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THESIS

INVESTIGATION OF THE DYEING AND FASTNESS PROPERTIES OF NATURAL DYES ON POLYESTER FABRICS

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A Thesis Submitted in Partial Fulfillment of
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The dyeing and fastness properties of natural dyes viz. Natural Orange, Natural Red Brown, turmeric and cassumunar dyes were investigated on PLA and PET fabrics. The water solubility and partition in water and octanol (log P) solvents of the dyes were examined. The results showed that water solubility and log P values of the dyes related to their dyeing properties on the polyester fabrics. The poor water-soluble dyes, turmeric and cassumunar, exhibited good dyeing properties on these polyester fabrics especially PLA while those having high water solubility and lower log P (Natural Orange and Natural Red Brown) could hardly dye on the fabrics. The spectroscopic property study of turmeric dye in organic solvents (ethyl acetate and methyl benzoate) could be used to explain the different color properties of the dye on PLA and PET. Turmeric and cassumunar dyes were also found to display fluorescence emission properties in particular on PLA. The color fastness of the turmeric and cassumunar dyes on PLA and PET were in a moderate-to-good level for fastnesses to washing, perspiration and rubbing but very poor light fastness was observed. Thus, an improvement of light fastness by using chitosan was studied.

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Vorabodee Sriumaoum
April 2013

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INVESTIGATION OF THE DYEING AND FASTNESS PROPERTIES OF NATURAL DYES ON POLYESTER FABRICS

INTRODUCTION

Poly(ethylene terephthalate), PET, is a conventional polyester being widely used in the industries including textiles. PET fiber has been accepted as a major synthetic fiber used in textile industry to date. PET polymer can be synthesized by either reacting terephthalic acid or dimethyl terephthalate with ethylene glycol in the condensation reaction. Producing the polymer into PET fiber can be achieved by melt spinning process. PET fiber is a strong fiber with the tensile strength in the range of 55–75 MPa (Hunt *et al*., 1993). It has a good resistance to chemicals used in textile processing. PET is a popular textile fiber as it has desired properties for textile applications. The chemical structure of PET is depicted in Figure 1 (Stoyko *et al*., 2002).

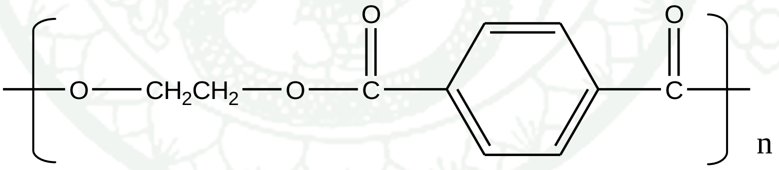


Figure 1 Chemical structure of PET.

Nowaday, an environmental awareness has brought about a textile production tendency toward the use of greener materials and manufacturing. The use of petroleum-based fiber has been claimed to cause an environmental burden. As a result, the materials derived from renewable resources have been in a great attention. As PET fiber is petroleum based fiber, it is not biodegradable. Therefore, an attempt to produce a more eco-friendly polyester fiber to substitute PET has been made.

Poly(lactic acid) (PLA) is an aliphatic polyester derived from renewable materials such as corn and sugar beet. Fermentation of such materials yields lactic acid. PLA can be produced by either direction condensation of lactic acid or ring-opening polymerization of lactide, a cyclic dimer of lactic acid. Figure 2 shows the chemical structure of PLA.

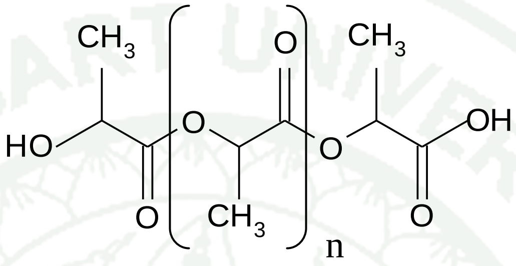


Figure 2 Chemical structure of PLA.

The properties of PLA have been studied in comparison with PET. PLA is a plant-based polyester, so it is biodegradable. At the beginning, it was expected to replace PET fiber in textile industry. However, some of its properties are inferior to those of PET. Table 1 illustrates the properties of PLA in comparison with PET. The tensile strength of PLA is slightly lower than that of PET. PLA has lower melting temperature than PET (170°C for PLA and 265°C for PET). Therefore, the temperature used in processing of PLA is lower as compared with PET. Young's modulus of PLA is 350 – 2,800 MPa while that of PET ranges from 2,000 to 2,700 MPa. The densities of PLA and PET are 1,210 – 1,430 kg/m^3 and 1,375 – 1,455 kg/m^3, respectively, indicating a lighter weight of PLA. Water absorption of PLA is 0.5 – 50 %, being more hydrophilic than PET(0.16% water absorption) (Middleton *et al*., 2000; Sodergard and Stott, 2002) .

Table 1 Properties of PLA in comparison with PET.

Properties	PLA	PET
Young's modulus (MPa)	350 – 2800	2000 – 2700
Tensile strength (MPa)	10 – 60	55 – 75
Melting temperature (°C)	150 – 170	250 – 265
Glass temperature (°C)	55 – 65	70 – 75
Density (kg/m^3)	1,210 – 1,430	1,375 – 1,455
Water absorption (%)	0.5 – 50	0.16

PLA and PET are dyeable with disperse dyes. The most important disperse dye class for polyester dyeing is azo-based type which covers about 60 – 70% of the commercial dyes used in dyeing industry. However, cleavage of the azo bond (−N=N−) in the dye molecule could generate a more toxic aromatic amines. Some of dye is suspected to cause cancer, reproductive or fertility problems in human.

Figure 3 illustrates cleavage of the azo bond in the dye molecule and the resulting aromatic amines. Apart from the generation of toxic aromatic amines, the dyes left after dyeing process often cause a serious problem to the effluent treatment. For this reason, greener dyestuffs are in demand. Natural dyes could be considered as an option for developing an eco-friendly textile dyeing.

$$\underset{\text{Azo dye}}{\text{R-N=N-R}'} \longrightarrow \underset{\text{Aromatic amine}}{\text{R-NH}_2 + \text{NH}_2\text{-R}'}$$

Figure 3 The chemical reaction of azo bond cleavage.

Natural dyes can be obtained from the color-providing materials in nature, viz. plants, animals and minerals. Natural dyes can be divided into organic and inorganic types. The organic dyes are mainly from plants and animals, e.g. lac, indigo, curcumin and madder whereas the inorganic ones are those from minerals, for example copper, coal and stone. Natural dyes are advantageous over synthetic dyes in the aspect of eco-friendliness, nontoxicity and no harm to environment. Nevertheless, the drawback of natural dyes is that they have relatively poor stability to light. Fading of the natural-dyed textile is often observed for most of the natural dyes. Therefore, improvement of such problem is needed in order to encourage the use of natural dyes in industrial textile dyeing.

The purpose of this research was to study the use of natural dyes for dyeing the polyester fabrics, PET and PLA, with the aim to establish a more eco-friendly dyeing process. The natural dyes used were those extracted from turmeric and cassumunar rhizomes and the commercial natural dyes. The solubility in water of the dyes was studied. The dyeing properties of the natural dyes on PET were compared with those on PLA. The color fastnesses to washing and light of the dyed PET and PLA were assessed. The effect of chitosan on the stability to light of the dyes was also investigated.

OBJECTIVES

1. To study the water solubility and partition in octanol: water mixture of the natural dyes.

2. To investigate the spectroscopic properties of natural dyes in organic solvents.

3. To investigate the dyeing properties of the natural dyes on the PET and PLA fabrics.

4. To investigate the color properties of the natural-dyed PLA in comparison with PET.

5. To study the color fastness properties of the natural dyes on PET and PLA fabrics.

6. To study the effect of chitosan on the dyeing and fastness properties of turmeric-dyed PLA fabric.

LITERATURE REVIEW

1. Polyester

1.1 Poly(ethylene terephthalate)

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester being widely used in packaging and textile applications. PET polymer can be divided according to its viscosity into two types, i.e. low-viscosity and high-viscosity PETs. The low viscosity type has viscosity in the range of 0.55-0.67 dl g^{-1} while that of the high viscosity type is 0.75-1.00 dl g^{-1} (Campbell, 1988). Low-viscosity PET is used in productions of textiles and packaging products, while the high-viscosity one is used for seat belt and cord production (Scheirs and Long, 2003). The textile fiber produced from PET has been accepted as a major synthetic fiber used in apparel and non-apparel textile industry.

Normally, PET polymer is produced by either reacting terephthalic acid with ethylene glycol in esterification reaction or by transesterification reaction between ethylene glycol and dimethyl terephthalate. Dimethyl terephthalate and terephthalic acid are in solid state and have melting point of 140.65°C and 300°C, respectively. The properties of terephthalic acid and dimethyl terephthalate are shown in Table 2. In the polymerization process, bis-(2-hydroxyethyl)-terephthalate monomer is generated as intermediate (Verschueren, 1983). Bis-(2-hydroxyethyl)-terephthalate monomer is then polymerized under pressure and heat conditions to attain PET polymer. Nowadays, PET is produced from terephthalic acid rather than dimethyl terephthalate. The advantage of using terephthalic acid is that the reaction from terephthalic acid is faster since the particle size of terephthalic acid is smaller than that of dimethyl terephthalate. The detailed mechanisms of PET synthesis are shown in the following section.

Table 2 Properties of terephthalic acid and dimethyl terephthalate.

Properties	Terephthalic acid	Dimethyl terephthalate
Melting point (°C)	300	140.65
Boiling point (°C)	-	284
Sublimation point (°C)	404	-
Sublimation enthalpy (kJ mol^{-1})	142	-
Burning enthalpy at 25°C (kJ mol^{-1})	-3,198	-4,685

1.1.1 Esterification reaction

Esterification reaction occurs throughout PET synthesis. Because it is an equilibrium reaction, the removal of the condensed water is important in order to minimize the hydrolysis of the formed ester groups. Polymerization is through a polycondensation reaction of terephthalic acid and ethylene glycol with water as a by-product (Figure 4). PET produced from esterification reaction has higher molecular weight than that synthesized by transesterification reaction.

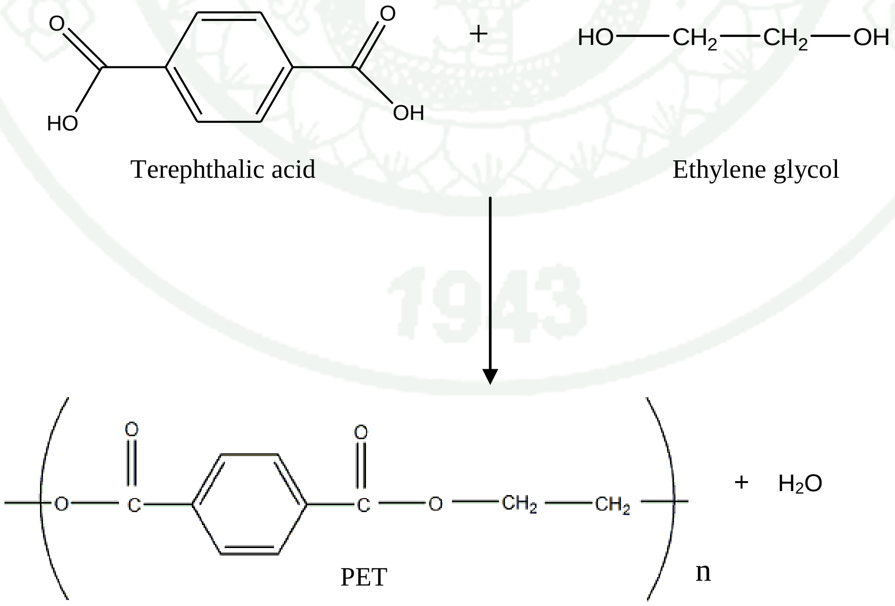


Figure 4 The esterification reaction of PET.

1.1.2 Transesterification reaction

Dimethyl terephthalate and ethylene glycol react to form poly(ethylene terephthalate) and methanol, which is evaporated to drive the reaction forward. Transesterification reactions are often catalyzed by the addition of an acid or base such as divalent salts of manganeses, cobalt, magnesium and zinc (Kroschwitz, 1990). The reaction is depicted in Figure 5.

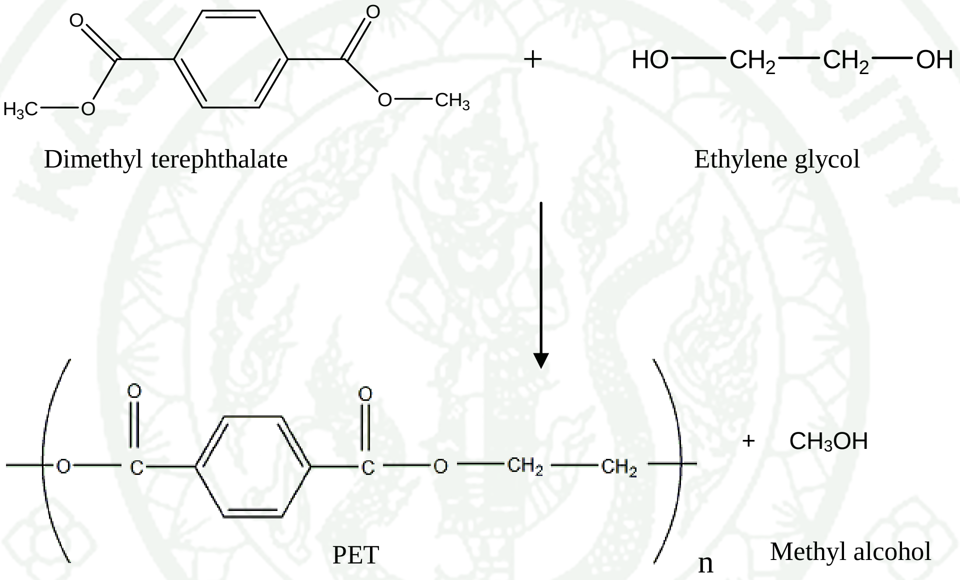


Figure 5 The transesterification reaction of PET.

PET has been produced into textile fiber with outstanding properties. PET fiber is strong, wrinkle resistant and durable. It is also resistant to chemicals especially acid except strong acid at high temperature but rather sensitive to hot alkali. PET fiber has been widely used in apparel production.

1.2 Poly(lactic acid)

Poly(lactic acid) (PLA) is an aliphatic polyester derived from natural renewable resources such as corn, sugar and cassava. Lactic acid which is a product from fermentation of the natural raw material is used as a monomer for PLA polymerization. Lactic acid has 2 forms of stereoisomers, viz. L-lactic acid and D-lactic acid (Figure 6). Production of cyclic lactide dimer results in three forms, viz. the D, D-lactide or D-lactide, L, L-lactide or L-lactide and L, D- or D, L-lactide called meso-lactide.

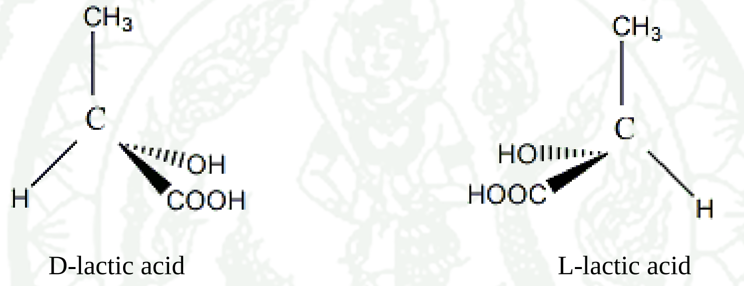


Figure 6 The stereoisomers of lactic acid.

1.2.1 Life cycle of PLA

The life cycle of PLA is a closed system with no emission of harmful substances to the environment (Figure 7). From natural resource-based materials like starch and sugar, lactic acid is produced and used as a monomer for PLA polymerization. As the raw materials used are renewable, PLA production is more substainable than the fossil-based materials where shortage of petroleum resource is in concern. After its service life, PLA can be disposed by hydrolysis into final products as CO_2 and H_2O which are then used in growing process of the starting raw material again.

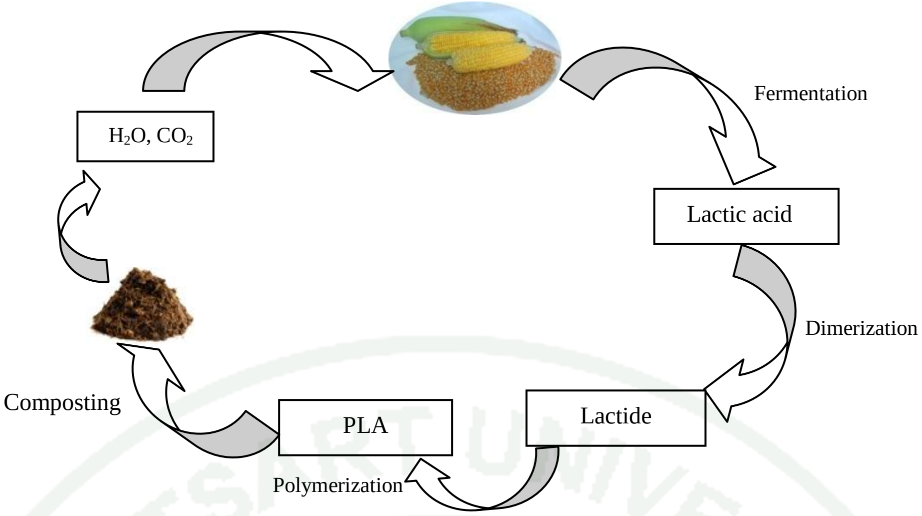


Figure 7 The life cycle of PLA.

