figure 3.14 shows typical tear strength graphs of tearing a flexible material like artificial leather, in which tear strengths of materials are decreasing by increasing the plasticizer quantity.

On the other hand, except TOTM, all plasticizers have similar tearing strength at 40 phr and 60 phr level (Figure 3.14 a-c). At 80 phr of plasticizer, TBC has the lowest tear strength, which can result from inadequate gelation, or presence of extra air bubble in test sample (Figure 3.14 c).

Among all levels of plasticizers, TOTM has the higher tear strength than others. If we put in order TOTM in itself, 40 phr > 60 phr > 80 phr, which means increasing plasticizer quantity leads to decrease tear strength, because the material become softer and more flexible which means PVC starts losing its properties (Figure 3.15 a-f).

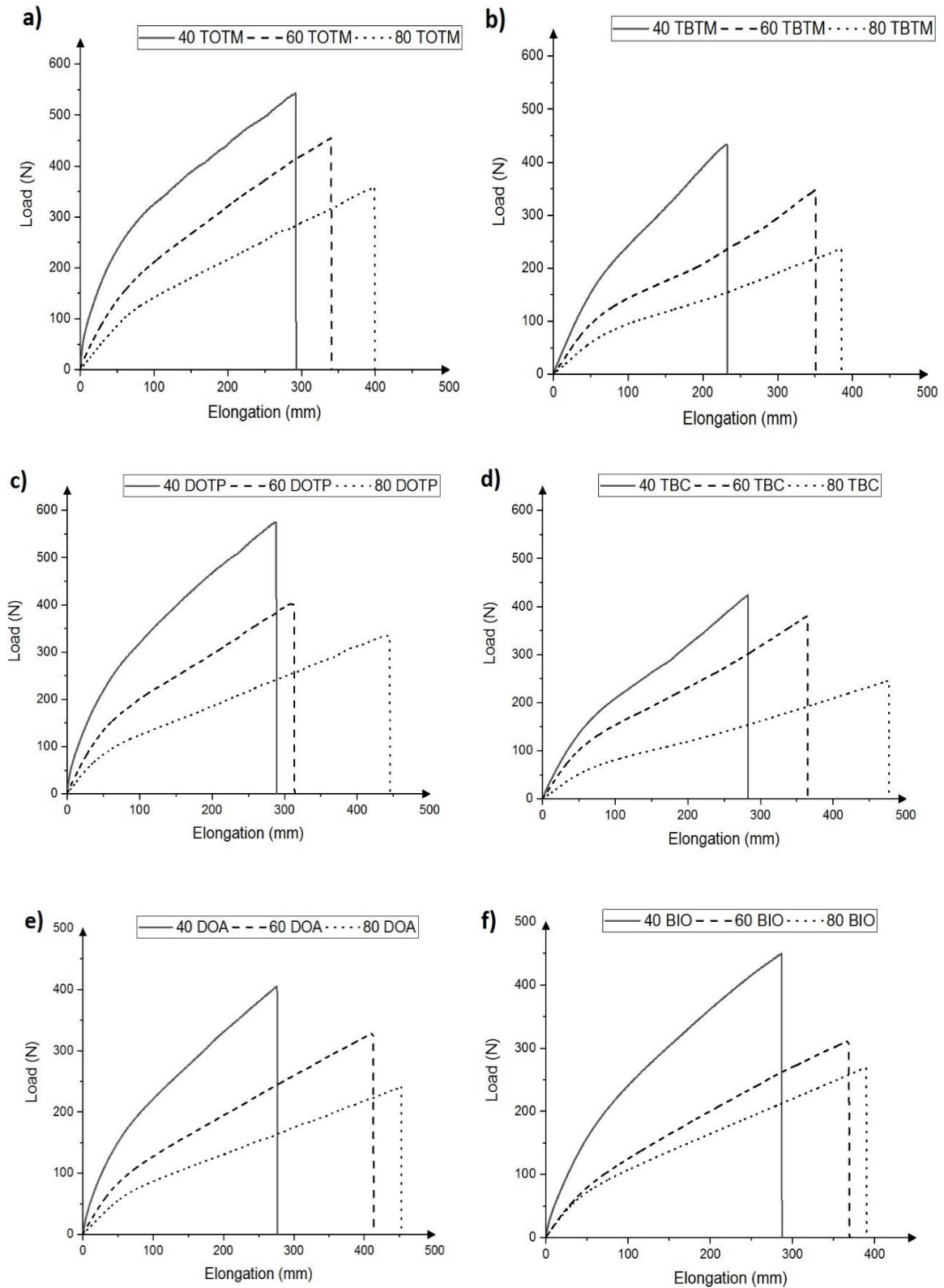


Figure 3.13. Change in tensile strength and elongation based on plasticizer level
a) TOTM, b) TBTM, c) DOTP, d) TBC, e) DOA, f) BIO.

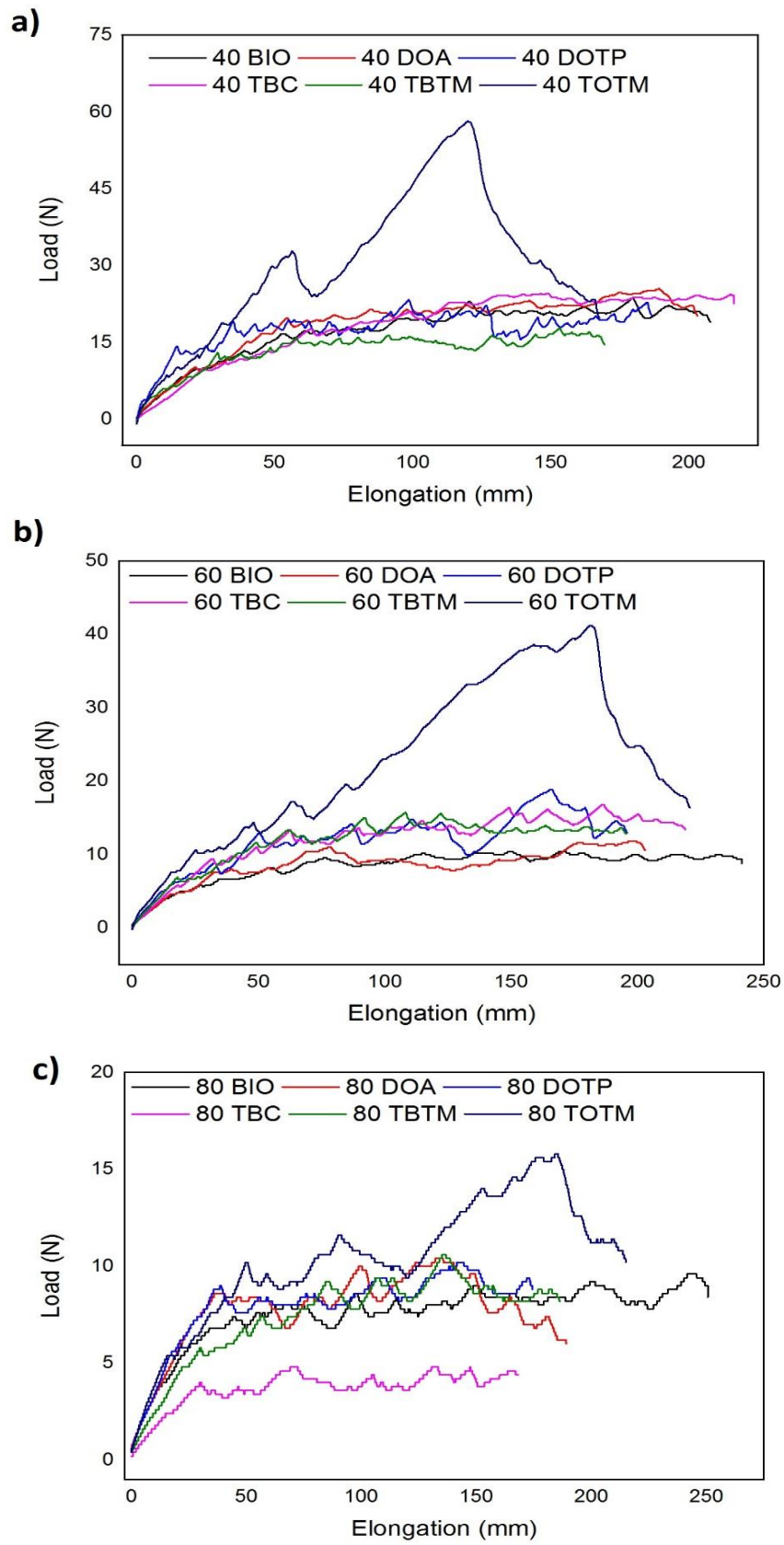


Figure 3.14. Tear Strength of PVC plasticized with a) 40 phr b) 60 phr c) 80 phr of 6 different plasticizers.

