A TECHNICAL GLANCE ON SOME COSMETİC OİLS

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Abstract

The properties of molecular structure, thermal behavior and UVA protection of 10 types of healthy promoting oils which are argania, almond, apricot seed, and jojoba, wheat germ, and sesame seed, avocado, cocoa, carrot and grapes seed oils were studied. FT-IR analysis was used for molecular structure. DSC analysis was used for thermal behavior and UV analysis was used for UV, visible and IR light absorption. Molecular structure and thermal behavior of avocado and cocoa are different from the others. Contrary to the spectra of avocado and cocoa on which the peaks belongs to carboxylic acid very strong, the spectra of the others do not involve carboxylic acid strong peaks. Almond, wheat germ and apricot seed oil absorb all UVA before 350 nm wave length. The UV protection property of grapes seed and cocoa is very well. Protection of wheat germ, almond and apricot seed oils to UVA is well respectively. Absorption of IR rate change from 7% to 25% for carrot, apricot seed, wheat germ, argania, avocado and grapes seed respectively.

Keywords: Cosmetic oils, thermal behavior, molecular structure, UV protection

Practical applications

Except avocado and cocoa oils the others may be used for production of inherently UV protection yarn. This type of yarn can be used for producing UV protection clothes. UV protection clothes are state of the art nowadays. These type of clothes are manufactured by finishing technique now. Inherently UV protection clothes may have more advantage than the clothes produced by finishing technique. Beside the UV protection properties, many benefits may be obtained by using these oils like moistening, vitamin emitted and the other healthy related conditions.

Introduction

The organic oils produced from plants are in state of art nowadays for using cosmetic areas. According to investigation on ancient cosmetics, these products contain a mixture of components of very different nature (organic and inorganic) and have some properties. From ancient texts or through archaeological findings, cosmetics' preparation ingredients have been recognized. Most of the mixtures of cosmetics described in the literature correspond to products formed with oils and/or resins, probably used as perfumes or unguents [1]. Fruit seed oils have been used as chemical additives in food, perfumes, and toiletries. Plant seed oils involve antimicrobial compounds and antioxidants [2,3].

Fatty acids can be in two different forms like saturated (no double bonds between the carbon atoms) or unsaturated (one or more double bonds). Unsaturated forms divided into three groups as monounsaturated, polyunsaturated and long-chain polyunsaturated. Most of the properties of the oils are controlled by fatty acid composition. These two forms determine the stability and property of the oil. Lauric (12:0), myristic (14:0), palmitic (16:0) and stearic acids (18:1) are high degree of saturated fatty acids. Oleic (18:1n-9), arachidonic (20:4n-6), linoleic acid (18:2n-6) are high degree of unsaturated fatty acids. Saturated oils are more stable and do not become rancid as quickly as unsaturated oils. However, unsaturated oils are smoother, more precious, less greasy, and better absorbed by the skin. Both form of natural oils are more difficult to build into emulsions, are unsoluble in alcohol (except castor oil) and require antioxidants (e.g. vitamin E or C) to prevent rancidity [4,5,6].

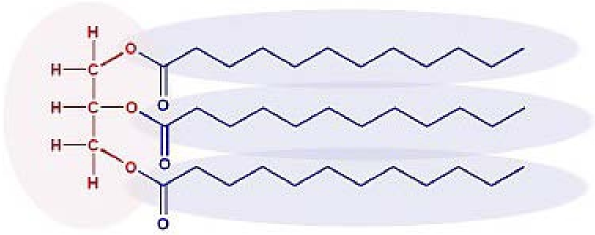

Fig.1: Glycerol (red) + 3 fatty acid chains (blue) =Triglyceride (natural oil) [4]

Although the scientists give most attention to the properties of fatty acid composition of the vegetable oils, they give minus attention to the lipid-soluble components which have significant contribution to the nutritional properties of these oils [7].