1.2.2 Polymerization of PLA

PLA can be produced by two different polymerization routes which are direct condensation and ring-opening polymerization processes. Figure 8 shows polymerization reactions of PLA.

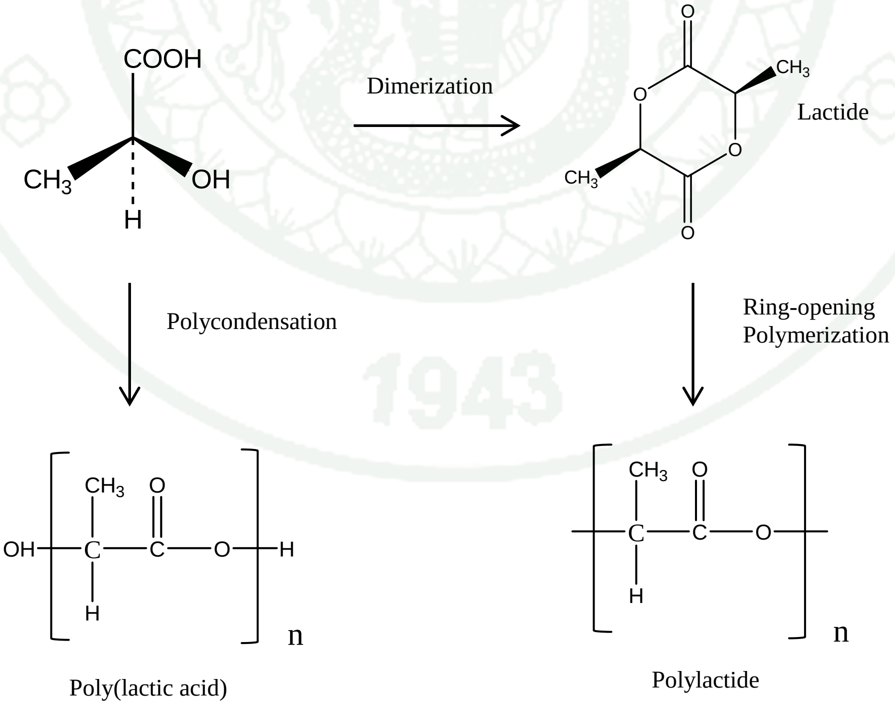


Figure 8 Polymerization of PLA.

1.2.2.1 Direct condensation polymerization of PLA

Direct condensation polymerization is an equilibrium reaction which produces PLA polymer of a low to medium molecular weight due to difficulties of removing water, the by-product from condensation reaction (Blackburn, 2005). The polymerization is performed in the presence of solvent at high temperature under vacuum condition.

1.2.2.2 Ring-opening polymerization of PLA

Ring-opening polymerization is an easy-to-control process which produces PLA with higher molecular weight. The ring-opening polymerization of PLA occurs via a coordination-insertion mechanism with ring opening of the lactide to the growing end of the polymer chain (Nijenhuis *et al.,* 1995). The advantages of ring-opening polymerization are that it yields PLA polymer with higher molecular weight and has a good reaction rate with organometallic compounds, Lewis-acid and metal-alkoxide catalysts (Jacobsen *et al*., 1999).

PLA has been produced into textile fiber with very interesting properties. It is expected to replace petroleum-based materials both on a cost and performance basis. PLA fiber has been developed with an attempt to produce a more eco-friendly synthetic fiber which can be used in a range of apparel and non-apparel fabric applications. Several properties of PLA are similar to PET viz. moisture absorption, dimensional stability and dyeing ability with disperse dyes (Suesat *et al*., 2011).

Table 3 Comparison properties of PLA and PET fibers.

Properties	PLA	PET
Young's modulus (MPa)	350 – 2,800	2,000 – 2,700
Tensile strength (MPa)	10-60	55-75
Melting temperature (°C)	150 – 170	250-265
Glass temperature (°C)	55 – 65	70-75
Density (kg/m^3)	1,210-1,430	1,375-1,455
Water absorption (%)	0.5 – 50	0.16
Strength (cN/tex)	40-55	35-50
Elongation at break (%)	30-40	30-50
Refractive index	1.35-1.45	1.54
Degradation (year)	0.5-2	Up to 1,000

Source: Middleton and Tipton (2000); Sodergard and Stott (2002); Choi and Seo (2006).

Table 3 shows the properties of PLA in comparison with PET. The tensile strength of PLA is slightly lower than that of PET. PLA has lower melting temperature than PET (170°C for PLA and 265°C for PET). Therefore, the temperature used in processing of PLA is lower. Young's modulus of PLA is 350-2,800 MPa while that of PET ranges from 2,000 to 2,700 MPa. The densities of PLA and PET are 1,210 – 1,430 kg/m^3 and 1,375 – 1,455 kg/m^3, respectively, indicating a lighter weight of PLA. Water absorption of PLA is 0.5 – 50%, being more hydrophilic than PET (0.16% water absorption) (Middleton and Tipton, 2000; Sodergard and Stott, 2002). The lower refractive index of PLA makes it exhibit a deeper shade as compared with PET when dyed with the same dyes. Dyeing PET is typically carried out by high-temperature process, where the temperature is raised to 130°C under pressure, while the dyeing of PLA is done at 110°C. Both polyester fibers are well dyeable with disperse dyes.

2 Spectroscopic properties of dye

2.1 The electromagnetic spectrum

The electromagnetic spectrum ranges from short wavelengths (containing gamma and x-rays) to long wavelengths (containing microwaves and radio waves). Table 4 illustrates the relationship between wavelength and frequency of electromagnetic spectrum (Lynch and Livingston, 2001). Dyes generally show an absorption band somewhere in the visible range of the electromagnetic spectrum between 360 and 750 nm. This absorption usually corresponds to an electronic transition in the molecule between the highest occupied electronic energy level and the lowest unoccupied electronic energy level. The absorbed electromagnetic radiation has energy equal to the energy difference between the occupied and unoccupied non-bonding. Figure 9 shows the visible spectrum of light from approximately 400 to 700 nm.

Table 4 The relationship between wavelength and frequency of electromagnetic spectrum.

Waves	Wavelength (nm)	Frequency (Hz)
Gamma Rays	$10^{-4} – 10^{-2}$	$> 3 \times 10^{19}$
X-Rays	10^{-2}- 1	$3 \times 10^{17} – 3 \times 10^{19}$
UV	10 - 400	$7.5 \times 10^{14} – 3 \times 10^{17}$
UV-Visible	400 – 700	$4.3 \times 10^{14} – 3 \times 10^{17}$
Infrared	700-10^{5}	$3 \times 10^{12} – 4.3 \times 10^{14}$
Microwave	$10^{5} – 10^{7}$	$3 \times 10^{9} – 3 \times 10^{12}$
Radio	10^{7} - 10^{9}	$< 3 \times 10^{9}$

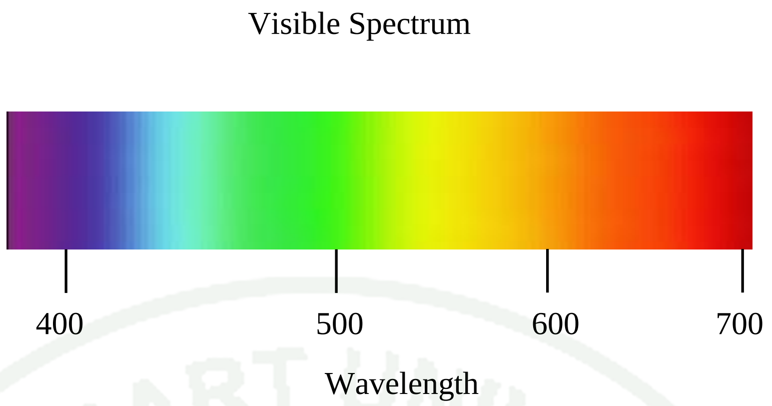


Figure 9 The visible spectrum of light.

Source: Lynch and Livingston (2001)

2.2 UV – Visible absorption spectrum

Normally, dyes can absorb ultraviolet and visible light. The visible region of the spectrum comprises photon energies of 36 to 72 kcal/mole and the near ultraviolet region extends this energy range to 143 kcal/mole. Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a tool for structural analysis.

2.2.1 Electronic transition

In the case of ultraviolet and visible spectroscopy of dye, the absorption of electromagnetic radiation in this region is for the transition between electronic energy. The energy is enough to excite dye molecules to a higher energy orbital. Therefore, absorption spectroscopy is the absorption of electromagnetic radiation in transition region between electron energy levels. When dye molecules absorb some of the light, energy will be absorbed as the electron is promoted to a higher energy orbital (Mohan, 2004).

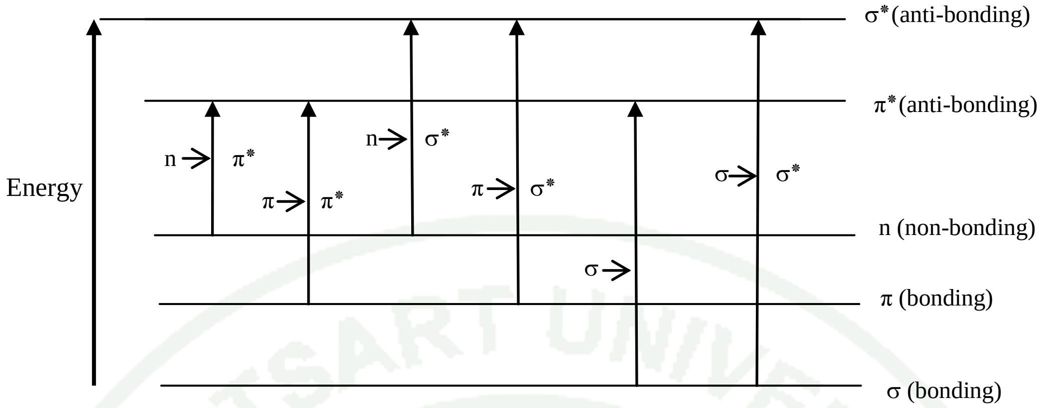


Figure 10 The electronic energy levels and electronic transitions.

2.2.1.1 Transition between bonding and anti-bonding orbitals

$\sigma \rightarrow \sigma^*$ Transition

The energy needed is large, corresponding to absorption in the far ultraviolet region in the range from 120-200 nm. This transition is found in saturated hydrocarbons, obtained σ bonds.

$\pi \rightarrow \pi^*$ Transition

This transition occurs with compounds containing double bonds, triple bonds, aromatic ring and azo group.

2.2.1.2 Transition between non-bonding and anti-bonding orbitals

$n \rightarrow \pi^*$ Transition

This transition occurs with compounds containing double bonds involving hetero-atoms bearing the unshared electron pair such as aldehydes, ketones and substitution on chromophore dyes.

$n \rightarrow \sigma^*$ Transition

Saturated compounds containing atoms with lone pair (non-bonding) electrons are capable of $n \rightarrow \sigma^*$ transitions. This transition occurs on nitrogen, oxygen and sulphur. Table 5 shows the electronic transition and absorption of some organic compounds.

Table 5 Electronic transition and absorption of some organic compounds**.**

Chromophore	**Example**	**Excitation**	**λ_{max} (nm)**
C = C	Ethene	$\pi \rightarrow \pi^*$	171
C = C	1-Hexene	$\pi \rightarrow \pi^*$	180
C = O	Ethanal	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180
N = O	Nitromethane	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200
C-X X = Br	Methyl bromide	$n \rightarrow \sigma^*$	205
X = I	Methyl Iodide	$n \rightarrow \sigma^*$	255

2.2.2 Absorption law (Beer – Lambert law)

2.2.2 Absorption law (Beer-Lambert law)

Figure 11 shows a monochromatic beam of light radiation of radiant power P_0, directed at a sample solution. Absorption takes place and the beam of radiation leaving the sample has radiant power P.

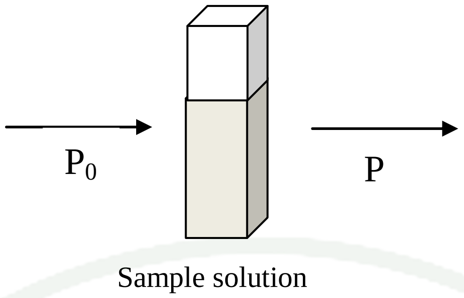


Figure 11 A monochromatic beam of light when directed at a sample solution.

The ratio of the light passing through a substance is measured as transmittance which can be calculated as P/P_0. The % transmittance is then calculated as:

$$\text{Transmittance (T)} \quad = \quad \frac{P}{P_0} \quad = \quad \frac{\text{Intensity of transmitted light}}{\text{Intensity of incident light}} \qquad (1)$$

Where P is intensity of transmitted light

P_0 is intensity of incident light

Absorbance is defined as the amount of light which is absorbed by the substance and is calculated as the negative logarithm of transmittance as shown in Equation 2 (anonymous, 2005).

$$\text{Absorbance} \quad = \quad -\log T = -\log \frac{P}{P_0} \qquad (2)$$

The Beer-Lambert law states that the absorbance of solution is directly proportional to the concentration of the absorbing species in the solution and the path length as seen in Equation 3. The molar absorptivity (ε) or the molar extinction coefficient is a property of the molecule undergoing an electronic transition and is a measure of a chemical ability to absorb light at a specified wavelength. (Pavia *et al.*, 2001). However, the law is not valid when high concentration and aggregation of the molecules in the solution are concerned.

$$A \quad = \quad \varepsilon bc \quad = \quad -\log \frac{P}{P_0} \qquad (3)$$

Where A is absorbance

$\mathcal{E}$ is molar extinction coefficient (l.cm^{-3}.mol^{-1})

c is concentration (mol.l^{-1})

b is path length of cell (cm)

P is intensity of transmitted light

P_0 is intensity of incident light

From Beer-Lambert law, the quantitative measurement of absorption and wavelength can build-up from concentration of a substance in solution.

2.2.3 Effects of substituent on the dye molecule

The absorption spectrum of the dye molecule depends on the type of solvent or substituent group on the dye molecules. Shift in spectral curves and change in their magnitudes are observed when the substituted group on the dye molecules is changed. The λ_{max} and $\mathcal{E}_{max}$ values vary depending on the degree of electron donating/withdrawing capacity of the substituted groups (Suesat *et al*., 2011). The shift in absorption bands are termed as follows.

- Bathochromic shift is a shift of the maximum absorption toward a longer wavelength due to the presence of auxochrome or by changing of solvent. It is also called “Red shift”.
- Hypsochromic shift is a shift of the maximum absorption toward a shorter wavelength. It is also called “Blue shift.
- Hyperchromic shift is an intensity increase of the band.
- Hypochromic shift is an intensity decrease of the band.

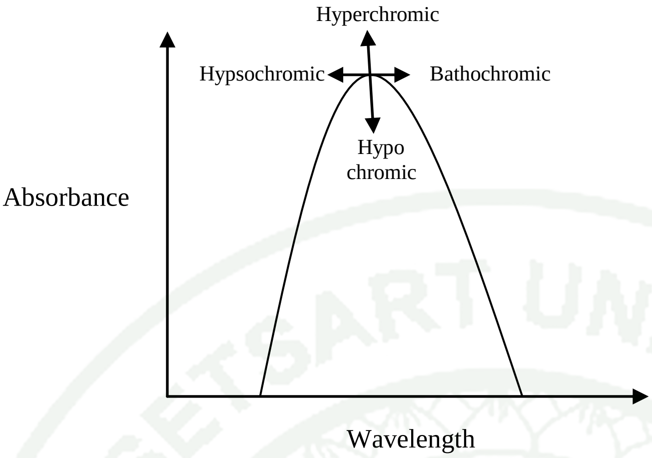
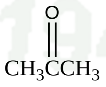
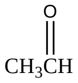
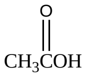


Figure 12 Shift of an absorption band.

The examples of some organic chromophores and the wavelength at their maximum absorption are illustrated in Table 6 (Skoog *et al*., 1988).

Table 6 Structures and wavelength at maximum absorption of some common organic chromophores.

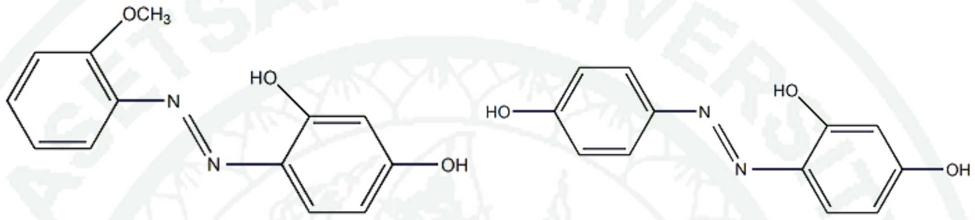
Chromophore	Example	Solvent	λ_{max} (nm)
Alkene	$C_6H_{13}CH=CH_2$	n-Heptane	177
Conjugated alkene	$CH_2=CHCH=CH_2$	n-Heptane	217
Alkyne	$C_5H_{11}C\equiv C–CH_3$	n-Heptane	178
Carbonyl	 $CH_3\overset{O}{\overset{\parallel}{C}}CH_3$	n-Hexane	186
	 $CH_3\overset{O}{\overset{\parallel}{C}}H$	n-Hexane	180
Carboxyl	 $CH_3\overset{O}{\overset{\parallel}{C}}OH$	Ethanol	204
Azo	$CH_3N=NCH_3$	Ethanol	339

2.2.4 Solvent effects

The choice of the solvents to be used in UV-vis spectroscopy is important. The first data for a good solvent is that it should not absorb ultraviolet radiation and UV-visible light range in the same region as the substance which spectrum is being examined. Solvents that do not contain conjugated systems are most suitable for this purpose. The non-polar solvent does not form hydrogen bonds with the solute, and the spectrum of the solute closely approximates the spectrum that would be produced in the gas state, where fine structure is observed. In polar solvent, the hydrogen bonding forms a soluble solvent complex, and the fine structure may disappear. The polar solvents do not form hydrogen bonds as readily with the excited states of polar molecules as with their ground states, and these polar solvents increase the energies of electronic transitions in the molecules. Polar solvents shift transitions of the $n \rightarrow \pi^*$ type to shorter wavelength. On the other hand, in some cases the excited states may form stronger hydrogen bonds than the corresponding ground states. In such a case, a polar solvent shifts absorption to longer wavelength, since the energy of the electronic transition is decreased. The polar solvents shift transitions of the $\pi \rightarrow \pi^*$ type to longer wavelength is shown in Table 6 (Amornsit, 2009; Pavia *et al*., 2001).