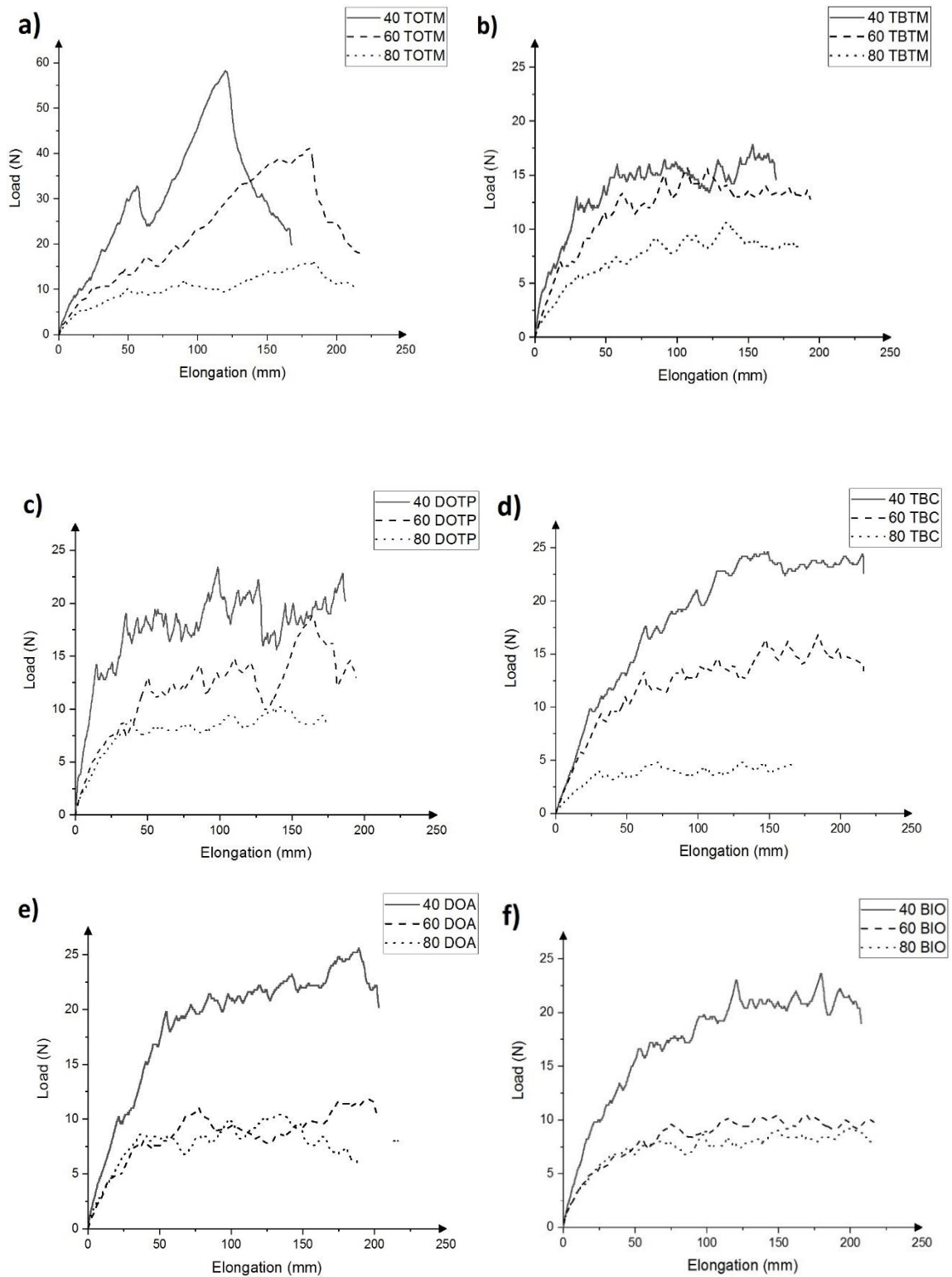


Figure 3.15. Change in tear strength based on plasticizer level a) TOTM, b) TBTM, c)DOTP, d) TBC, e) DOA, f) BIO