Avocado oil obtained from the fresh fruit. Due to its stability and high level of vitamin E, the use of avocado oils in the cosmetic industry is a state of art. The volume of avocado oil is nearly 2000 tones/year. The major advantages in respect to skin care of the avocado oil are its softening, soothing and notable absorption. Avocado oil involves at least 60% of the mono-unsaturated and 10% poly-unsaturated fatty acid. The composition of the fatty acids in avocado are palmitic and stearic as a saturated, palmitoleic and oleic as mono-unsaturated and linolenic and linoleic as poly-unsaturated. There are many extraction methods of the avocado oil; most popular one in this century is cold pressing method. [8]

Grapes seed oil is generally used in food and cosmetics areas, because it includes fatty acid and bioactive components. Grapes seed oil is commonly extracted from side product press cake of the juice and wine production. There are several technique for extraction oil from seeds like cold-pressing, hot-pressing, solvent extraction, super critical fluid extraction with CO_2. The last technique has advantage for enriching α-tocopherol, but only a few manufacturers used this technique due to the cost. This oil is rich in linoleic acid, plant steols, tocopherol and provitamin A. Grapes seed oil was classified in the polyunsaturated nutritional class. This oil has several subclasses, based on the content of linoleic, α-linolenic and monounsaturated fatty acid [6].

Sesame oil is the first oil known and consumed by human being. Sesame seed includes oil about %50, protein about %25, mineral ash, crude fiber, oxalates, soluble carbohydrates and phytate. Sesame oil has more resistance to oxidation than the other vegetable oils. Sesame oil is used in various areas like drugs, perfumes, cosmetics, creams, lubricants, insecticides and fungicides. Sesame oil can cause allergic problems when it use in cosmetic products. Sesame oil can be extracted by cold press technique and solvent extracted technique to get crude oil. Crude (unrefined) sesame oil contains high level free faty acids. Sometimes crude sesame oils are refined (neutralization, acid bleaching and deodorization). Refined oil properties are different from crude oil. Sesame oils involve triacylglycrols (90%), diacylglycrols, free fatty acids and phospholipids. The fatty acid is composed of palmitic acid, stearic acid, oleic acid, linoleic acid. In sesame seed oils saturated fatty acids are higher level than tri- and di-acylglycrols [9, 10, 11].

Wheat germ oil is a product obtained from germ part of the wheat. The wheat consists of endosperm (81-84%), bran (14-16%) and germ (2-3%). According to the reports brand and germ components have nutritional and health benefits. Wheat germ oil is used generally for nutritional due to its high level of vitamin E content. This oil can be use in wide range of applications like cosmetics, toiletries and pharmaceuticals. The concentration range of wheat germ oil in cosmetic products is 0,1-50%. Wheat germ oil can be extracted via some techniques like mechanical expelling, organic solvent extraction and super critical fluid extraction with CO_2. Solvent extracted wheat germ oil is more stable than the oil which is extracted mechanically, due to its lower lipid content. The wheat germ contains about 15% oil. The fatty acid composition is varied based on the wheat type, growth conditions, extraction method and storage conditions. Wheat germ consists of unsaturated and polyunsaturated fatty acid [12].

Carrot seed oil can be extracted via cold press or solvent extraction. Carrot seed oil contains oleic acid, linoleic acid and palmitic acid. Carrot seed oil has not so good oxidative stability. Monounsaturated fatty acid fraction is 82%, polyunsaturated fatty acid fraction is 13% and total saturated fatty acid is 4,6% in carrot seed oils [13].

There are two methods for extraction of argania oil; one of them is the traditional method which is carried out by crushing roasted kernels and then kneading into paste or dough with hot water and then pressed by hand, the other is half-industrialized or semiautomatic method which is carried out by mechanical cold-pressed without water addition. The oil produced using traditional method includes less linoleic and oleic acids than the oil produced half- industrialized method. The argania oil includes polyphenols as an antioxidant and minor component such as sterols, carotenoids, xanthophylls, and squalene for nutrition and health [14].

Jojoba oil can be produced by solvent extraction method. It is used generally in the cosmetic industry. Jojoba oil contains 38:2, 40:2, 42:2, 44:2 and 46:2 wax esters and stearic acids, Eicosenoic acid (20:1), Erucic acid (22:1) and Nervonic Acid (24:1) fatty acids. The structure of jojoba oil is such that it acts as a natural skin-softener. Consequently, jojoba oil is incorporated into many personal care formulations. Some chemical modification of the oil has occurred and has been geared toward polyunsaturated derivatives via bromination followed by dehydrohalogenation to produce alkynes and tetraene intermediates [15].

Almonds are considered to be a great source of proteins, dietary fibre, health-promoting unsaturated fatty acids, vitamin E, other vitamins, minerals; they are also low in saturated fats, and contain no cholesterol. The main monounsaturated fatty acid was oleic acid with substantial levels of palmitoleic acid present in the macadamia nut. The main polyunsaturated fatty acids present were linoleic acid and linolenic acid. alpha-Tocopherol was the most prevalent tocopherol except in walnuts [16, 17].