When dyes are dissolved in different solvents, the color of the dye solutions are different. The absorption spectra of dyes shows a bathochromic shift when polarity of the solvents increases. The solvatochromic effect happens as a consequence of polarity of the solvent used, influencing λ_{max} to shift towards shorter or longer wavelengths depending on types of the interaction between the solvent and the dye molecule in its ground and excited states. For the dye molecules, their excited state is more polar than their ground state. When polar solvent interacts with the molecules in their excited state. (Suesat *et al.*, 2011).

Sidir *et al.* (2009) studied the electronic absorption spectra of dyes dissolved in different solvents. The dyes dissolved in polar solvent (DMSO) exhibited bathochromic shift. The bathochromic shift was not observed in nonpolar solvent (n-hexane). The result indicated that more polar solvent affected the change of energy which showed $\pi\rightarrow\pi^*$ and n $\rightarrow\pi^*$ transitions depending on the solvent. It was found that the AZO3 and AZO4 showed a bathochromic shift when increased polarity of the solvent (Figure 13). The azoaromatic derivatives were more polar in the excited state than in the ground state. AZO3 exhibited a maximum absorption at a longer wavelength than AZO4 in the same solvent. It was found that the monoazo disperse dye molecules showed $\pi\rightarrow\pi^*$ and n $\rightarrow\pi^*$ transition depending on solvent effect.



2´,4´-dihydroxy-2-methoxyazobenzene
AZO3

4,2´,4´-trihydroxyazobenzene
AZO4

Figure 13 The structure of investigated azoaromatic molecules.

Suesat *et al.* (2011) studied the spectroscopic properties of the synthesized azo disperse dyes in two ester solvents (ethyl acetate and methyl benzoate) in order to obtained an explanation in the dye properties when applied on PLA and PET polymers (fibers) by using ethyl acetate and methyl benzoate as representatives, respectively.

Table 7 Spectroscopic properties of the synthesized dyes in ethyl acetate and methyl benzoate.

Dyes	**Substituted groups**			**λ_{max} (nm)**		**Exhaustion (%)**		**K/S**	
	X	**Y**	**R_1**	**In ethyl acetate**	**In methyl benzoate**	**On PLA**	**On PET**	**On PLA**	**On PET**
A1	H	H	C_2H_5	482	496	99.5	92.1	17.2	12.4
A2	H	H	C_2H_4OH	478	489	85.0	65.9	5.2	4.9
A3	H	H	$C_2H_4OCOCH_3$	454	467	99.7	95.9	11.8	8.2
A4	H	CH_3	C_2H_5	492	510	96.1	99.1	19.7	12.8
A5	H	CH_3	C_2H_4OH	488	500	84.9	74.1	9.4	6.5
A6	H	CH_3	$C_2H_4OCOCH_3$	464	476	97.5	97.2	10.5	8.6
B1	Cl	H	C_2H_5	504	520	98.8	98.7	17.5	13.1
B2	Cl	H	C_2H_4OH	500	511	88.0	87.6	8.1	7.4
B3	Cl	H	$C_2H_4OCOCH_3$	474	486	97.5	97.2	11.5	8.3
B4	Cl	CH_3	C_2H_5	516	531	99.1	97.8	15.9	13.3
B5	Cl	CH_3	C_2H_4OH	512	524	87.2	85.1	9.3	8.7
B6	Cl	CH_3	$C_2H_4OCOCH_3$	485	499	99.6	98.2	10.9	8.4
C1	CN	H	C_2H_5	529	545	98.9	90.2	20.4	16.1
C2	CN	H	C_2H_4OH	527	538	82.7	70.0	5.6	5.4
C3	CN	H	$C_2H_4OCOCH_3$	505	516	94.8	91.8	13.1	9.6
C4	CN	CH_3	C_2H_5	542	557	94.3	99.6	18.1	15.5
C5	CN	CH_3	C_2H_4OH	540	551	98.8	84.5	7.7	7.7
C6	CN	CH_3	$C_2H_4OCOCH_3$	516	528	98.2	98.9	11.7	9.5

Table 7 shows the spectroscopic properties of the synthesized dyes in ethyl acetate and methyl benzoate. The λ_{max} of the dyes dissolved in methyl benzoate was shifted to a longer wavelength (bathochromic shift) as compared with those in ethyl acetate. This can be explained the influence of solvents on the absorption properties of the dyes. For the dyeing study, the visual color yields for those dyes having approximately the same high level of exhaustion were different. The shade of the dyed PLA was darker and a trace brighter than the dyed PET. These differences correlated well with the solvatochromic study of the dyes in ethyl acetate and methyl benzoate solution. The molecular structures of the dyes also affected the absorbance of the dyes. The λ_{max} values were changed when the substituted group changed. The absorption spectra of the dyes showed a bathochromic shift when the polarity of solvents increased. This was reported to be caused by different spectroscopic properties of the dyes when applied on different type of polyester fibers.

2.2.5 Fluorescence

Fluorescence is electron emission processes which occur during molecular relaxation from excited states. When radiation of an appropriate wavelength is used to irradiate molecules in a sample, certain electronic transitions take place. As excited molecules return to the ground state they emit radiation of longer wavelength. The emitted radiation is referred to as fluorescence.

Electrons in the ground state (S_0) absorb energy from an incident radiation and are excited to S_1 or S_2 excited states. Vibrational relaxation (VR) results in the placement of the electron at the S_1, the main electronic level. Vibrational relaxation is a radiationless deactivation process where excess energy is consumed as kinetic energy or heat. A second collisional deactivation process can take place and the electron returns to the ground state by a radiationless deactivation (RD) process to S_0. The other possibility involves direct transition of the electron from the S_1 excited state to S_0 ground state and excess energy is emitted as photons at specific wavelengths called fluorescence (Atkins and Paula, 2000).

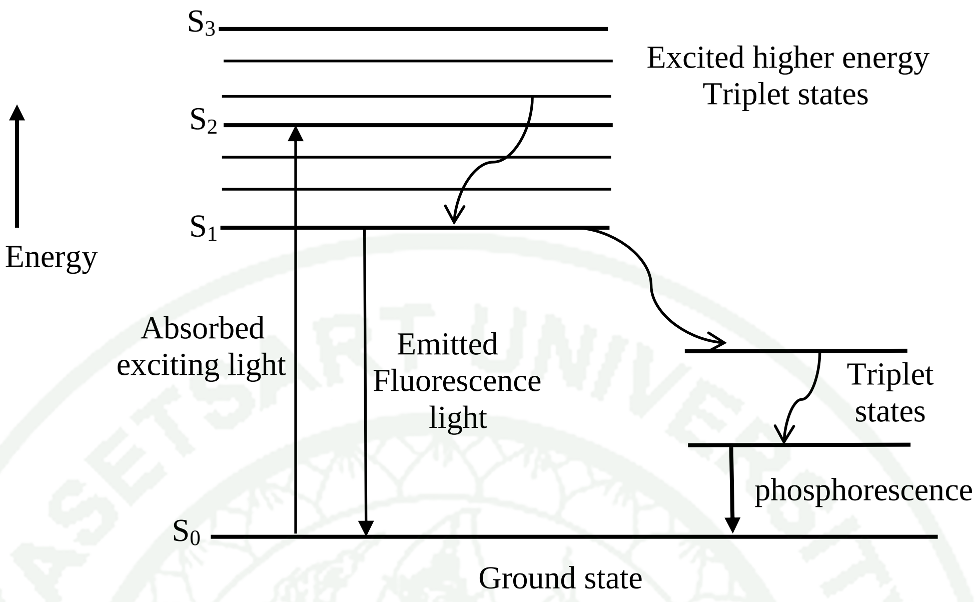


Figure 14 Fluorophore excitation, radiative decay and nonradiative decay pathway.

Source: So and Dong, 2002

3. Natural dyes and fastness properties

3.1 Natural dyes

Natural dyes can be obtained from the color-providing materials in nature, viz. plants, animals and minerals. Natural dyes can also be divided into organic and inorganic types. The organic dyes are mainly from plants and animals, e.g. lac, indigo, curcumin and madder whereas the inorganic ones are those from minerals, for example copper, coal and stone. Natural dyes are advantageous over the synthetic dye in the aspect of eco-friendliness, nontoxicity and no harm to environment. Nevertheless, the major drawback of these dyes is their relatively poor stability to light. Fading of the natural-dyed textile are often observed for most of the natural dyes. So, improvement of such problem is needed in order to encourage the use of natural dyes in industrial textile dyeing.

3.1.1 Classification of natural dyes

3.1.1.1. Indigoids dyes

Indigo is the most important group of natural dyes (Vankar, 2000). The color that indigo provided is blue. Indigo is classified as a vat dye. It is water insoluble. The general chemical structure of indigoid dye is shown in Figure 15.

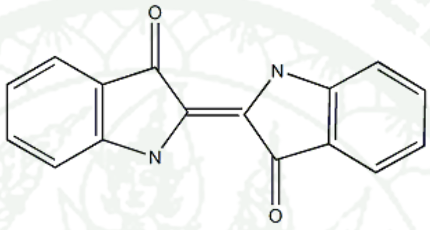


Figure 15 The chemical structure of indigoid dye.

3.1.1.2 Anthraquinone dyes

These dyes are important natural red dyes which are obtained from both plants and insects such as madder, cochineal and lac. They have good light fastness properties as compared with other natural dyes (Vankar, 2000). Alizarin or 1,2-dihydroxyanthraquinone obtained from madder is the example of anthraquinone dye. The structure of alizarin is shown in Figure 16.

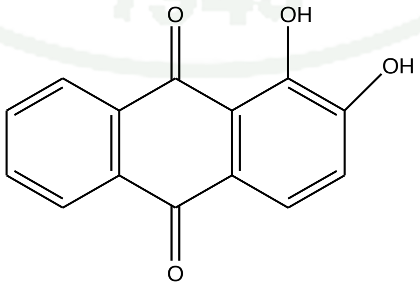


Figure 16 The chemical structure of alizarin.

3.1.1.3 Naphthoquinone dyes

Naphthoquinone dyes are derived from juglone for green to brown dyes and from henna for red dyes (Sequin-Frey, 1981). The chemical structure of 2-hydroxy-1,4-naphthoquinone dye from lawsone is shown in Figure 17.

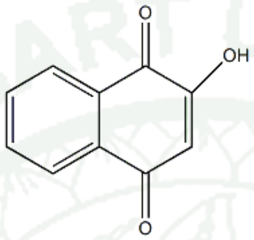


Figure 17 The chemical structure of 2-hydroxy-1,4-naphthoquinone dye.

3.1.1.4 Flavone dyes

These dyes are important yellow colorant. The examples of hydroxyl and methoxy containing flavones are weld, fustic, osage, etc. The basic structure of flavones dye is shown in Figure 18.

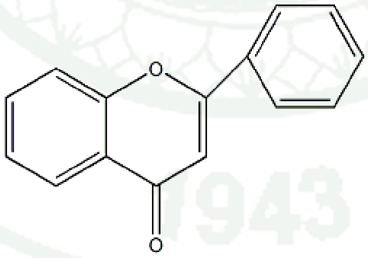


Figure 18 Basic structure of flavone dye.

3.1.1.5 Flavonoid dyes

Flavonoids provide the largest class of natural dyes obtained from old fustic, still de grain and sap green. Anthocyanins are the example of natural dye belonging to this flavonoid class. The basic structure of flavonoid dye is shown in Figure 19.

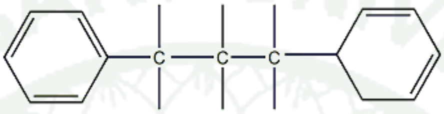


Figure 19 Basic structure of flavonoid dye.

3.1.1.6 Neoflavonoid dyes

Neoflavonoid dyes are isomer of flavonoids which belong to a class of polyphenolic compounds. It is derived from brazilwood and logwood. The chemical structure of brazilein from brazilwood is shown in Figure 20.

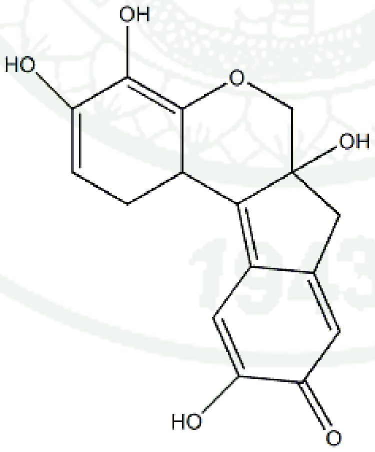


Figure 20 The chemical structure of brazilein.

3.1.1.7 Carotenoid dyes

The chemical structure of a carotenoid dye contains a long conjugated double bond. The examples of carotenoid dyes are those dyes derived from annatto and saffron. β-carotene is an example of carotenoid dye and its chemical structure is shown in Figure 21.

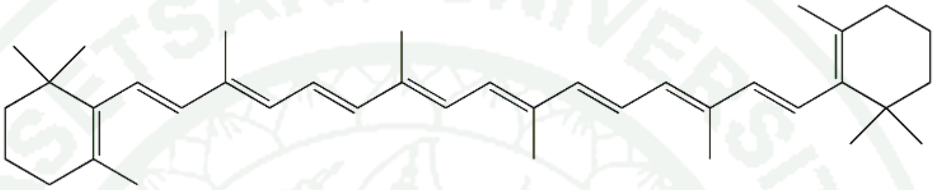


Figure 21 The chemical structure of β-carotene dye.

3.1.1.8 Xanthone dyes

Xanthones are a class of biologically active polyphenolic compounds structurally similar to bioflavonoids. Most xanthone dyes are derived from the mangosteen fruit. The general structure of xanthone dye (α-mangostin) from mangosteen is shown in Figure 22.

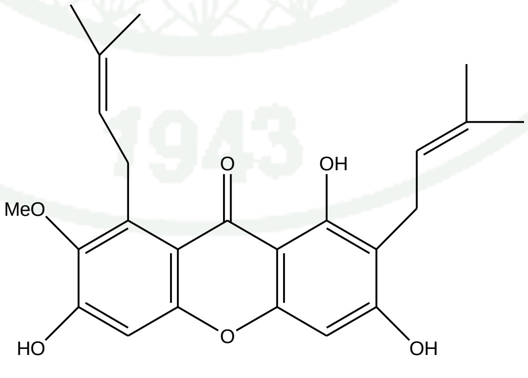


Figure 22 The chemical structures of α-mangostin from mangosteen.

3.1.1.9 Curcuminoid dyes

Curcuminoids are a partially purified natural complex of diaryl heptanoid derivatives isolated from turmeric. They are compounds of natural phenols and give yellow color. The chemical structure of curcumin, the curcuminoid dye, is shown in Figure 23.

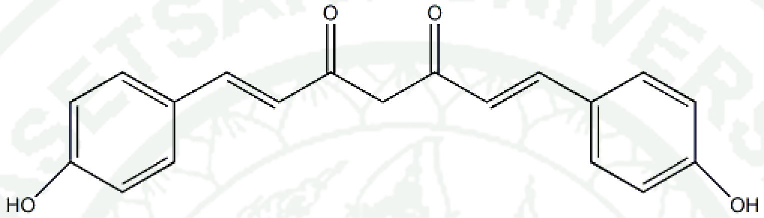


Figure 23 The chemical structure of curcumin.

3.1.2 Curcumin and its derivatives

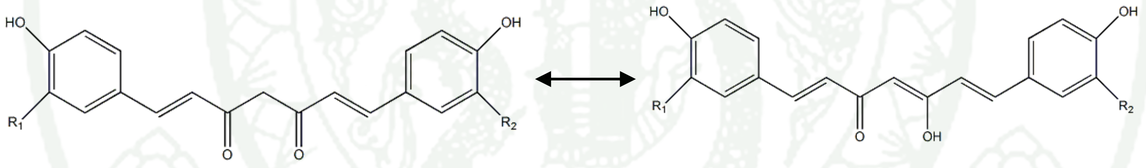
Curcumin is a yellow colorant that is derived from *Curcuma longa L*. and Zingiberaceae plants. Turmeric is rhizomes of *Curcuma longa L*. which has been intensively researched to be used in various fields, especially medical and pharmaceutical. Turmeric is considered a natural dye providing a yellow color which can be used for food and textile coloration (Sriumaroum *et al*., 2011). The yellow dye contains in turmeric is curcumin.

Cassumunar is a rhizome of Zingiber cassumunar which is a species of plant in the ginger family. It is important is medical application and is used medicinally in massage. Cassumunar is considered a natural dye providing a yellow color as well as turmeric. The dye contains in cassumunar rhizome is cassumunarin, a complex curcuminoids.

Normally, curcumin is derived from rhizome of turmeric and cassumunar by solvent extraction (Stankovic, 2004). The three important colorant components of curcumin are all dicinnamoylmethane derivatives:

- 1,7-Bis-(4-hydroxy-3-methoxyphenyl)-hepta-1,6-diene-3,5-dione or called “diferuloylmethane”.
- 1-(4-Hydroxyphenyl)-7-(4-hydroxy-3-methoxyphenyl)-hepta-1,6-diene-3,5-dione or called “*p*-hydroxycinnamoylferuloylmethane”.
- 1,7-Bis-(4-hydroxyphenyl)-hepta-1,6-diene-3,5-dione or called “*p*,*p*-dihidroxydicinnamoylmethane”.