3.4. Migrability

Migration of plasticizer from PVC can lead to unwanted results such as weakening products flexibility, becoming more brittle and shortening its physical life. This behavior of plasticizers also results in environmental pollution and health effect, when it occurs in life place, i.e. skin contact with migrated plasticizer and their penetration into body while handling them. In this work, an easy way was obtained to put in order migrability level of plasticizer. In all plasticizer levels, migrability of plasticizers are measured indirectly and obtained by the methodology described above (section 2.7 migration test). The arrow marks on Figure 3.16 and 3.17 were used for expressing the color change by the migration.



Figure 3.16. Color changes of artificial leathers obtained by using TOTM, TBTM, DOTP after 70 °C heat treatment a) initial b) after 24 hours

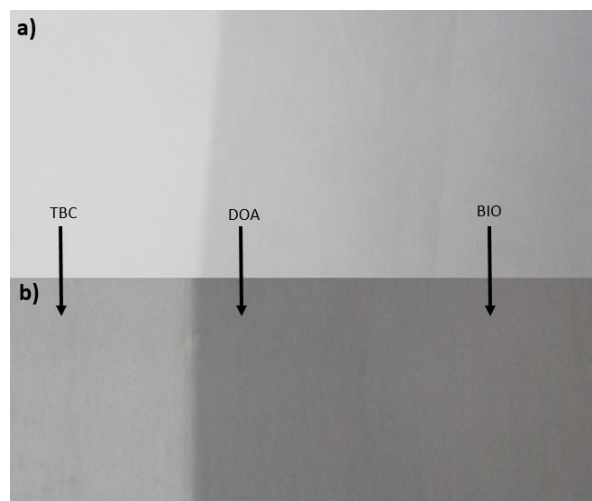


Figure 3.17. Color changes of artificial leathers obtained by using TBC, DOA, BIO after 70 °C heat treatment a) initial b) after 24 hours

Table 3.1. Spectrophotometric lightness change of artificial leathers after 70 °C heat treatment at 40 phr plasticizer level.

Time of measurement	L value 40 TOTM	L value 40 TBTM	L value 40 DOTP	L value 40 TBC	L value 40 DOA	L value 40 BIO
Initial	95.97	94.34	95.34	94.49	95.28	94.80
3 hours	95.10	93.89	94.63	93.63	89.87	89.25
6 hours	95.06	93.77	93.89	92.42	83.54	81.97
24 hours	92.46	87.86	82.63	76.38	64.53	63.91

Table 3.2. Spectrophotometric lightness change of artificial leather after 70 °C heat treatment at 60 phr plasticizer level

Time of measurement	L value 60 TOTM	L value 60 TBTM	L value 60 DOTP	L value 60 TBC	L value 60 DOA	L value 60 BIO
Initial	94.05	94.02	93.96	93.70	94.08	94.42
3 hours	91.72	90.95	88.73	87.28	70.87	74.12
6 hours	89.29	88.95	83.09	80.07	62.34	66.57
24 hours	69.84	65.80	60.99	60.64	55.88	57.59

Table 3.3. Spectrophotometric lightness change of artificial leather after 70 °C heat treatment at 80 phr plasticizer level

Time of measurement	L value 80 TOTM	L value 80 TBTM	L value 80 DOTP	L value 80 TBC	L value 80 DOA	L value 80 BIO
Initial	96.15	93.98	94.06	94.32	93.22	93.36
3 hours	92.00	85.30	82.36	74.22	63.49	65.02
6 hours	88.23	77.96	73.37	66.55	58.80	59.62
24 hours	71.08	57.31	59.11	57.13	55.34	56.22