Natural oils have been used in cosmetic products and some cosmetic products could be used as UV protection materials. UV light is part of the light spectrum emitted by the sun. Below is a diagram that shows the light spectrum & the bands it is divided into. You will notice that the Ultra Violet band is broken into three catorgories. UVA, UVB & UVC.

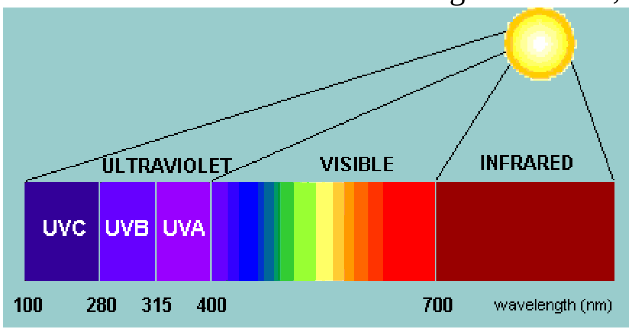

Fig.2: electromagnetic spectrum [18]

Experimental

In this study we used 10 types of healthy promoting oils which are argania, almond, apricot seed, jojoba, wheat germ, sesame seed, avocado, cocoa, carrot and grapes seed oils. The properties of these oils are given in the table 1. We studied UV transmission properties, FT-IR analysis based on predominant molecular structure and DSC analysis for thermal behavior of these different 10 natural oils.

DSC Analysis

Perkin Elmer Sapphire II model Differential Scanning Calorimeter (DSC) having heat flux method were used

Test Condition

Initial temperature: 30 °C,

Purge gaseous : nitrogen,

Heating rate : 10 °C /min,

Heating type : first heating (as-received)

Final temperature: 550 °C

Sample mass : approximately 5 mg,

Sample pan : open aluminum pan

FT-IR Analysis

Fourier transform infrared (FT-IR) spectra obtained by using Perkin Elmer -Spectrum 2000 Explorer model device with Pike- MIRacle model ATR auxiliaries. The spectra were taken between 4000–650 cm^{-1} wave numbers.

UV Analysis

UV spectra obtained by using Varian Cary 5000 UV-VIS-NIR Spectrophotometer with GTA Tubes auxiliaries. The spectra were taken between 800–180 nm in transmission mode. The scan rate was 600 nm/min and data interval was 5.0 nm

Table 1: The properties of oils.

Oil Name	Manufacturer	Production Method	Ingredient	Production date	Serial Number
Argania	BHS group	Cold press	%100	01/2012	0001
Almond	Gençay	Cold press	%100	02/2012	01
Apricot Seed	Kardelen	Cold press	%100	05/2011	008
Jojoba	Kardelen	Cold press	%100	09/2011	014
Wheat Germ	Kardelen	Cold press	%100	02/2011	013
Sesame Seed	Gençay	Cold press	%100	12/2011	01
Avocado	Kardelen	Cold press	%100	06/2011	013
Cocoa	Kardelen	Cold press	%100	09/2011	013
Carrot	Kardelen	Extraction	%100	08/2011	012
Grape Seed	Kardelen	Cold press	%100	09/2011	010

Result and discussion

According to FT-IR spectra the dominant molecular structure of all oils, except avocado and cocoa oil, are similar. There is also similarity between FT-IR spectra of avocado and cocoa oils. As seen from figure 3, there are five main differences between avocado and cocoa oils, and the others. One of them is the broad peak located at 3300 cm^{-1} which is related -OH- group only on the spectra of avocado and cocoa oils, two of them are the narrow peak located at 1738 cm^{-1} which is related -C=O- group and 718 cm^{-1} which is related $–CH_2$-CH_2-CH_2- chain group only on the spectra of argania, almond, apricot seed, jojoba, wheat germ, sesame seed, carrot and grapes seed oils, the fourth one is peaks between 1136-802 cm^{-1} only on the spectra of avocado and cocoa oils and the last one is peaks between 1237-1099 cm^{-1} only on the spectra of argania, almond, apricot seed, jojoba, wheat germ, sesame seed, carrot and grapes seed oils.