Curcumin possibly exhibits tautomerism reaction. It shows to be sesquiterpene ketones and alcohols as called “keto-enol tautomerism”. Figure 24 illustrates keto-enol tautomerism of curcumin. The keto-enol tautomerism refers to a chemical equilibrium between a keto form (a ketone or an aldehyde) and an enol form (an alcohol). The keto and enol forms are said to be tautomers of each other. The interconversion of the two forms involves the movement of an alpha hydrogen and the shifting of bonding electrons.



Keto form Enol form

Figure 24 Keto-enol tautomerism of curcumin.

Normally, curcumin shows keto-enol tautomerism depending on the type of solvents. More than 95% exhibits an enol form at pH levels of 1-7. Water solubility of curcumin is very low and curcumin solution appears in yellow. At pH 7.5, the color changes from brownish yellow to red.

Dyeing textiles with natural dyes have long been over half century ago, especially for natural fibers like cotton and silk. Most of natural dyes are well soluble in water, so they can readily dye on hydrophilic textile fibers. Natural dyes rarely found in use for dyeing synthetic fibers as these fibers are rather hydrophobic.

Han and Yang (2004) studied the use of curcumin as an antimicrobial finish by dyeing on wool fabric. It was found that curcumin provided a good antimicrobial properties to the fabric. Antimicrobactial ability of the wool fabric increased with curcumin concentration.

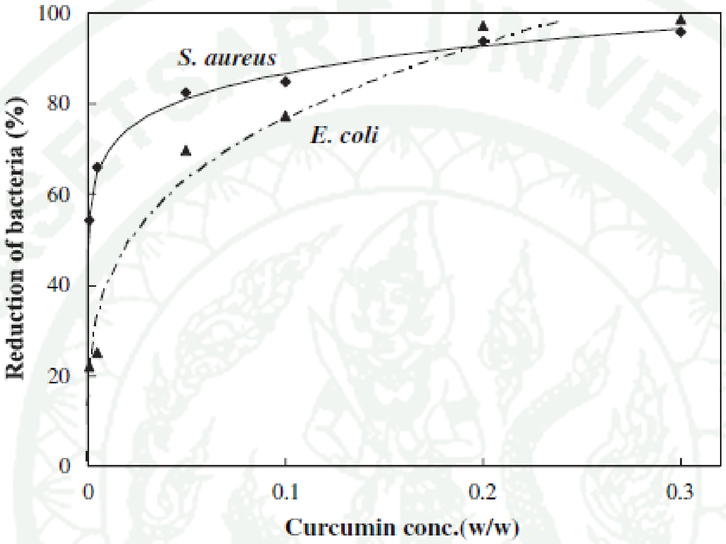


Figure 25 Relationships between curcumin concentration and antimicrobial activity of wool fabric treated with curcumin against S. *aureus* and E. *coli*.

Figure 25 showed the relation between curcumin concentration on wool and the antimicrobial activity of the treated fabric against E. *coli* and S. *aureus*. Less than 0.01% of curcumin inhibited 70% S. *aureus* growth. Effective inhibition of E. *coli* required a higher concentration of curcumin. For an inhibition rate of 70% against E. *coli*, 0.05% of curcumin was necessary. An inhibition rate of more than 95% was obtained against both S. *aureus* and E. *coli* when 0.2% of curcumin was applied to the fabric. The antimicrobial ability of curcumin-finished wool was moderately durable, more durable to home laundering than to light exposure. The inhibition rates against S. *aureus* and E. *coli* were 45% and 30%, respectively, after 30 cycles of home laundering.

Singh *et al*. (2005) performed an antimicrobial activity test of some natural dyes with a view to develop protective clothing. The natural dyes were highly effective antimicrobial agents as the minimum inhibitory concentration (MIC) for most of these lies in region of 5-40 mg. *Rumex maritimus* was active only against *Klebsiella pneumonia* and showed a small zone of inhibition. *Rubia cordifolia* showed little activity against *Klebsiella pneumoniae* at highest test concentration (40 mg). It was observed that *Quercus infectoria* had excellent antimicrobial properties with significantly low concentration required (5 μg) on wool fabrics. Table 8 shows zone of inhibition for each natural dyes against microbes.

Table 8 Zone of inhibition for natural dyes against microbes.

Dye	**Conc. (μg)**	**Zone of inhibition (diameter in cm)**				
		Pseudomonas aeruginosa	***Bacillus subtilis***	***Proteus vulgaris***	***Klebsiella pneumonia***	***Escherichia coli***
Quercus infectoria	5	0.9	2.5	1.2	2.0	0.7
	10	1.3	2.6	1.5	2.2	1.4
	20	1.6	2.7	1.7	2.4	1.9
	40	1.8	2.9	2.0	2.6	2.1
Acacia catechu	5	-	-	0.8	1.2	0.5
	10	-	0.6	0.9	1.4	0.8
	20	-	1.1	1.2	1.5	1.3
	40	-	1.3	1.3	1.6	1.5
Rumex maritimus	5	-	-	-	0.9	-
	10	-	-	-	0.9	-
	20	-	-	-	1.1	-
	40	-	-	-	1.2	-
Rubia cordifolia	5	-	-		-	-
	10	-	-		-	-
	20	-	-		-	-
	40	-	-		0.7	-

EL-Shishtawy *et al.* (2009) studied the modification of acrylic fiber to improve natural dyeing properties. The modified acrylic fiber containing amidoxime groups was obtained and was dyed with curcumin and madder. It was found that the dyeability of the acrylic fibers depended on amidoxime content. The optimum pH for dyeing was 2.0 and 5.0 for madder and curcumin, respectively. Under acid conditions, madder bonded to modified acrylic by mainly ionic bonds, while curcumin attached to the fiber via both physical bonds together with ionic bonds.

3.1 Fastness properties

Natural agencies such as light, weather, oxygen and other atmospheric gases can destroy certain dyes. In addition, there are many chemicals and finishing treatments used in wet processing of textiles which may influence fastness of dyes to some degree. Most natural dyes are organic compounds and are, therefore, poor in varying degree to the action of destructive agents. The light fastness of the natural-dyed samples are normally in the range from poor to fairly good (Gupta, 1996). The poor light fastness can be attributed to the sensitivity of the dye chromophore to photochemical oxidation (Teli *et al.*, 2000). The absorption of one quantum of light of 400 nm represents an increase in energy of molecule by about 77 Kcal. When this is compared with bond energies (C-C 58.6, C-O 70.0, C=C 100.00 Kcal/mole), it is clear that energy particularly UV is adequate for rupturing of covalent bond in organic molecule (Gohl and Vilensky, 1980).

Fading of natural dye in sunlight may be due to some of breakdown in energy absorption capacity of the electron of chromophores or a breakdown in the structure of dye molecule. When sunlight energy is absorbed, the loosely held electrons of the chromophores are raised to higher energy level that they become more active. Fading in sunlight is also due partly to ultraviolet radiation which initiates chemical degradation of dye molecule through the loosely held electrons of the chromophores.

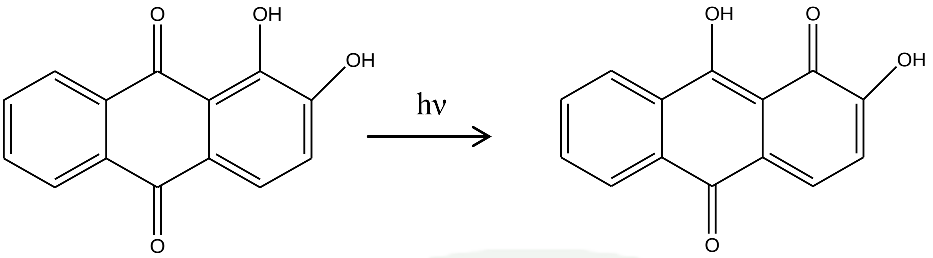


Figure 26 Photochemical reaction of Rheum

The hydrogen bonds could form in the molecules of some natural dyes such as Rheum. When exposed to sunlight, a possible photochemical reaction of the natural dyes could occur as shown in Figure 26. The sunlight could provide sufficient energy to cause breakdown of hydrogen bonds and make fabric color pale.

In the case of wet fastness properties, natural dyes itself normally provide low-to-medium level when applied on textile fiber. An improvement in fastness properties is typically achieved by the aid of mordants such as alum, iron and tannin (from natural materials).

4. Chitosan

Chitosan is an aminopolysaccharide derived from chitin which is a natural polysaccharide found in exoskeleton of shellfish e.g. crab and shrimp and in cell wall of fungi. Chitosan composes of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). Deacetylation reaction of chitin in a concentrated alkaline solution under elevated temperature produced chitosan with the degree of deacetylation (%DD) varying depending on the deacetylation condition.

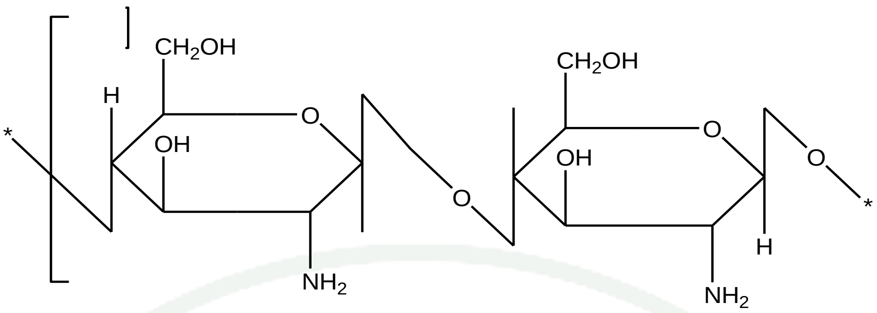


Figure 27 The chemical structure of chitosan (poly-glucosamine).

Figure 27 shows chemical structure of chitosan. Chitosan is a natural polymer which has good properties for example biocompatibility, biodegradability, non-toxicity and antimicrobial properties. Chitosan can be easily dissolved into solution in diluted acetic acid and formic acid. Its compatibility and antimicrobial properties bring chitosan into biomedical application.

In textile application, chitosan has been researched to be used as a dyeing auxiliary to enhance the dyeability on textile. As chitosan has ability to resist microorganism, it is used as an antibacterial finishes for textiles. Chitosan is also tempting for use in textile printing because its viscose solution has a potential to be used as a thickener for printing process (Choomchit *et al*., 2013).

Samanta *et al*. (2003) studied the dyeing of cotton with natural dyes, viz. turmeric, myrobolan, madder and red sandalwood and mordanting in pre-, post- and simultaneous processes was investigated. Mordant used was aluminium sulphate. Some samples were also dyed with a combination of turmeric with madder or red-sandalwood, and a combination of myrobolan with madder or red sandalwood in different proportions. Turmeric being a direct dye type, exhibited very well visual color when applied by the simultaneous-mordanting method, either single or in combination with other dyes but it showed low wash fastness. So, the turmeric-dyed fabric was improved to some extent by the after-treatment with a cationic dye fixing agent and the combination of turmeric with other dyes of better fastness.

Lee (2007) extracted natural colorant from *Coffea Arabica L.*, using water as extractant at 90°C for 90 min. Studies have been made on the dyeing, color fastness, and deodorization properties of cotton, silk, and wool fabrics dyed with *Coffea Arabica L.* extract solutions. The best mordants were found to be $FeSO_4$, $CuSO_4$, and $SnSO_4$ for improving the color strength (K/S) of cotton, silk, and wool fabrics. Mordants for cotton (Rating 3) $MnSO_4$, $ZnSO_4$, and $NiSO_4$, all mordants for silk (Rating 3) except $MnSO_4$ and mordants for wool (Rating 4) $CuSO_4$, $FeSO_4$, $CoSO_4$, $Al_2(SO_4)_3$, and $MnSO_4$ were the best mordants to improve the light fastness. It was found that $FeSO_4$ and $CuSO_4$ were the best mordants for the improvements of color strength (K/S) and light fastness for silk and wool fabrics. In addition, it was found that cotton, silk, and wool fabrics dyed with the *Coffea Arabica L.* extract showed good deodorization performance.

Mitra (2008) studied the stabilizing effect of chitosan on curcumin. They found that binding affinity of curcumin to chitosan was pH-sensitive. The chitosan-curcumin complex formed at higher pH and this complex formation occurred via electrostatic interaction between $–NH_2$ of chitosan and the phenolic –OH of curcumin. The chitosan-curcumin complex helped protect curcumin from alkali or UV light.

MATERIALS AND METHODS

Materials

1. Fabrics

1.1 40 Ne interlock-knitted PET fabric

1.2 40 Ne interlock-knitted PLA fabric

2. Reagents

2.1 Acetone (Carlo Erba, Italy)

2.2 Acetic acid (Carlo Erba, Italy)

2.3 Cassumunar Powder (Srimasok, Co Ltd., Thailand)

2.4 Chitosan Powder with %DD of 94 (TaMing Enterprises, Thailand)

2.5 Disodium hydrogen orthophosphate dodecahydrate ($Na_2HPO_4.12H_2O$)

2.6 Ethyl acetate (Carlo Erba, Italy)

2.7 Heal's ECE formulation phosphate reference detergent (James H. Heal &Co Ltd., UK)

2.8 *1*-histidine monohydrochloride monohydrate (Ajax Finechem, Australia)

2.9 Methyl benzoate (Carlo Erba, Italy)

2.10 Natural Orange (Brenntag Company, Thailand)

2.11 Natural Red Brown (Brenntag Company, Thailand)

2.12 n – Hexane (Fisher, UK)

2.13 Sera Wash (non – ionic surfactant, Dystar Thai Ltd., Thailand)

2.14 Sodium carbonate (Carlo Erba, Italy)

2.15 Sodium chloride (Carlo Erba, Italy)

2.16 Sodium dihydrogen orthophosphate dodecahydrate (Ajax Finechem, Australia)

2.17 Turmeric Powder (Srimasok, Co Ltd, Thailand)

2.18 1-Octanol 99% Pure (Acros, UK)

3. Equipments

3.1 Rotavapor R-114 rotary evaporator (Heidolph, Germany)
3.2 Color-Eye 7000 spectrophotometer (GretagMacbeth, USA)
3.3 F & P Model MD drying machine (F&P, China)
3.4 Grey scales of staining and color change
3.5 LS 55 Fluorescence spectrometer
3.6 MU 504 A Padder machine (MU504A, China)
3.7 Perspiration tester (Goodbrand, UK)
3.8 Rotawash machine (Rochdale, UK)
3.9 Starlet Daelim Infrared dyeing machine (Daelim Starlet Co., Ltd., Korea)
3.10 UV/visible spectrophotometer (Specord, USA)
3.11 Xenotest alpha (ATLAS, USA)

Methods

1. Preparation and property study of natural dyes

1.1 Extraction of the natural dyes from turmeric and cassumunar

Turmeric and cassumunar rhizomes are a source of brilliant yellow colorant. By extracting these materials with acetone, the yellow dyes were obtained.

Figure 28 Soxhlet extraction**.**

In this research, the natural dyes used were from 2 sources, viz. the natural dyes extracted from natural raw materials i.e. turmeric and cassumunar rhizomes, and commercial natural dyes viz. Natural Orange and Natural Red Brown. The natural dyes from turmeric and cassumunar were prepared by extracting the turmeric and cassumunar powders in a soxhlet extraction apparatus using acetone as an extracting solvent. About 10-15 g of cassumunar and turmeric were placed in a thimble and then put into a soxhlet extraction unit (Figure 28). The extraction was performed until no colored solution was generated. After the extraction, the solution was evaporated using a rotary evaporator. The natural dye pastes obtained were oven-dried at 80˚C for 4-6 hr. Then, removal of oil from the natural dyes was done by agitating the dye in hexane for 48 hr and oven-dried at 60˚C for 24 hr. The turmeric and cassumunar dyes were then used to dye the polyester fabrics (PLA and PET) in comparison with the commercial natural dyes. The commercial natural dyes were used directly in their as-received powder form. The extraction method of turmeric and cassumunar are shown in Figure 29. The characteristics of the natural dyes used in this research are shown in Table 9 and Figure 30.