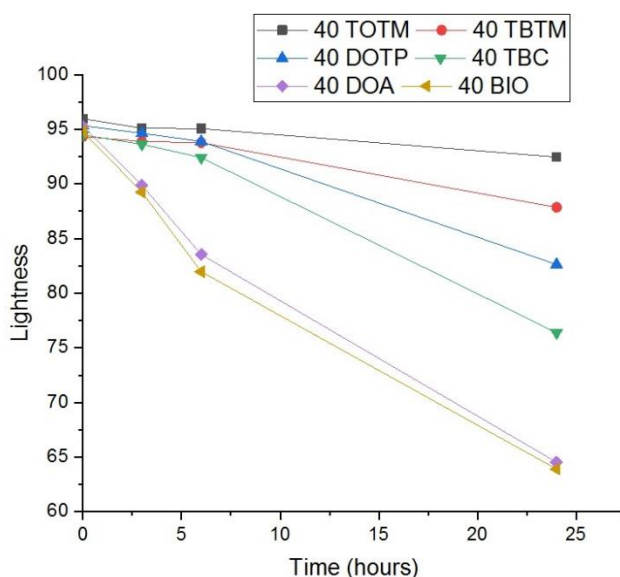


Figure 3.18. Lightness decrease of 40 phr plasticizer level by the migration

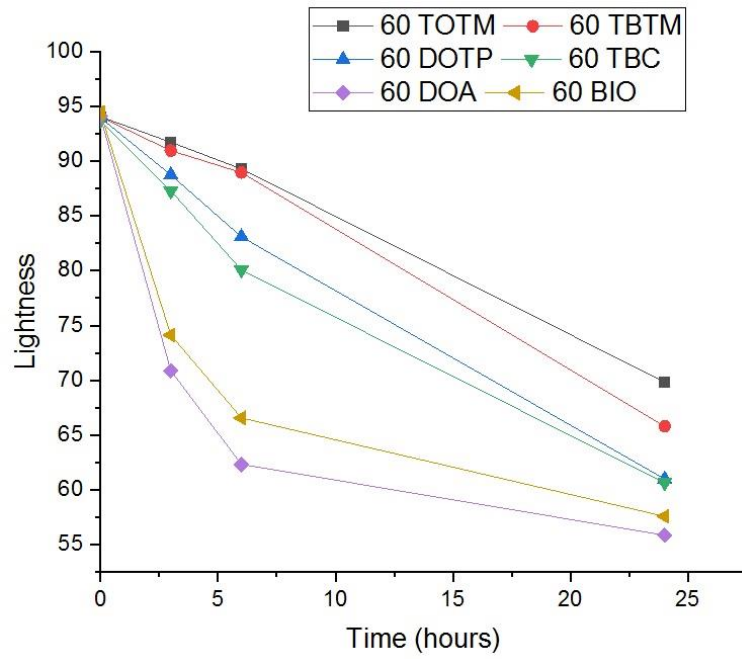


Figure 3.19. Lightness decrease of 60 phr plasticizer level by the migration

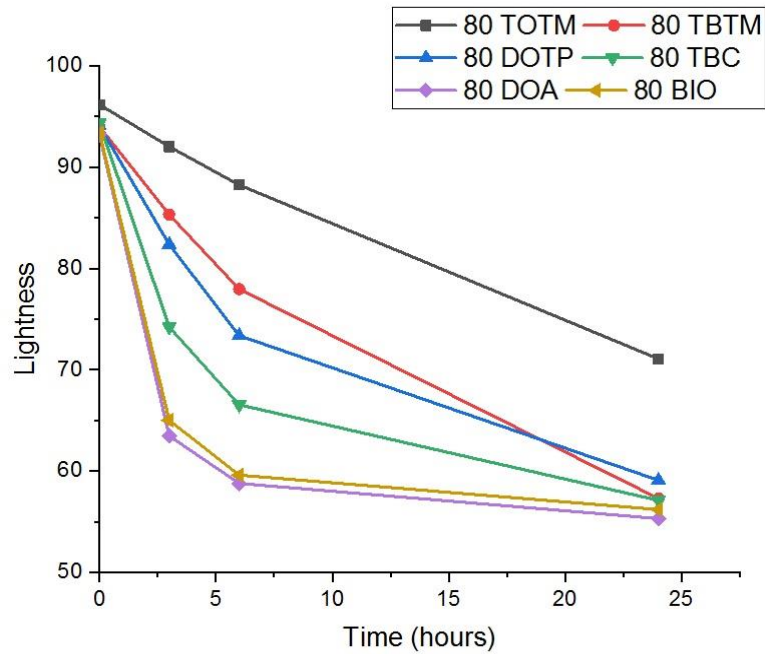


Figure 3.20. Lightness decrease of 80 phr plasticizer level by the migration

Table 3.4. Summary lightness change of artificial leather based on spectrophotometric measurements

Plasticizers	ΔL at 40 phr level	ΔL at 60 phr level	ΔL at 80 phr level
TOTM	2.46	24.21	25.07
TBTM	6.48	28.22	36.67
DOTP	12.71	32.97	34.95
TBC	18.11	33.55	37.19
DOA	31.37	38.20	37.88
BIO	34.24	36.83	37.14

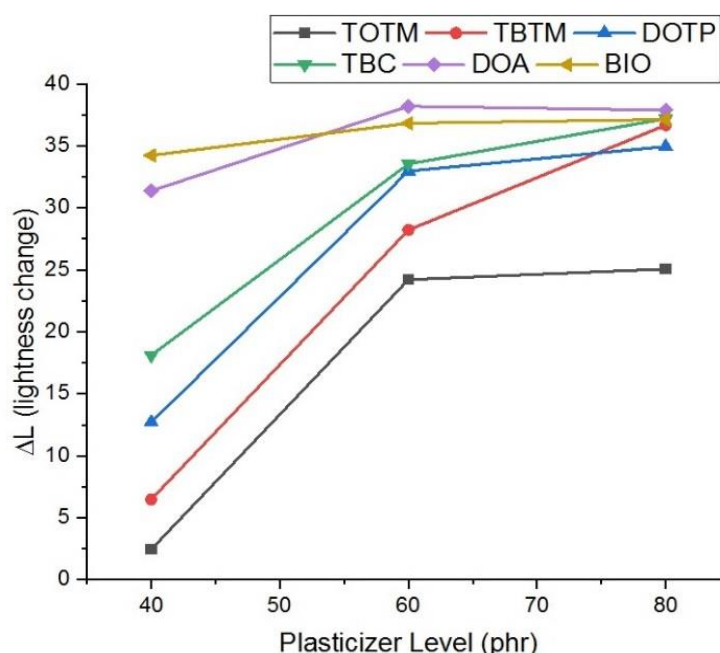


Figure 3.21. Lightness change based on plasticizer kind and level

For all concentrations, decreasing lightness of artificial leather with time is observed because of migration of fabric dye with help of plasticizers migrability (Figure 3.16 and Figure 3.17). The lightness change of artificial leather has directly proportional with the migration of plasticizers. All migration properties have different magnitudes for each plasticizer kind and each concentration, which explains migration depends on their chemical structure, molecular weight, compability and their concentration in formulation with PVC resin (Table 3.1 - 3.3 and Figure 3.18 - 3.20).

Considering TOTM and TBTM, which are from the same family, migration decreases by increasing molecular weight which are about 546.789 g/mol and 378.465 g/mol respectively. Although TBTM has lower molecular weight than DOTP (390.564 g/mol), it shows less migrability because of its branched butyl structure. TBC also has more branched structure than DOA and BIO, which leads to less migration at low level

plasticizer concentration, despite its lower molecular weight (360.447 g/mol) than that of DOA (370.574 g/mol) but higher with comparing to BIO's molecular weight (342.520 g/mol).

Using higher level concentrations of plasticizers affect migration to increase as expected, but lower molecular weighted and linear plasticizers (i.e. DOA, BIO) show higher migration at low level of usage because of their nature (Table 3.4 and Figure 3.21).