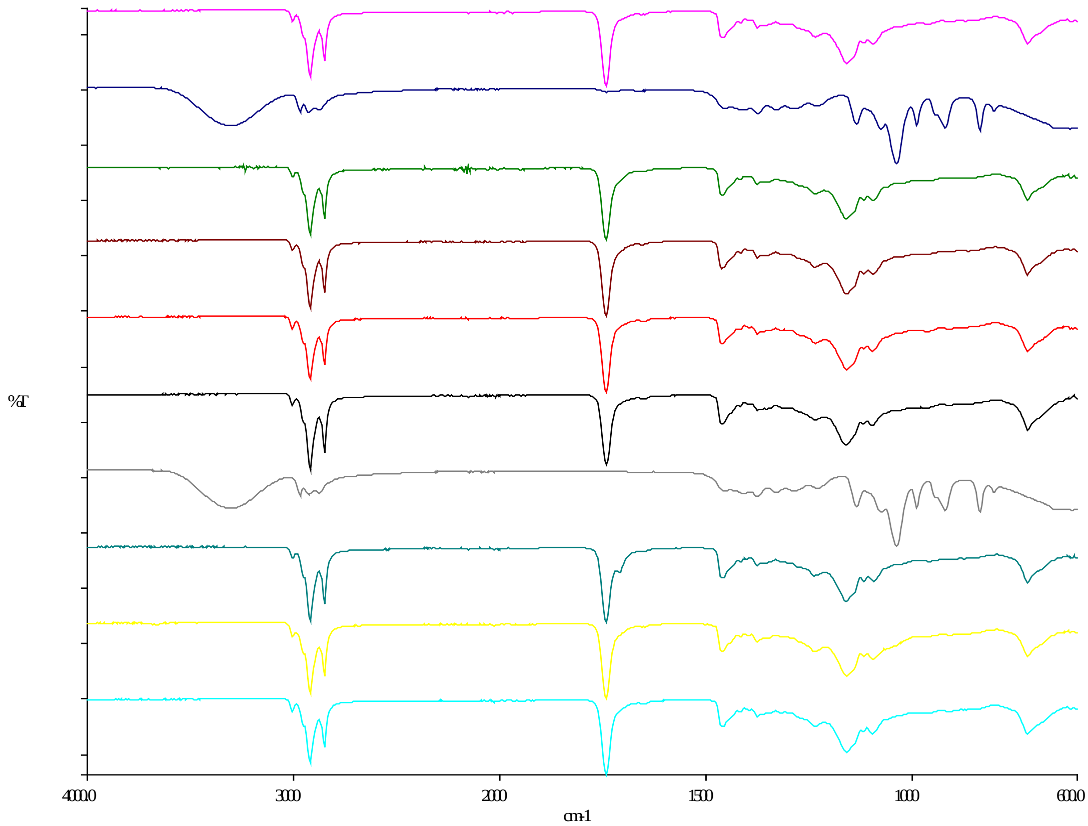

Figure 3: FT-IR spectra of all oils:

From top to bottom: 1. spectrum: argania oil, 2.spectrum: avocado oil, 3. spectrum: almond oil, 4. spectrum: wheat germ oil, 5. spectrum: carrot oil, 6. spectrum: jojoba oil, 7. spectrum: cocoa oil, 8. spectrum: apricot seed oil, 9. spectrum: sesame seed oil, 10. spectrum: grapes seed oil

The peaks located at 2923 cm^{-1} and 2850 cm^{-1} which are related $-CH_2-$ group are weak on the spectra of avocado and cocoa oils, but that peaks are strong on the spectra of the other rest oils. Although the peak at 1459 cm^{-1} on the all oils' spectra except avocado and cocoa oils was strong which is belongs to $-CH_2-$ and the peak related to $–CH_3-$ was weak. On the spectra of avocado and cocoa oils between 1455 -1233 cm^{-1}, a number of weak peak combination and overtone bands were occurred. The intensity of $-CH_2-$ and $-CH_3-$ group frequencies were decreased by the group of -OH- frequency in the region of 1455 -1233 cm^{-1} a bands. Spectra of all oils involve strong peaks at 1240-1030 cm^{-1} which are related to -C-O-C- group. It was supposed that the peaks between 991-802 cm^{-1} on the spectra of avocado and cocoa oils are related to carboxylic acid. The carboxylic acid group peaks was not observed from spectra of the other rest oils like the spectra of avocado and cocoa oils. There were only very weak peaks.