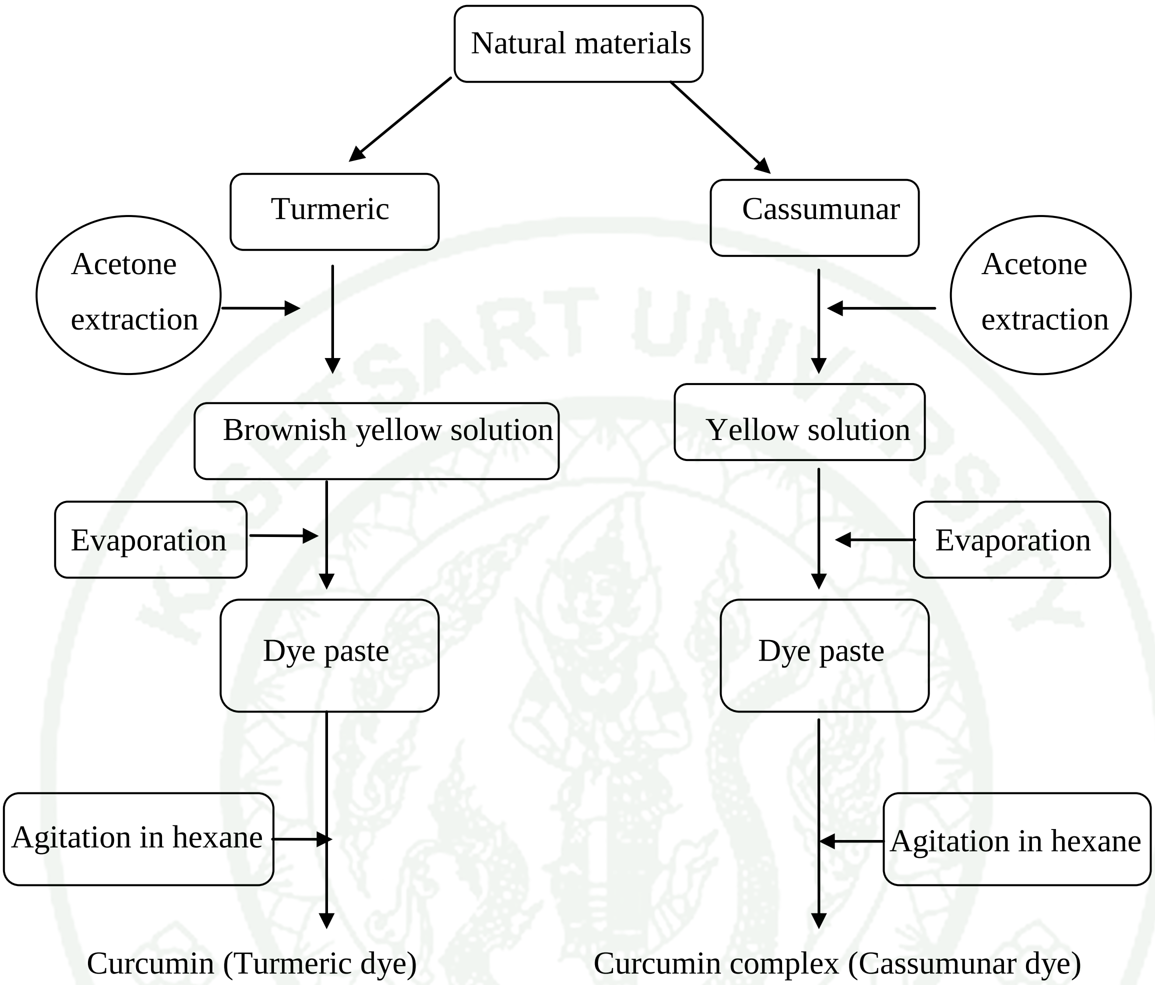


Figure 29 The extraction method of turmeric and cassumunar dyes.

Table 9 Characteristics of the natural dyes used.

Raw material	Characteristics	
	Dyes obtained	Water solubility
Turmeric	Brownish yellow solid	Sparingly soluble
Cassumunar	Brown solid	Sparingly soluble
Natural Orange	Orange powder	Highly Soluble
Natural Red Brown	Reddish brown powder	Highly Soluble

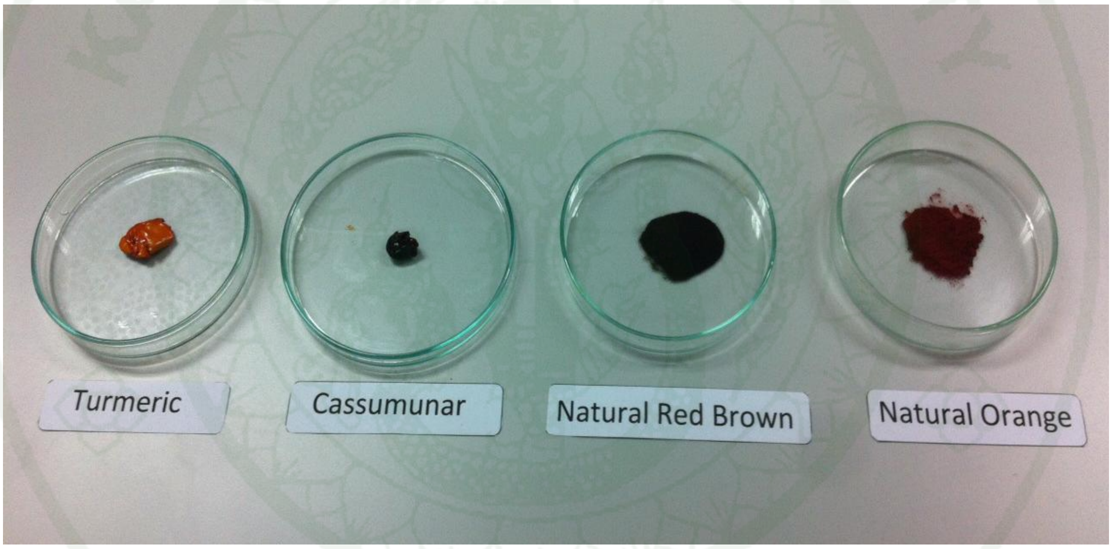


Figure 30 The natural dyes used in this research.

1.2 Study of water solubility of the natural dyes

Water solubility of the natural dyes, viz Natural Orange, Natural Red Brown, turmeric and cassumunar dyes was evaluated by dissolving 50 mg of dyes in 50 ml distilled water and stirring for 24 hr. After that, the insoluble part was filtered and dried in an oven at 80˚C for 4 hr. The weight of the dried solid (W_1) was used to calculate the percent dye soluble in water against the total dye weight (W_0) as shown in Equation 4.

$$\text{Water solubility of the dye (\%)} = \frac{(W_0 - W_1)}{W_0} \times 100 \qquad (4)$$

Where W_0 = the total dye weight, g

W_1 = the weight of the dried solid, g

Partition of the dyes in octanol:water (log P) was analyzed following shake-flask method (Anonymous, 1985). Dye (0.5 g) was put into a mixture of n-octanol and water and stirred for 24 hr. The extent of the dye partitioned in octanol and water was measured from the dye weights related to absorbance of dye dissolved in octanol and water. The absorbances of the dye solutions in octanol and water were measured by a Specord UV/vis spectrophotometer. The absorbance values were converted into the weight by using the calibration graph of the dyes in octanol and water. The partition coefficient (log P) was then calculated from Equation 5.

$$\log P_{\text{(octanol/water)}} = \log \frac{\text{weight of dye soluble in octanol}}{\text{weight of dye soluble in water}} \qquad (5)$$

log P values of the dyes were analyzed in order to correlate with the dyeing properties on PLA and PET fabrics.

1.3 Analysis of spectroscopic properties of turmeric dye in organic solvents

Turmeric dye was chosen as a representative of natural dyes for spectroscopic study. The absorbance properties of turmeric dye were studied in organic solvent media viz. ethyl acetate and methyl benzoate, being chosen as representatives of PLA and PET, respectively. This study was performed to mimic the absorbance properties of turmeric dye in the two polymers as ethyl acetate and methyl benzoate had nearly similar polarity to PLA and PET, respectively. The solutions of turmeric dye in ethyl acetate and methyl benzoate were prepared at the concentration of 6.25 mg/l. The absorbance of the solutions was examined using a Specord UV/vis spectrophotometer.

2. Dyeing of natural dyes on PLA and PET fabrics

2.1 Dyeing process

The PLA and PET fabrics were scoured in a bath containing 1 g/l Sera Wash and 1 g/l sodium carbonate at 60˚C for 15 min. After scouring, the polyester fabrics were rinsed with water and dried at room temperature. The fabrics were dyed with the natural dyes viz. Natural Orange, Natural Red Brown, turmeric and cassumunar dyes at the concentrations of 0.5, 1.0, 2.0, 3.0 and 5.0 %owf using a liquor ratio of 10:1 in a Starlet Daelim Infrared dyeing machine. The PLA fabrics were dyed at 110˚C for 30 min. While the PET fabrics were dyed at 130˚C for 30 min. After dyeing, the polyester fabrics were rinsed with water and dried at room temperature. The dyeing processes for PET and PLA are shown in Figures 31 and 32, respectively.

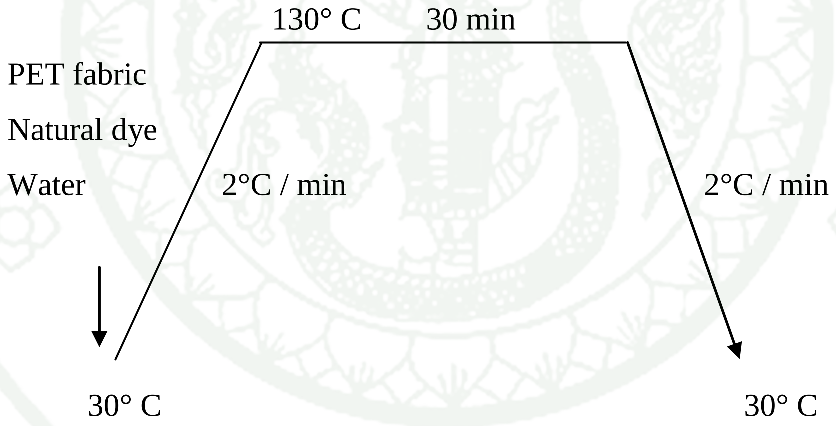


Figure 31 Dyeing profile of natural dye on PET fabric.

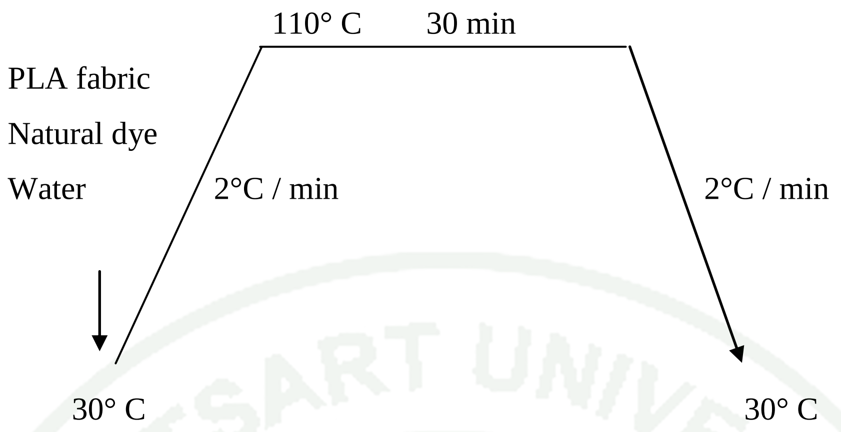


Figure 32 Dyeing profile of natural dye on PLA fabric.

Figure 33 Starlet Daelim Infared dyeing machine.

The color values (L*, a*, b*, C and H) and the visual color yield (K/S value) of the dyed fabrics were measured using a McBeth ColorEye 7000 Spectrophotometer. The build-up curves of the natural dyes on PLA and PET fabrics were made by plotting the graph between concentration of the natural dyes (% owf) and the K/S values obtained.

2.2 The % exhaustion of the natural dyes on PLA and PET fabrics.

The % exhaustion of the natural dyes on PLA and PET fabrics was determined by measuring the absorbance of the dyebath solution before and after dyeing with a Specord UV/vis spectrophotometer. The % exhaustion was calculated from Equation 6.

$$\% \text{ Exhaustion} = \left[\frac{A_1 - A_2}{A_1}\right] \times 100 \qquad (6)$$

Where A_1 is the absorbance of the dyebath solution before dyeing

A_2 is the absorbance of the dyebath solution after dyeing

3. Study on the fluorescence emission properties of the turmeric and cassumunar dyes

The PLA and PET fabrics were dyed with turmeric dyes to the level of K/S values of 5, 10, 15 and 20 while cassumunar was applied to the level of K/S value of 5. The dyeing profiles used were those illustrated in Figures 32 and 33. The fluorescence emission spectra of the dyed fabrics were determined using LS 55 fluorescence spectrometer. The excitation wavelength of 360 and 420 nm were used for cassumunar- and turmeric-dyed fabrics, respectively.

4. Fastness properties of the natural-dyed fabrics

4.1 Wash fastness

Wash fastness was determined according to the ISO 105: C01 test method in a rotawash machine. The fabric samples were cut into rectangular shape of 4x10 cm^2. The multifiber and the test fabrics having the same size were sewn together. The wash bath contained 5 g/l ECE detergent solution and the pH was adjusted to 8 using sodium carbonate. The ratio of the liquor and test specimen was 50:1. The test was performed at 40˚C for 30 min. After the wash fastness test, the test fabric and multifiber adjacent were separated, rinsed with water and then dried. The level of staining on the multifiber fabric was assessed visually using a McBeth Color-Eye 7000 Spectrophotometer and grey scales of staining and color change rating from 1 to 5. Level 1 on the scale refers to the highest degree of staining or shade change whereas level 5 refers to no staining or no shade change.

Figure 34 Rotawash machine.

4.2 Perspiration fastness

Alkaline perspiration fastness was tested by means of ISO 105-E04:1994 test method. The artificial perspiration solution was prepared by dissolving 0.5 g/l *1*-histidine monohydrochloride dodecahydrate ($C_6H_9O_2N_3.HCl.12H_2O$), 5.0 g/l disodium hydrogen orthophosphate dodecahydrate ($Na_2HPO_4.12H_2O$) and 5.0 g/l sodium chloride (NaCl) together in distilled water. The pH of the solution was adjusted to 8 with 0.1 M sodium hydroxide (NaOH).

Acid perspiration fastness was also tested according to the ISO 105-E04:1994 test method. The acid perspiration solution containing 0.5 g/l *1*-histidine monohydrochloride monohydrate ($C_6H_9O_2N_3 \cdot HCl \cdot H_2O$), 2.2 g/l sodium dihydrogen orthophosphate dihydrate ($NaH_2PO_4.2H_2O$) and 5 g sodium chloride (NaCI) was prepared. The pH of the solution was adjusted to 5.5 with 0.1 M sodium hydroxide (NaOH).

The dyed fabric samples to be tested and the multifiber fabric were sewn together, being the same as in the case of the wash fastness test. The dyed fabric samples were wetted with an artificial perspiration solution separately at a liquor ratio of 50:1 for 30 min at room temperature and after that the liquor was poured off. The specimen was then placed between two glass plates pressed together with a force equivalent to 10 Lb (4.536 kg) and allowed to stand in an oven at 37±2˚C for 4 hr.

After perspiration fastness testing, the dyed fabric samples and multifiber were dried at room temperature. The degree of alkaline and acid perspiration fastnesses was assessed by using grey scales.

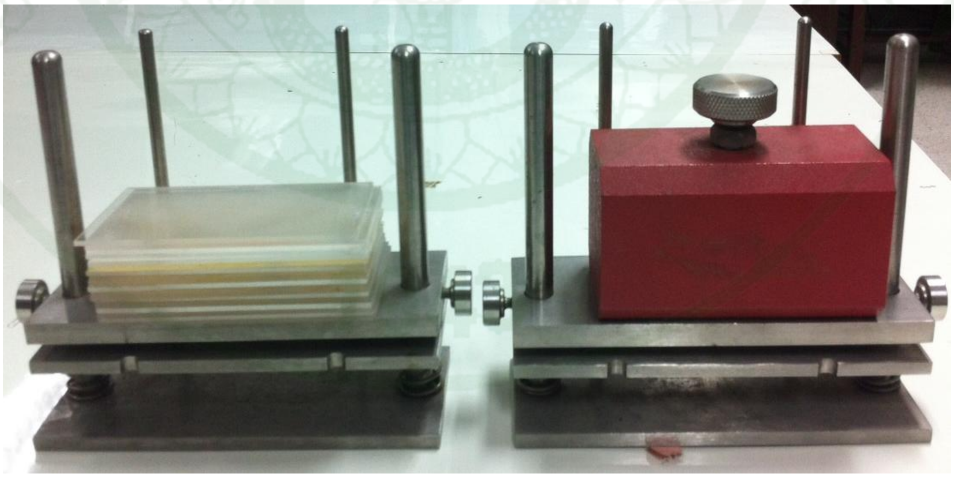


Figure 35 Perspiration tester.

4.3 Rubbing fastness

Rubbing fastness was determined according to the BS 1006X12 105 test method. A device used was a crockmeter. The fabrics samples were cut into a rectangle shape of 14 x 5 cm^2. The white standard cotton fabric of 5 x 5 cm^2 was fixed to the finger of rubbing device of a crockmeter. The specimen was rubbed back and forth with a force of 9 N in a straight line of 10 cm for 10 times. Dye staining on standard cotton fabric both in wet and dry rubbing was assessed by grey scale of staining.

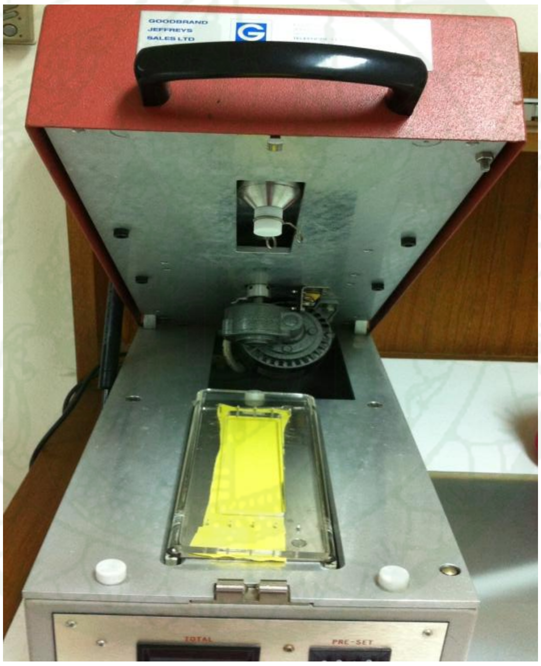


Figure 36 Crockmeter.