3.5. Cold Flexibility

The cold flexibility performance of plasticizers directly depends on their structure i.e. linearity and molecular weight [8]. In this work, six plasticizers from 5 different families were studied for low temperature flexibility. Among three set of materials, the highest plasticizer used specimens were performed cold flexibility test because of their being most flexible at room temperature. At -20 °C, TBTM plasticized PVC cracked after 100000 flex. DOA, BIO and TBC showed most cold flexible character, about 550000, 450000, 390000 flex, which verifies their elongation behavior at room temperature. Other two plasticizers TOTM and DOTP showed nearly same property at -20 °C, which is about 300000 flex.

3.6. Summary of Results

Table 3.5, 3.6, and 3.7 show average maximum tensile strength, elongation and their migrability order based on their used level and Table 3.8 shows maximum tear force of materials based on their used level per hundred PVC resin.

Table 3.5. Maximum load, elongation and migration order at 40 phr plasticizers

Plasticizer (40 phr)	Average Maximum Tensile Force (N)	Elongation at Max. Force (mm or %)	Migration Order
TOTM	542.4	290.8	6
DOTP	560.0	285.2	4
TBTM	433.4	231.1	5
TBC	423.8	281.7	3
DOA	404.8	275.7	2
BIO	449.2	287.0	1

Table 3.6. Maximum load, elongation and migration order at 60 phr plasticizers

Plasticizer (60 phr)	Average Maximum Tensile Force (N)	Elongation at Max. Force (mm or %)	Migration Order
TOTM	455.2	339.9	6
DOTP	360.4	254.0	5
TBTM	348.4	350.5	4
TBC	380.2	364.5	3
DOA	240.2	266.1	1
BIO	326.2	379.2	2

Table 3.7. Maximum load, elongation and migration order at 80 phr plasticizers

Plasticizer (80 phr)	Average Maximum Tensile Force (N)	Elongation at Max. Force (mm or %)	Migration Order
TOTM	359.4	409.6	6
DOTP	335.8	444.1	4
TBTM	237.4	384.9	5
TBC	246.0	476.0	3
DOA	240.6	452.0	1
BIO	268.6	391.1	2

Table 3.8. Maximum tear force at three plasticizer levels

Plasticizer Types	Average Max. Tear Force at 40 phr Plasticizer (N)	Average Max. Tear Force at 60 phr Plasticizer (N)	Average Max. Tear Force at 80 phr Plasticizer (N)
TOTM	58.2	38.6	15.6
DOTP	22.8	14.8	12.0
TBTM	17.8	15.6	10.6
TBC	24.4	14.6	6.0
DOA	25.6	11.8	10.4
BIO	22.8	10.4	9.6

CHAPTER 4

CONCLUSION

In this work, number of procedures to monitor plasticizer characterization which are used in artificial leather were presented. Variations in mechanical properties and migration processes, and also infrared spectral changes were obtained according to used plasticizer types e.g. TOTM, TBTM, DOTP, TBC, DOA and BIO.

Based on infrared spectral changes of plastisols, less compatibilities of TBC, TOTM and TBTM were observed compared to the other three plasticizers. When plasticizer families are studied, it can be roughly stated that migration decreases and mechanical strength increases when molar mass of plasticizer increases. For high tensile, tear strengths, and low migration, TOTM is the most useful plasticizer among six plasticizers which were studied in this work. Although DOA, BIO and TBC have high migration property, their ability of giving flexibility to PVC is higher than others when comparing other plasticizers under same load of stress.

When considering only tear resistance, TOTM shows a quite difference by its having high endurance for tearing. At low 40 phr level, DOTP, TBC, DOA and BIO have close resistance, but TBTM has less. By increasing plasticizer quantity, the tear resistances of materials reduce. The big decrease occurs in TOTM and TBC materials as nearly 75 % when comparing 40 phr and 80 phr samples.

Additionally, flexible materials, such as artificial leather, being hard to breakable at low temperature is very important characteristic if we consider using them in cold season or in cold area, they must be still wearable and useable for long time. DOA, TBC and BIO have more resistance to cold area according to its cold flexibility test with its high flexibility at room temperature. Other plasticizers except TBTM showed nearly same characteristic in cold flex. TBTM plasticized PVC cracked earlier than others, it can be resulted from its low compatibility and worse gelation behavior under same condition of plasticization steps.

By considering these properties, the choice of plasticizers must meet the requirements that desired for final product, using them separately at specific ratio or they can be mixed together to improve performance of the final product.

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