Figure 4: FT-IR spectra of avocado and cocoa oils

Figure 5: FT-IR spectra of all oils except avocado and cocoa oils

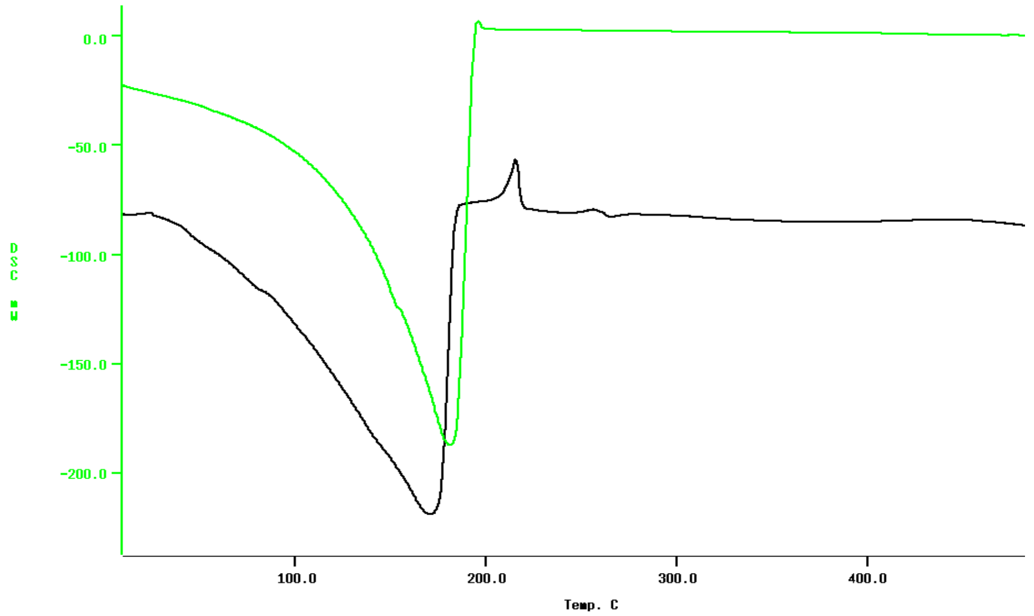

Figure 6: DSC thermograms of oils:
From top to bottom: 1. thermogram: avocado oil, 2.thermogram: cocoa oil

According to DSC thermogram, there are two main differences between the thermogram of avocado and cocoa oils, and the thermogram of the others rest. First one is the broad endothermic peak located between 70-180 ^{0}C which is related to loss of low molecular weight substances (water or solvent), only on the spectra of avocado and cocoa oils. The other is the endothermic narrow peak combination located 400-480 ^{0}C which is related to melting crystalline region of molecular chain, only on the spectra of argania, almond, apricot seed, jojoba, wheat, sesame, carrot and grapes seed oils. Endothermic peak combination shows that there is a different molecular chain length in the oil, the crystal structure length is short and crystallinite size distribution looks like a single crystal.