4.4 Light Fastness

Light fastness was determined according to the ISO 105: B02 standard method. A light source used in this method was a xenon lamp. The samples of PLA and PET fabrics were compared using blue wool reference levels of 1 to 8. Level 1 refers to the poorest light fastness and level 8 refers to the highest light fastness.

Figure 37 Xenotest machine.

5. Study on the effect of chitosan on light fastness properties of the turmeric-dyed fabrics

The effect of chitosan on light fastness properties of the natural-dyed fabric was studied with turmeric dye. The polyester fabrics were dyed with turmeric dye at the concentration of 5.0 % owf. The dyeing methods are shown in Figure 38. The chitosan solutions were prepared by dissolving chitosan with 2% acetic acid at the concentrations of 0.25, 0.5, 1.0 and 2.0 %w/v. PLA and PET fabrics were padded with chitosan solutions using MU 504 A Padder. After padding, the fabrics weight was measured. The % wet pick up was calculated from Equation 7. Then, the fabrics were dried at 80˚C for 5 min and cured at 100˚C for 5 min. After that, weight of the cured fabric was determined. The % add-on was calculated from Equation 8. The light and wash fastnesses according to the ISO 105: B02 and ISO 105:C01 test method respectively, were compared between the chitosan-treated fabrics and the untreated ones.

Figure 38 MU 504 A Padder.

$$\% \text{ Wet pick up} = \left(\frac{W_1 - W_0}{W_0} \right) \times 100 \qquad (7)$$

Where

W_0 = Initial weight of the fabric

W_1 = Weight of the padded fabric

$$\% \text{ Add on} = \frac{\% \text{ concentration of chitosan} \times \% \text{ wet pick up}}{100} \qquad (8)$$

RESULTS AND DISCUSSION

1. Preparation and property study of the natural dyes

1.1 Extraction of natural dyes from turmeric and cassumunar

Two yellow dye solutions were extracted from turmeric and cassumunar rhizome powders. The solutions obtained were yellowish brown with that of turmeric being a stronger brownish shade (Figure 39). After the solvent was evaporated, the dye powder was collected. Table 10 shows % yields of the extracted dyes from turmeric and cassumunar.

Turmeric solution Cassumunar solution

Figure 39 Turmeric and cassumunar solutions.

The % yields of the extracted dye from cassumunar (26.53%) was higher than that from turmeric (15.40%). However, turmeric provided a dye with stronger yellow shade. A lower % yield of the extracted dye from turmeric can be explained by its chemical composition as compared with cassumunar. Turmeric composes of 6.6% curcumin, 60-65% polyphenol (Braga *et al*., 2003) and about 5-8% essential oil (Aggarwal *et al*., 2006) while, cassumunar contains 22-65% curcuminoid, 4-30% terpinol (Braga *et al*., 2003) and about 2-3% essential oil (Aggarwal *et al*., 2006). For the commercial dyes, Natural Orange showed a brownish orange shade whereas Natural Red Brown is reddish brown.

Table 10 % Yield of the natural dyes extracted from turmeric and cassumunar rhizome powders.

Raw material	**Yield (%)**
Turmeric	15.40±1.91
Cassumunar	26.53±1.93

1.2 Study of the water solubility of natural dyes

The water solubility properties and log P $_{\text{(octanol/water)}}$ of the natural dyes viz. Natural Orange, Natural Red Brown, turmeric and cassumunar dyes were investigated and the results are shown in Table 11.

Table 11 The % natural dyes dissolved in water and logP $_{\text{(octanol/water)}}$ of the natural dye

Dye	**Water solubility (%)**	**log P**
Turmeric	0.69±0.08	1.90±0.44
Cassumunar	2.16±0.10	1.49±0.29
Natural Orange	89.12±1.83	-1.23±0.53
Natural Red Brown	96.70±1.63	-1.79±0.57

The commercial dyes showed a very good water solubility being 89.12 and 96.70% for Natural Orange and Natural Red Brown, respectively, while the turmeric and cassumunar dyes exhibited a very poor water solubility of 0.69 and 2.16%, respectively (Sriumaroum *et al*., 2011). The log P values indicates the degree of dye partition between octanol and water. The higher the log P values are, the more hydrophobic the dye is. The log P of each dye inversely corresponded to their water solubility ability. The data on the partition in octanol and water (log P) exhibited a varying degree for each natural dye. Natural Orange and Natural Red Brown had negative log P of -1.23 at 488 nm and -1.79 at 500 nm, respectively. It indicated that the commercial dyes did prefer to stay in water whereas the turmeric and cassumunar dyes exhibited higher log P of 1.90 at 423 nm and 1.49 at 421 nm, respectively. This infers the more hydrophobicity of these dyes comparing to the commercial ones.

Natural Orange Natural Red Brown Turmeric Cassumunar

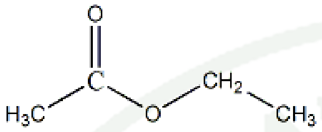
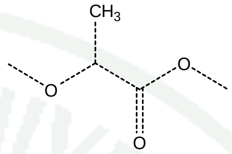
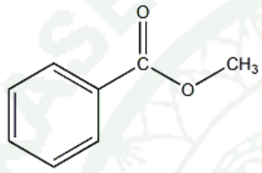
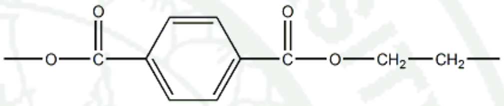
Figure 40 The natural dyes dissolved in octanol/water mixture.

Figure 40 shows the partition of each dye in octanol/water mixture, the commercial dyes, Natural Orange and Natural Red Brown, have excellent water solubility (most of the dye dissolve in water) and they can be regarded as hydrophilic dyes. Turmeric and Cassumunar dyes go into octanol rather than water (high log P) suggested that they are hydrophobic dyes.

1.3 Analysis of spectroscopic properties of turmeric dye in organic solvents

The spectroscopic properties of the turmeric dye in the selected organic solvents were investigated so as to study solvatochromism. The polarity of ethyl acetate and methyl benzoate are 0.795 and 0.836, respectively (Suesat *et al*., 2011). Table 12 shows the chemical structure of ethyl acetate and methyl benzoate in comparison with PLA and PET, respectively.

Table 12 Comparison between the chemical structure of the selected solvents and the fibers.

Solvent	**Fiber**
 Ethyl acetate	 PLA
 Methyl benzoate	 PET

The absorbance properties of turmeric dye was studied in organic solvents viz. ethyl acetate and methyl benzoate, being chosen as representatives of PLA and PET, respectively. Figure 41 shows the absorbance curves of turmeric dye solutions in ethyl acetate and methyl benzoate.

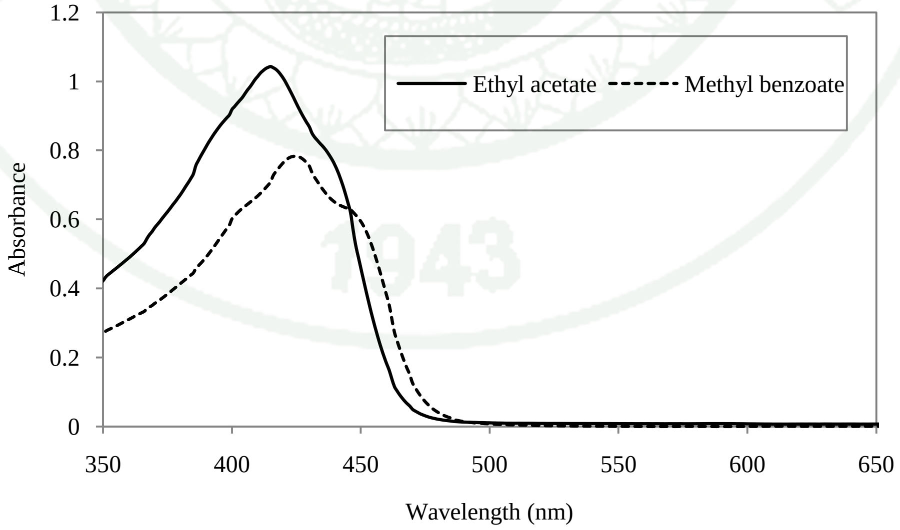


Figure 41 Absorbance spectra of 6.25 mg/l turmeric solutions in ethyl acetate and methyl benzoate.

The effect of solvents on the absorption characteristic of the dyes (solvatochromism) was observed. Turmeric dissolved in methyl benzoate showed bathochromic shift, which absorbed maximum at longer wavelength as compared with turmeric dissolved in ethyl acetate because of the increase in polarity of solvent from ethyl acetate to methyl benzoate. The absorption maxima is at 415 and 425 nm for turmeric in ethyl acetate and methyl benzoate, respectively. The bathochromic shift was observed when polarity of solvent increased from ethyl acetate (0.79) to methyl benzoate (1.13) (Suesat *et al.*, 2011; Sriumaroum *et al.*, 2011).

Table 13 The absorbance properties of turmeric dye dissolved in organic solvents at concentration of 6.25 mg/l.

Solvent	**Absorbance**	**λ_{max} (nm)**	**Color of solution**
Ethyl acetate	1.13	415	
Methyl benzoate	0.79	425	

The difference in absorbance values and λ_{max} of turmeric dye in ethyl acetate and methyl benzoate is illustrated in Table 13. Visually observed color of turmeric dye solutions in these two solvents was also different. At the same concentration, a higher absorption capacity of turmeric dye was found when ethyl acetate was employed as a solvent medium as compared with methyl benzoate. This result elucidates the influence of the organic solvent on the spectroscopic properties of turmeric dye.

As mentioned previously that the two organic solvents were chosen as representatives of PLA and PET in order to simulate the influence of these two polymers on turmeric dye properties and the above results confirmed the effect of solvents on spectroscopic properties of the dye, this infers that the PLA and PET polymer may exhibit the same effect on color properties of the dye.

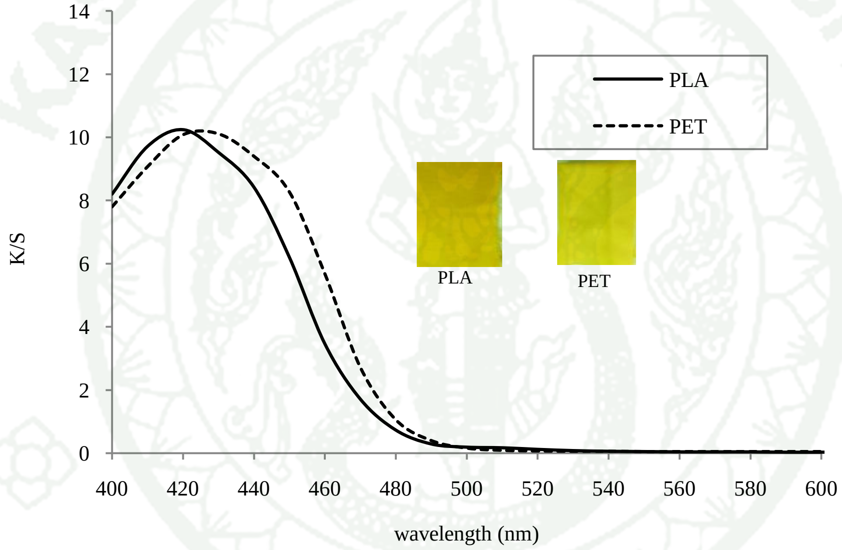


Figure 42 K/S curves of the turmeric-dyed PLA and PET fabrics at the same K/S level (10).

Table 14 Concentrations of turmeric applied on PLA and PET fabrics to achieve K/S 10 and the color values of the resulting dyed fabrics.

Fiber	**Concentration of turmeric applied (%owf)**	**λ_{max} (nm)**	**Color values of the dyed fabric**				
			L*	**a***	**b***	**C**	**H**
PLA	0.42	420	84.83	-5.17	74.58	74.76	93.97
PET	1.41	430	84.60	-12.52	76.33	77.35	99.32

The K/S curves of the turmeric-dyed PLA and PET fabrics at the same K/S level are depicted in Figure 42. A bathochromic shift observed when the dye was applied on PLA as compared with methyl benzoate (respresentative of PET).

The effect of polymer (fiber) on the color properties of turmeric dye are shown in Table 14. To achieve the same K/S value, a significantly lower concentration of turmeric dye was required for PLA (0.42%owf) than PET (1.41%owf). The λ_{max} and the color values (L*, a*, b*, C and H) indicated a shade difference obtained on PLA and PET. Therefore, it is conclusive from the results that the solvent and polymer (fiber) media do influence on the spectroscopic and color properties of the turmeric dye.

2. Dyeing of natural dyes on PLA and PET fabrics.

In this section, the dyeing properties of the natural dyes on PLA and PET fabrics were investigated. The degree of exhaustion, build-up and color properties of the dyes on PLA and PET were compared.

2.1 The % exhaustion of the natural dyes on PLA and PET fabrics

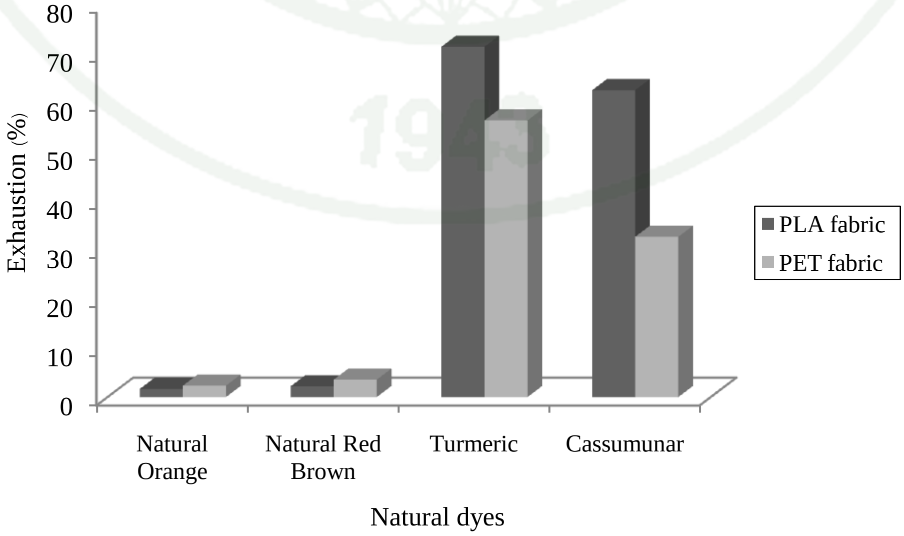


Figure 43 % Exhaustion of natural dyes on PLA and PET fabrics at 2%owf.

The % exhaustion of the dyes when applied at 2 % owf on PLA and PET is depicted in Figure 43. Comparing with the commercial dyes, turmeric and cassumunar dyes exhibited a significantly higher degree of exhaustion. Turmeric dye could exhaust well on both PLA and PET with the degree of exhaustion of 71.42 and 56.40 %, respectively. Cassumunar dye showed a good exhaustion on PLA (62.56 %) but lower than turmeric dye while it exhibited relatively poor exhaustion on PET (32.67 %). From the results, it can be seen that the poorly water soluble dyes which are turmeric and cassumunar displayed good dyeing ability on these polyester fabrics. Whereas the highly water soluble dyes (Natural Orange and Natural Red Brown) prefered to stay in water rather than diffusing into the hydrophobic polyester fibers. This infers that the natural dyes with poor water solubility would dye well on PLA and PET fabrics.

Figures 44 and 45 show the build-up curves of the dyes on PLA and PET, respectively. The turmeric dyes showed excellent build-up properties on both PLA and PET fabrics. A relatively poor build-up of cassumunar dye was found on PLA and PET fabrics whereas the commercial dyes could hardly build-up on both polyester fabrics.

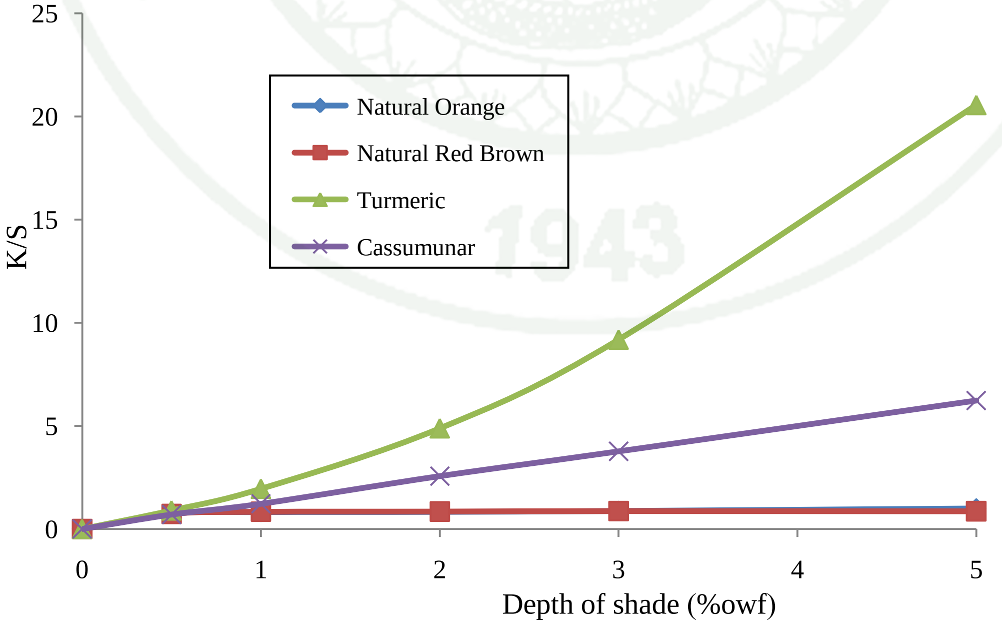


Figure 44 Build-up curves of natural dyes on PLA fabrics.