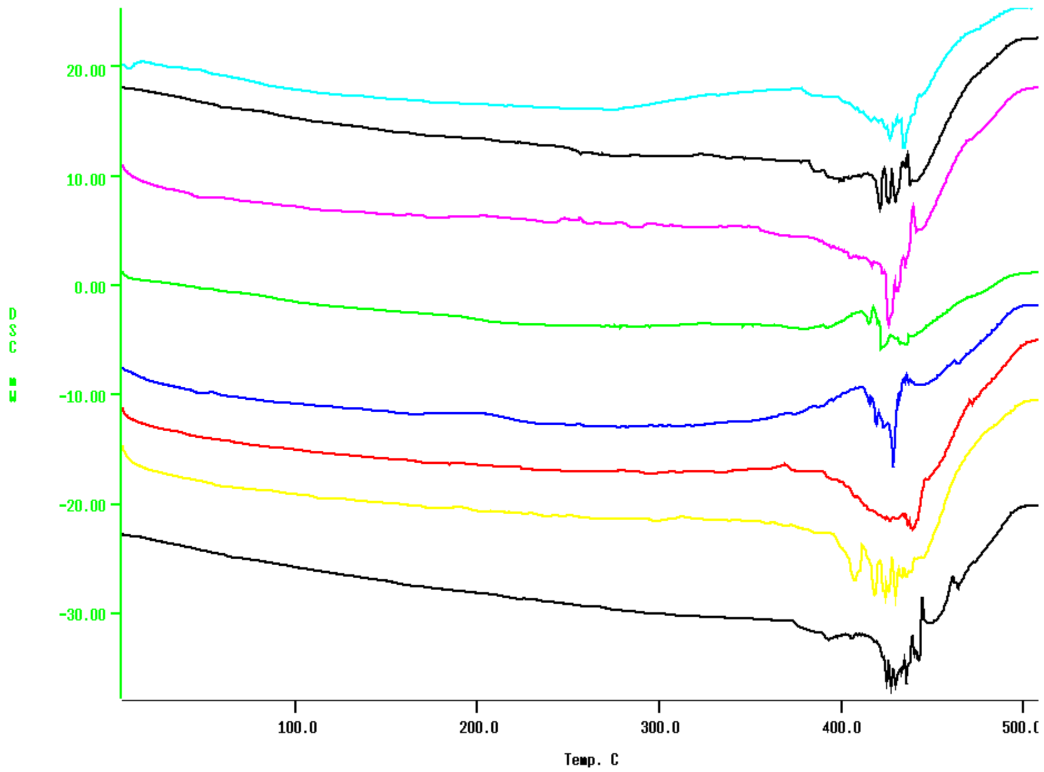

Figure 7: DSC thermogram of oils

From top to bottom: 1. thermogram: apricot seed oil, 2. thermogram: sesame oil, 3. thermogram: jojoba oil, 4. thermogram: grapes seed oil, 5. thermogram: carrot oil, 6. thermogram: wheat oil, 7. thermogram: almond oil, 8. thermogram: argania oil

All oils absorb UVB and UVC light. Because of that transmission ratio of this light is under %1. UVB and UVC could not arrive to earth surface. They are absorbed by stratospheric ozone and cloud. Only UVA reach to the earth. UVA can enter through glass and skin surface to epidermis. This light causes ageing and being cancer of the skin. Because of that UV protection properties of material directly related to UVA absorption ratio [19].

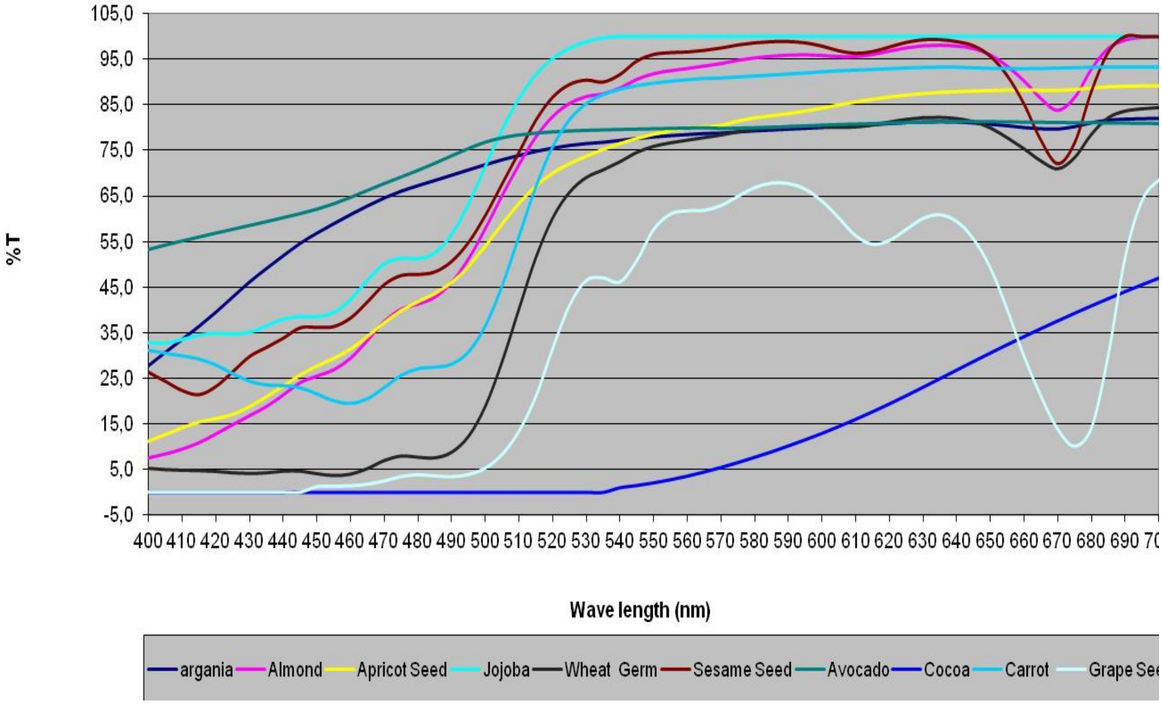

Figure 8: Light Transmission Ratios of oils at visible area (700-400 nm)

Cocoa oil absorbs all visible light after 540 nm wave length. Between 540-700 nm wave lengths, the absorption rate increase by decreasing wave length. Minimum absorption rate is 50% occurred at 700 nm. About 680 nm the spectra of grape seed, wheat germ, sesame seed and almond involve a peak. The peak dept which is related to absorption level was high at grape seed, sesame seed, almond and wheat germ respectively. About this wave length, these oils absorb more light than that they absorb at the other regions. At 680 nm the most absorption rate belongs to grapes seed oil, about 90%. The other oils did not absorb meaningfully visible light until the wave length of 520 nm. After 520 nm all oils begin to absorb light in different levels. Grapes seed and wheat germ oils absorb nearly all visible light after 500 nm. The ratio of absorption of the other oils increase, by decreasing wave length of light after 500 nm. Absorption of light rate change from 45% to 5% for avocado, argania, carrot, jojoba, sesame seed, apricot seed and almond respectively (figure 8)

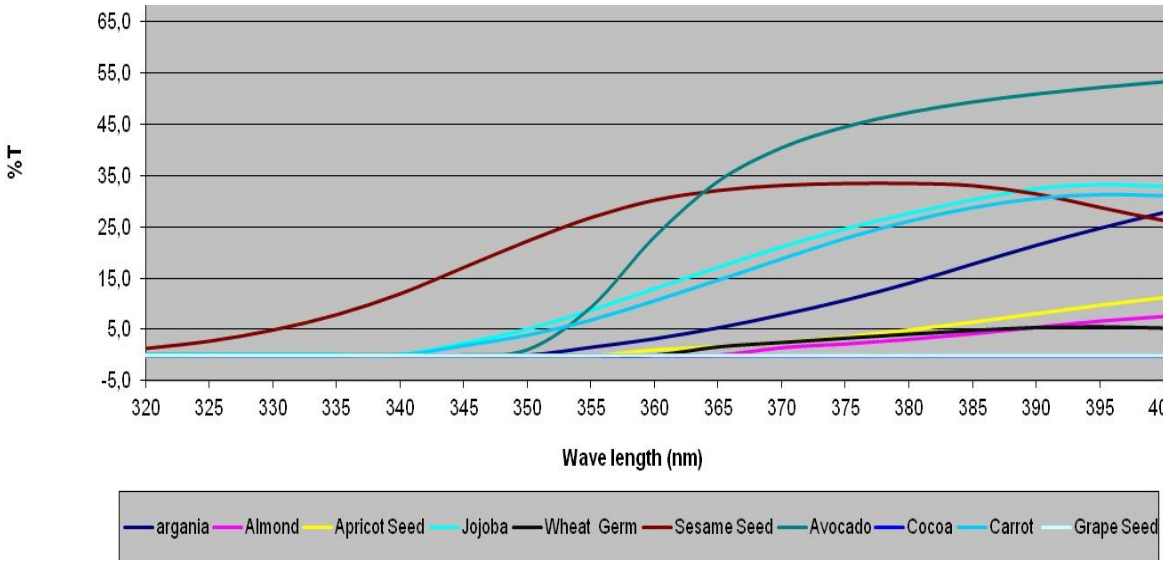

Figure 9: Light Transmission Ratios of oils at UVA area (400-320 nm)

Except sesame seed, all oils absorb all UVA light after 345 weave length. Sesame oil absorbs all UV light after 320 nm which is end of the UVA light. The absorption rate of all oils was altered by changing wave length. Decreasing wave length leads to an increase in the UVA absorption ratio. Grapes seed and cocoa oils absorb all UVA light. Although almond, wheat germ and apricot seed oil absorb all UVA before 350 nm wave length, they absorb UVA light nearly 95% after this wave length (figure 9). The UV protection property of grapes seed and cocoa is very well. Protection of wheat germ, almond and apricot seed oils to UVA is well respectively.