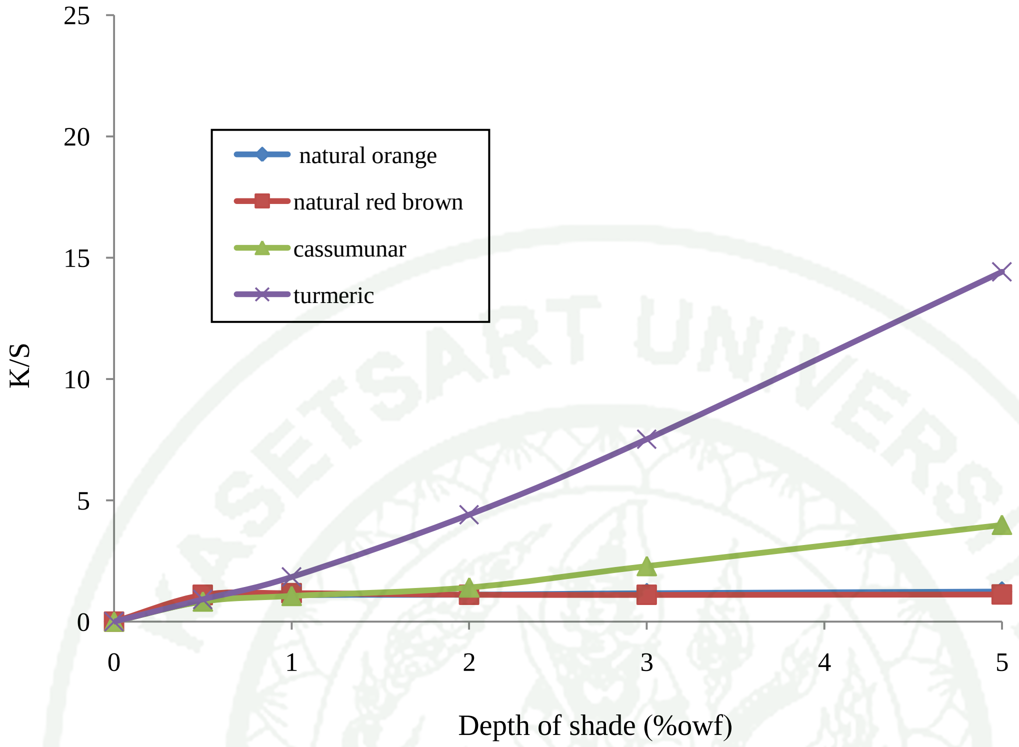


Figure 45 Build-up curves of natural dyes on PET fabrics.

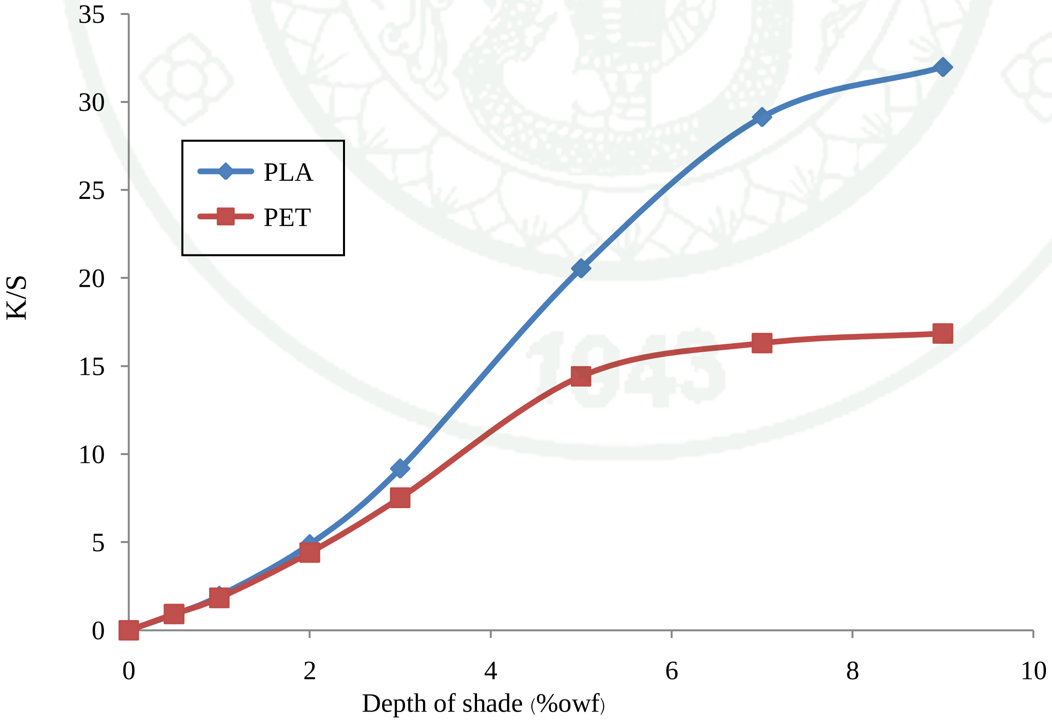


Figure 46 Build-up curves of turmeric on PLA and PET fabrics.

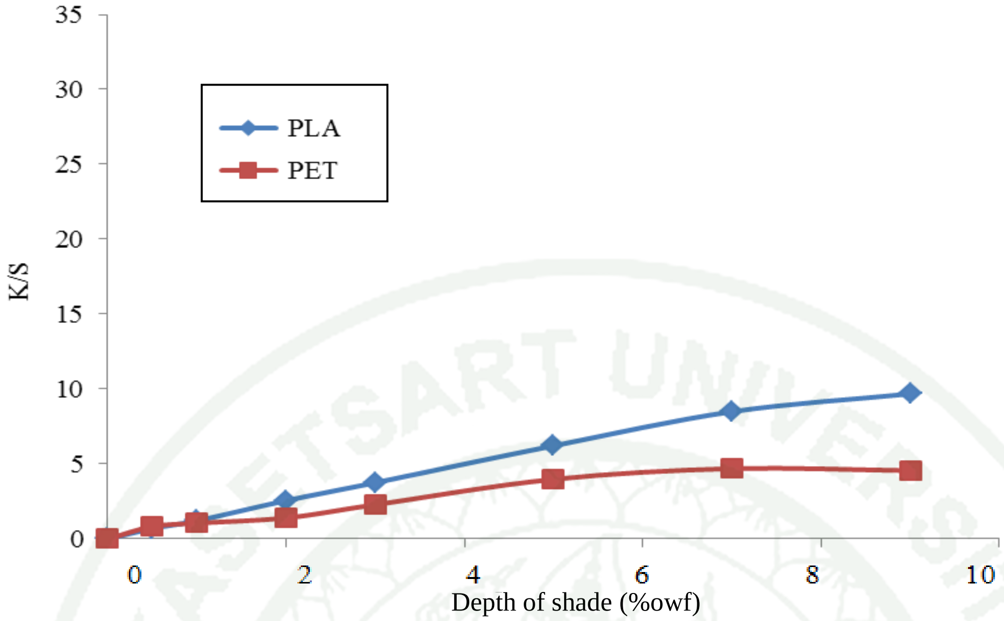


Figure 47 Build-up curves of cassumunar on PLA and PET fabrics.

Figures 46 and 47 compares the build-up curves of turmeric and cassumunar dyes on PLA and PET fabrics, respectively. The build-up properties of the dyes on PLA fabrics were different from on PET fabrics, especially turmeric dye. The dyes applied on PLA fabric exhibited higher build-up than on PET fabric (Sriumaoum *et al*., 2011).

From the results, the higher degree of dye exhaustion was observed on both PLA and PET fabrics for turmeric and cassumunar dyes whereas the commercial dyes had poor the % exhaustion on both PLA and PET fabrics. The color yield (K/S) observed on PLA and PET fabrics correlates with the % exhaustion. Natural Red Brown and Natural Orange had poor both the % exhaustion and color yield. While, the turmeric and cassumunar dyes showed a better dyeing properties on polyester fabric.

This point can be concluded that the dyes with poor water solubility could dye very well on PLA and PET fabrics (Suesat and Suwanruji, 2011). Turmeric and cassumunar dyes are natural dyes with low water solubility being recommended for dyeing these two hydrophobic polyester fabrics. The dye extracted from turmeric was reported to be curcumin which can be used as a natural dye for dyeing textile fiber both natural and synthetic fabrics, while cassumunar dye was reported to be cassumunarin, a complex curcuminoids (Jitoe *et al.,* 1994). However, cassumunar dye did not perform well on the polyester fabrics as compared with turmeric dye.

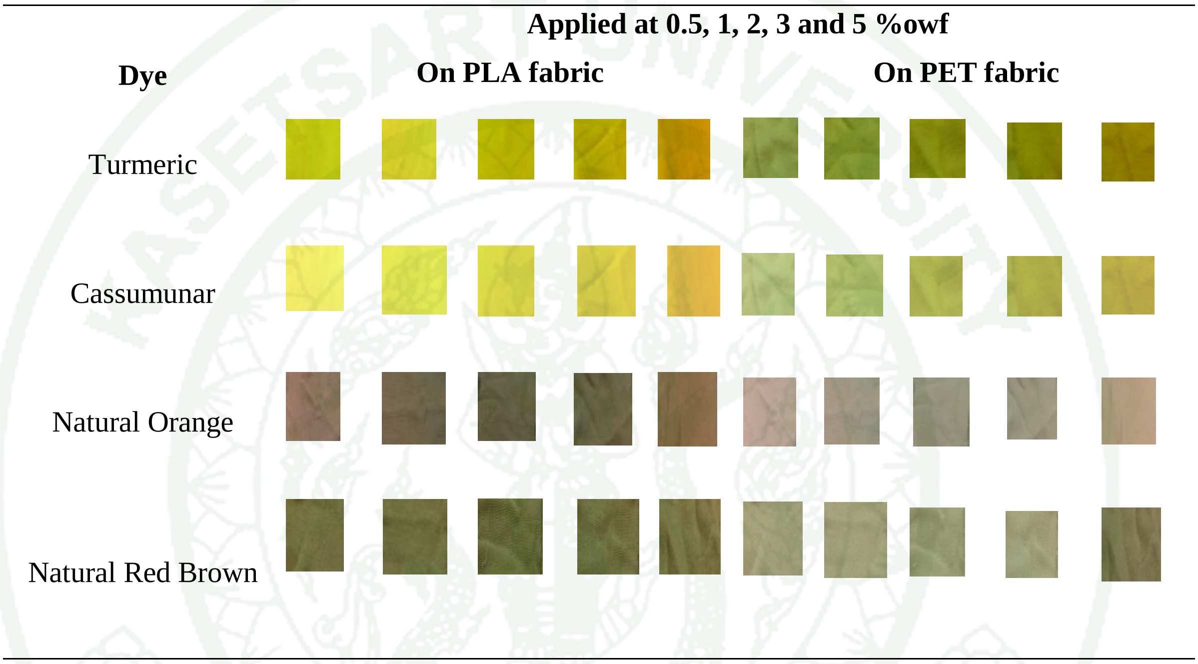
Table 15 Dyeing properties of the natural dyes on PLA and PET fabrics when applied at 2 % owf.

Dye	Fabrics	% Exhaustion	Color Properties					
			K/S	L*	a*	b*	C	H
Turmeric	PLA	71.42	4.88	77.89	47.97	48.09	94.07	98.41
	PET	56.40	4.41	79.16	-8.06	51.23	51.87	90.94
Cassumunar	PLA	62.56	2.56	83.65	-3.88	27.94	28.21	97.96
	PET	32.68	1.41	86.95	-0.58	18.59	13.6	91.8
Natural Red Brown	PLA	2.19	0.84	71.97	9.03	11.43	14.58	51.57
	PET	3.55	1.11	72.27	5.93	10.92	12.43	61.48
Natural Orange	PLA	1.66	0.82	71.20	9.87	14.22	17.31	55.24
	PET	2.32	1.11	70.94	7.92	11.88	14.27	56.29

The data on the % exhaustion and the color properties (K/S, L*, a*, b*, C and H) of the natural dyes applied at 2%owf obtained on the PLA and PET fabrics are showed in Table 15. As mentioned previously, the commercial dyes exhibited a very low color yield developed on the polyester fabrics. Their pale shade corresponded to their low degree of exhaustion. In the case of turmeric and cassumunar dyes, they showed a much better color yield (high exhaustion) on the fabrics.

The shade variation of each dyes obtained on PLA and PET fabrics can be noticed from the color values (L*, a*, b*, C and H). This can be explained by the influence of polyester polymer on the spectroscopic properties of the dye as mentioned in Section 1.3.

Table 16 PLA and PET fabrics were dyed with natural dyes at various applied concentrations (% owf).



The shades of the dyes obtained on PLA and PET fabrics are depicted in Table 16. At the same applied depth of shade, a slightly different shade of each dye was observed on PLA comparing with PET. This shade variation occurred on different polyester fabrics are explained by the influence of the polyester polymer (fiber). The same dye applied on different fiber type could display a shade variation due to the effect of different dye-fiber interaction. A deeper shade observed on PLA was attributable to its lower refractive index, compared with PET. It points out from the results that the shade of the natural dyes obtained on PLA fabric is slightly different from that on PET fabric (Suesat *et al*., 2011).

3. Study on the fluorescence emission properties of the turmeric and cassumunar dyes on polyester fabrics

The fluorescence properties of turmeric and cassumunar dyes were investigated on PLA and PET fabrics being dyed to the same K/S value so that the fluorescence properties could be compared. Figure 48 shows the fluorescence emission curves of the cassumunar-dyed on PLA and PET fabrics at the same K/S of 5 and the fluorescence emission curves of the turmeric-dyed PLA and PET fabrics at the K/S values of 5, 10, 15 and 20 are depicted in Figures 49 to 52, respectively.

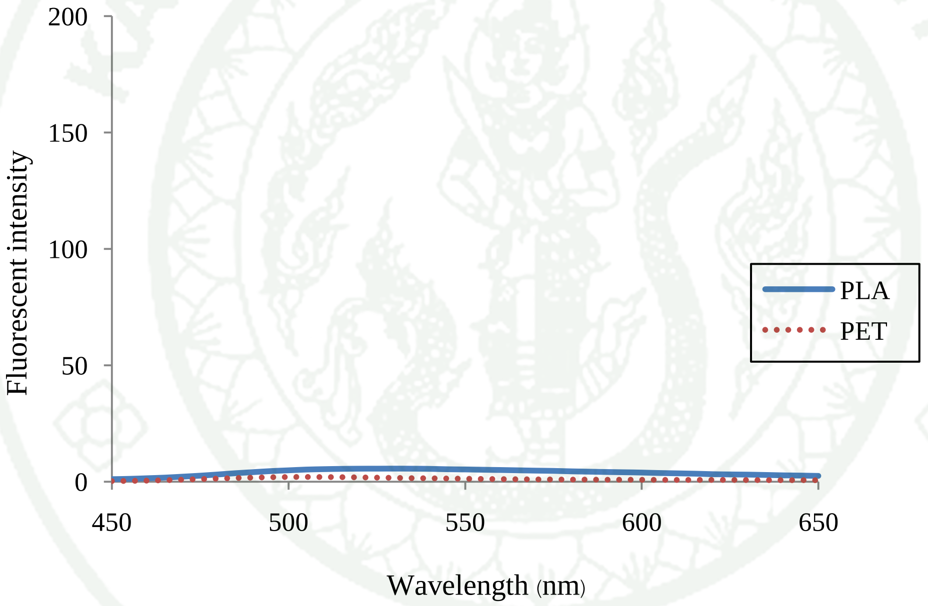


Figure 48 Fluorescence spectra of PLA and PET fabrics dyed with cassumunar dye at the same K/S level of 5.

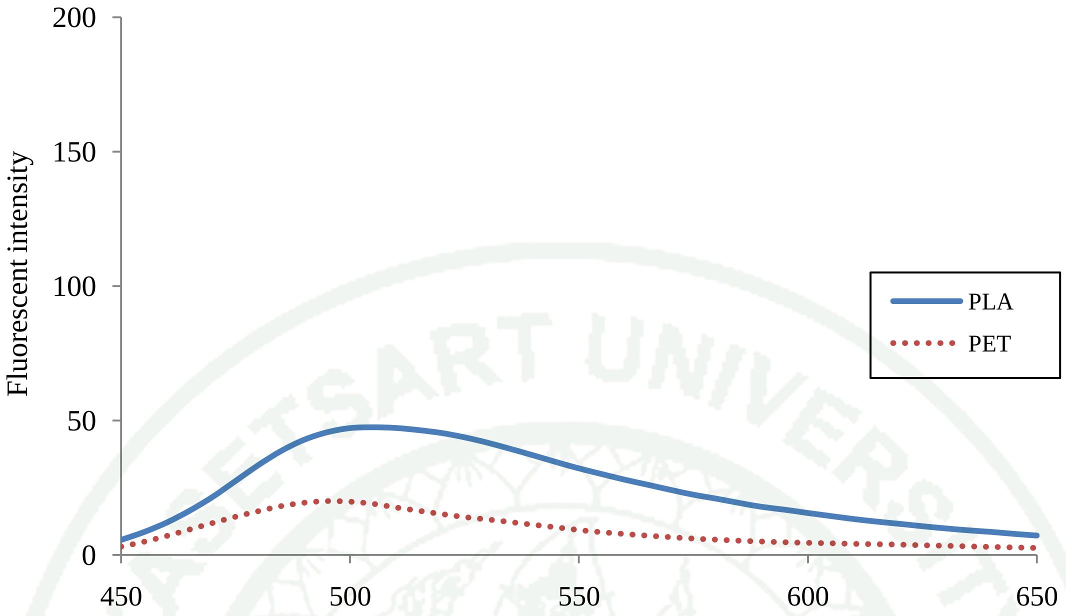


Figure 49 Fluorescence spectra of PLA and PET fabrics dyed with turmeric dye at the same K/S level of 5.