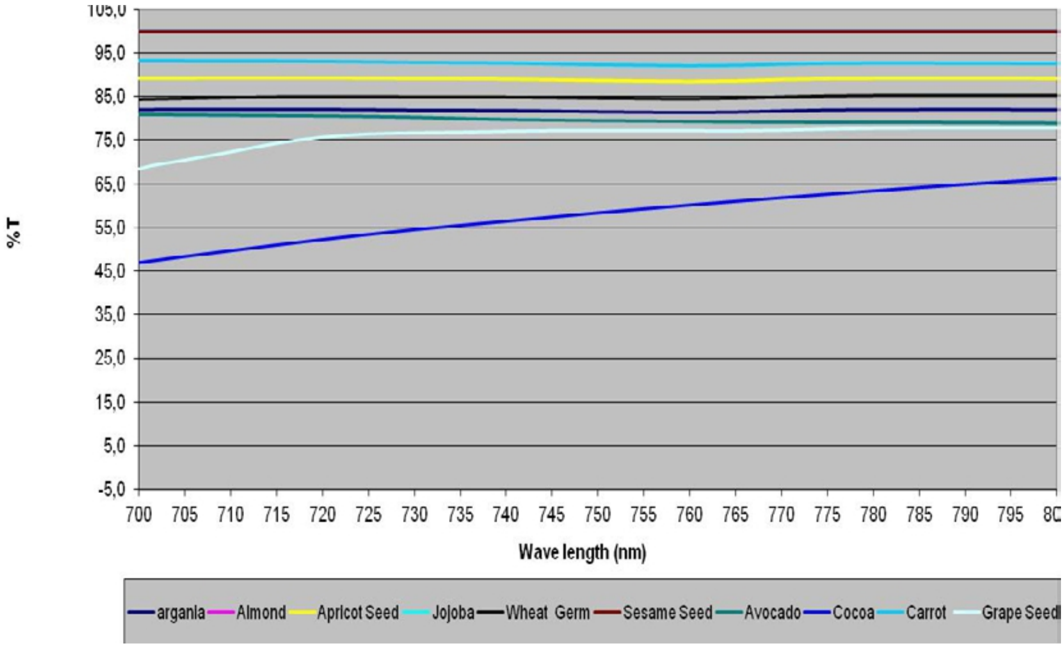

Figure 10: Light Transmission Ratios of oils at IR area (700-800 nm)

Cocoa oil absorbs more IR light than others. It absorbs about 50% of IR light. Sesame seed, jojoba and almond oils do not absorb IR light. Absorption of IR rate change from 7% to 25% for carrot, apricot seed, wheat germ, argania, avocado and grapes seed respectively. Except grapes seed and cocoa oils the absorption rate of IR of other oils do not change according to IR wave length (figure 10).

Conclusion

The dominant molecular structure of all these oils are similar each other except avocado and cocoa oils. The molecular structure of these two oils is looks like each other. This difference can be observed from DSC thermogram too. Unlike cocoa and avocado oils, the other oils does not include -OH- group. Because of this group, DSC thermograms of these two oils involve a big broadly peak. From DSC thermograms it was easily seen that there was no decomposition, melting and loss of volatile matter of all oils except avocado and cocoa oils under inert atmosphere before 400 ^{0}C. Grapes seed, cocoa, wheat germ, apricot seed and almond oils can be used as a UV protection agent. Due to the color and thermal behavior using cocoa oil may be not suitable. But the grape seed, wheat germ, apricot seed and almond oils can be used. The thermal behavior of these oils also permits using these oils in fiber production. The conventional thermoplastic synthetic fiber like polyamide, polyethylene terephthalate, polypropylene, etc. production are made under 400 ^{0}C. Because of that, if these oils can be added to extruder under inert condition, inherently UV production yarn could be produced. This type of UV protection may have more advantages than UV protection textile which is produced by finishing. Inherently UV protection property of textiles is more durable than UV protection property gained by finishing. Beside the UV protection properties, many benefits may be obtained by using these oils like moistening, vitamin emitted and the other healthy related conditions. Determination of this state a lot of work must be carried out. Cacao and grapes seed oils can be used also in the smart textiles for the use of the protection against hot atmosphere condition due to IR light absorption properties. This type of application may be used for production of hats and blouses.

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