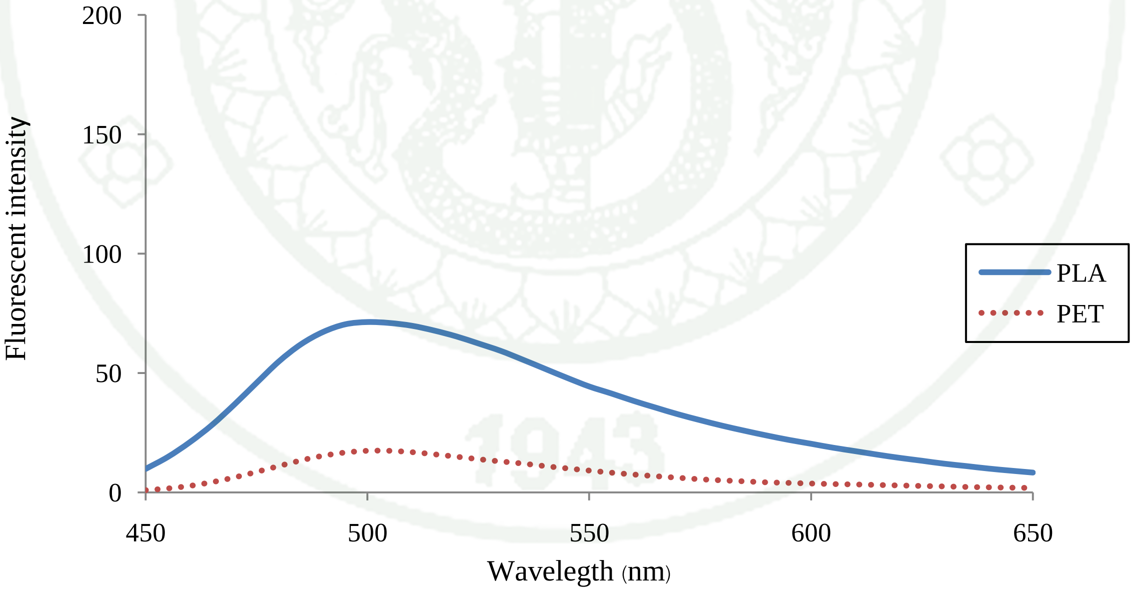


Figure 50 Fluorescence spectra of PLA and PET fabrics dyed with turmeric dye at the same K/S level of 10.

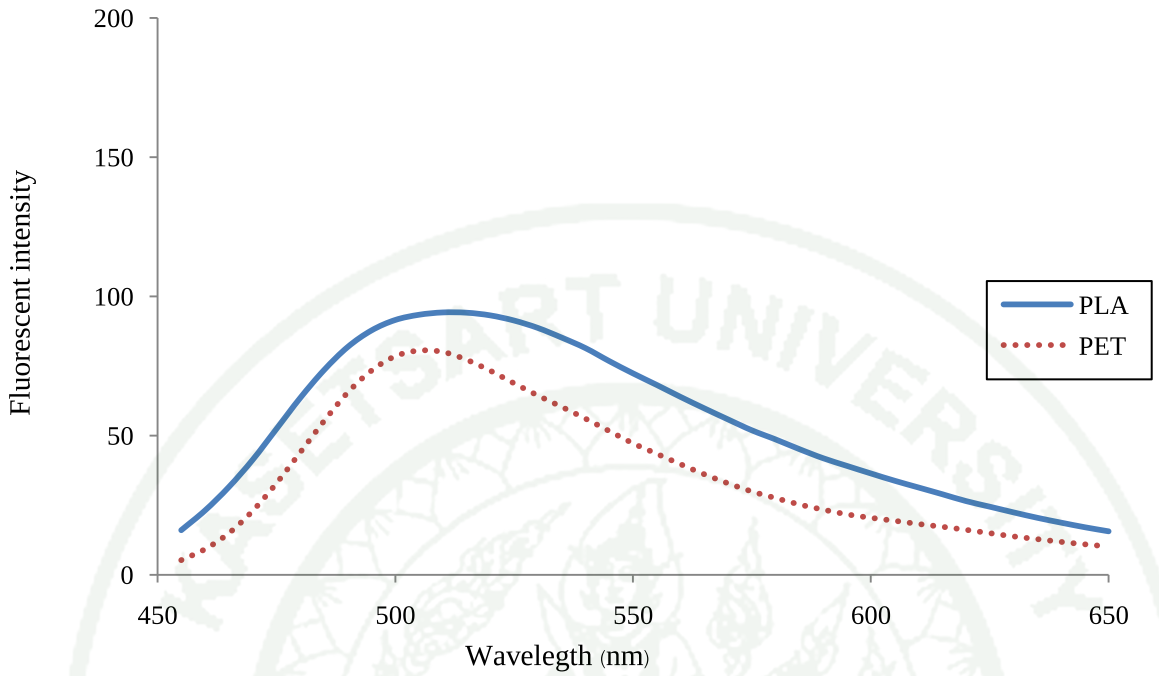


Figure 51 Fluorescence spectra of PLA and PET fabrics dyed with turmeric dye at the same K/S level of 15.

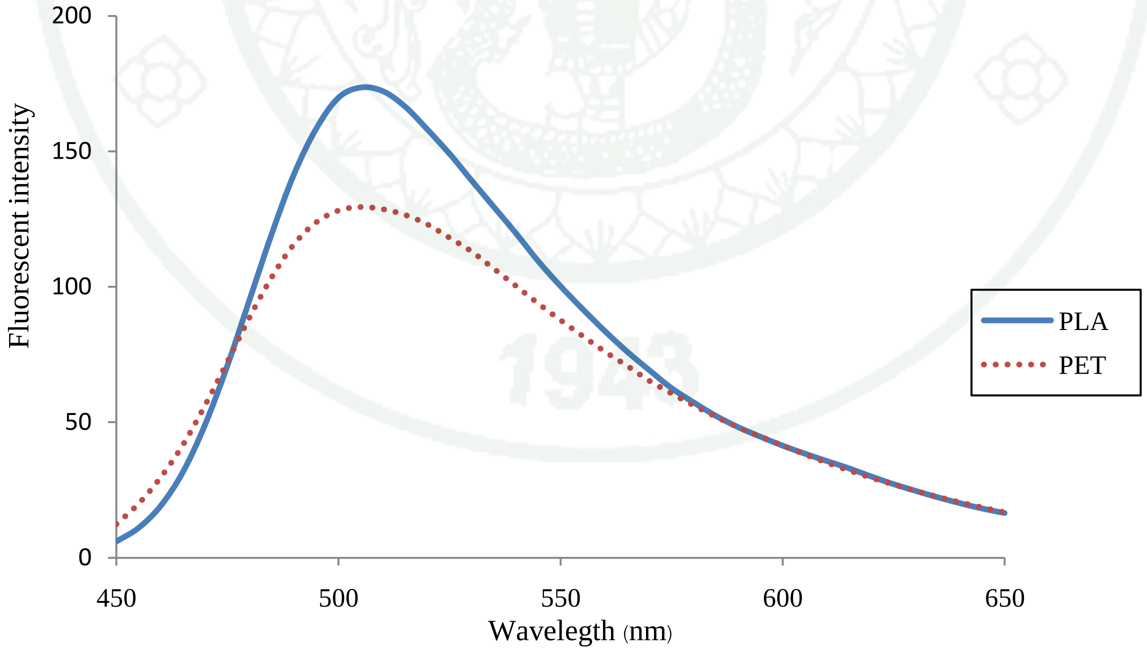


Figure 52 Fluorescence spectra of PLA and PET fabrics dyed with turmeric dye at the same K/S level of 20.

The fluorescence emission took place at the wavelength between 490- 510 nm for both turmeric and cassumunar. A higher emission was observed on PLA as compared with PET for both turmeric and cassumunar dyes at all K/S values. The fluorescence properties of the dyes were influenced by the fibers. It was reported that the polarity of the surrounding environment affected fluorescence properties of fluorophore molecule. As a result of the difference in polarity of PLA and PET, the fluorescence characteristics of the dyes were influenced to a different extent. It seemed that the dyes exhibited a stronger fluorescence emission on the less polar PLA than PET for both turmeric and cassumunar dyes. The yellow dye from turmeric is curcumin. This curcumin is a fluorophore molecule, so it glows when exposed to UV light and makes turmeric dyes be a fluorescence dye. Cassumunar dye was claimed to be a complex curcuminoids (Jitoe *et al*., 1994), however, it showed less fluorescence properties on both fabrics, especially PET, fluorescence nearly disappeared.

Figures 49 to 52 shows the fluorescence emission properties of turmeric dye on PLA and PET fabrics at different K/S levels. The data found that the turmeric dye exhibited pronounced fluorescence properties on PLA than PET especially at a higher K/S levels. The fluorescence emission capacity of turmeric dye increased with increasing K/S values. It means that the higher amount of the dye is applied, the higher the fluorescence emission obtains on the fabric. It can be said that turmeric dye is a potential fluorescence dye for polyester fabrics, in particular for PLA.

4. Fastness properties of the natural-dyed fabrics

In this section, the color fastness properties viz. washing, perspiration, rubbing and light on the natural dyes on polyester fabrics were discussed as follows.

4.1 Wash fastness (ISO 105/C01)

The wash fastness of the PLA and PET fabrics dyed with turmeric and cassumunar at various K/S values are shown in Table 17. From a pale to heavy depth of shade, the turmeric-dyed PLA and PET fabrics exhibited a moderate fastness to washing (3/4 on grey scale of staining). The cassumunar-dyed fabrics which could be obtained only in a pale shade (K/S 5), gave a slightly better fastness to washing. For the degree of shade change, the turmeric-and cassumunar-dyed fabrics were in a good level (grey scale of 4). From this result, it elucidates that the two natural dyes especially turmeric have a good wash fastness properties on PLA and PET fabrics.

Table 17 ISO 105-E04 wash fastness of turmeric and cassumunar dyed on PLA fabrics and on PET fabrics at various K/S levels.

	Dyes	Grey scale of shade change	Grey scale of staining on					
			Wool	**Acrylic**	**PET**	**Nylon**	**Cotton**	**Acetate**
PLA	Turmeric of K/S 5	4/5	4/5	4	4	4	3/4	4/5
	Turmeric of K/S 10	4/5	4/5	4	4	4	3/4	4/5
	Turmeric of K/S 15	4/5	4/5	4/5	4	4	3/4	4/5
	Turmeric of K/S 20	4	4/5	3/4	3/4	4	4	4/5
	Cassumunar of K/S 5	4	5	4	4	4	4	4
PET	Turmeric of K/S 5	4/5	4/5	4/5	3/4	4/5	4	4/5
	Turmeric of K/S 10	4/5	4/5	4	3/4	4/5	4	4/5
	Turmeric of K/S 15	4	4/5	4	3/4	4	3/4	4/5
	Turmeric of K/S 20	4	4/5	3/4	3/4	4	3/4	4/5
	Cassumunar of K/S 5	4/5	5	4/5	4	4/5	4	5

4.2 Perspiration fastness

The alkaline and acid perspiration fastnesses of the turmeric- and cassumunar-dyed PLA and PET fabrics are depicted in Tables 18 and 19, respectively. Cassumunar dye showed a good perspiration fastness on both PLA and PET because it had only pale shade. In the case of turmeric, the perspiration fastness was not as good as its wash fastness properties on PLA and PET. A higher degree of staining was observed especially for alkaline perspiration of those heavy depth (K/S 20). It seems that turmeric dye is rather sensitive to alkaline perspiration than the acid one. A higher staining was noticed on nylon adjacent at 2/3-3 on grey scale whereas a better result was found in an acid perspiration (about 1 unit grey scale higher).

This may be explained by the effect of pH on the color of turmeric dye. It is reported that when the pH of the surrounding medium is changed from neutral to alkaline, the color of turmeric alteres from brilliant yellow to brownish yellow. Therefore, under alkaline testing condition, the color of turmeric dye on the fabric is changed to a brownish shade, resulting in a visually stronger staining observed.

Table 18 ISO 105-E04:1994 alkaline perspiration fastness of turmeric-and cassumunar dyed on PLA and PET fabrics at various K/S levels.

Dyes		Grey scale of staining on					
		Wool	**Acrylic**	**PET**	**Nylon**	**Cotton**	**Acetate**
PLA	Turmeric of K/S 5	5	5	5	5	4	4/5
	Turmeric of K/S 10	5	5	5	4	3/4	3/4
	Turmeric of K/S 15	4/5	4/5	4/5	4	3/4	3/4
	Turmeric of K/S 20	4/5	4	4/5	3	3	5
	Cassumunar of K/S 5	5	5	5	4/5	4	4/5
PET	Turmeric of K/S 5	5	4/5	4/5	4/5	4/5	4/5
	Turmeric of K/S 10	5	5	5	4/5	4	4/5
	Turmeric of K/S 15	4/5	4/5	4/5	3	3/4	4
	Turmeric of K/S 20	4/5	4/5	4/5	2/3	2/3	3/4
	Cassumunar of K/S 5	4/5	5	5	4/5	4/5	4/5

Table 19 ISO 105-E04:1994 acid perspiration fastness of turmeric-and cassumunar dyed on PLA and PET fabrics at various K/S levels.

Dyes		Grey scale of staining on					
		Wool	**Acrylic**	**PET**	**Nylon**	**Cotton**	**Acetate**
PLA	Turmeric of K/S 5	5	5	5	5	4/5	5
	Turmeric of K/S 10	5	5	5	4/5	4	4/5
	Turmeric of K/S 15	4/5	4/5	4/5	4	3/4	3/4
	Turmeric of K/S 20	4/5	4/5	4/5	3/4	3	3/4
	Cassumunar of K/S 5	5	5	5	5	5	5
PET	Turmeric of K/S 5	5	5	5	4/5	4	4
	Turmeric of K/S 10	4/5	4/5	5	4/5	4	4/5
	Turmeric of K/S 15	4	4/5	4	3/4	3	3/4
	Turmeric of K/S 20	4	4/5	4	3/4	4	3/4
	Cassumunar of K/S 5	4/5	5	5	4/5	4	4

4.3 Rubbing fastness

The data on rubbing fastness study are shown in Table 20. In the dry rubbing fastness, turmeric-and cassumumar-dyed PLA and PET fabrics were rated on the grey scale of staining at 4 to 4/5, being a good level. In the wet rubbing fastness, the fabrics were rated to be poorer (grey scale of 3/4), showing moderate wet rubbing fastness. With increasing color yield (K/S value), the degree of staining as a result of rubbing was higher for turmeric dye. In this result, it indicates a moderate to good rubbing fastness of the dyes on PLA and PET fabrics.

Table 20 BS 1006X12 rubbing fastness of turmeric-and cassumunar dyed on PLA fabrics at various K/S level.

Fabrics	**Dyes**	**Dry**	**Wet**
PLA	Turmeric of K/S 5	4/5	4/5
	Turmeric of K/S 10	4/5	4
	Turmeric of K/S 15	4	3/4
	Turmeric of K/S 20	4	3/4
	Cassumunar of K/S 5	4/5	4
PET	Turmeric of K/S 5	4/5	4/5
	Turmeric of K/S 10	4	4
	Turmeric of K/S 15	4/5	3/4
	Turmeric of K/S 20	4/5	3/4
	Cassumunar of K/S 5	4	4

4.4 Light fastness

Table 21 shows the light fastness of the turmeric and cassumunar-dyed PLA and PET fabrics determined according to ISO 105:B2 standard. The results found that these turmeric and cassumunar dyes had a very poor color fastness to light (Blue wool scale of 1) on both PLA and PET fabric even at a heavy depth of shade. This is a typical drawback of natural dyes that they tend to fade easily when exposed to light.

From the color fastness assessment, it can be summarized that turmeric and cassumunar dyes display a moderate to good fastness to washing, perspiration and rubbing but very poor light fastness on PLA and PET fabrics.

Table 21 ISO 105-B02 light fastness of turmeric-and cassumunar- dyed on PLA and PET fabrics at various K/S levels.

Fabrics	**Dyes**	Blue Wool scale
PLA	Turmeric of K/S 5	1
	Turmeric of K/S 10	
	Turmeric of K/S 15	
	Turmeric of K/S 20	
	Cassumunar of K/S 5	
PET	Turmeric of K/S 5	1
	Turmeric of K/S 10	
	Turmeric of K/S 15	
	Turmeric of K/S 20	
	Cassumunar of K/S 5	

5. Study on the effect of the chitosan on light fastness properties of turmeric-dyed PLA fabrics

5.1 Effect of chitosan on color properties of turmeric-dyed on PLA fabric

The color properties of turmeric-dyed PLA fabric treated with chitosan at various concentrations are shown in Table 22. The shade difference was noticed between the chitosan-treated and the untreated fabrics. A duller, greener and less yellow shade was found on turmeric-dyed PLA fabric with increasing chitosan concentration. The effect of chitosan concentration on the color yield of turmeric-dyed PLA is also found as in Figure 53. Higher color yield (deeper shade) was obtained on the dyed fabric when treated with chitosan. The result shows that chitosan treatment can cause a shade alteration and higher color yield turmeric-dyed PLA fabric.

Table 22 Color properties of turmeric-dyed PLA fabric at 5%owf treated with chitosan solutions.

%Chitosan	dyeing → chitosan treatment			Shade
	L*	a*	b*	
0	84.92	-8.04	35.60	🟨
0.25	82.81	-8.85	53.18	🟨
0.5	80.82	-8.04	54.68	🟨
1	80.39	-7.19	53.57	🟨
2	80.23	-5.20	53.50	🟨

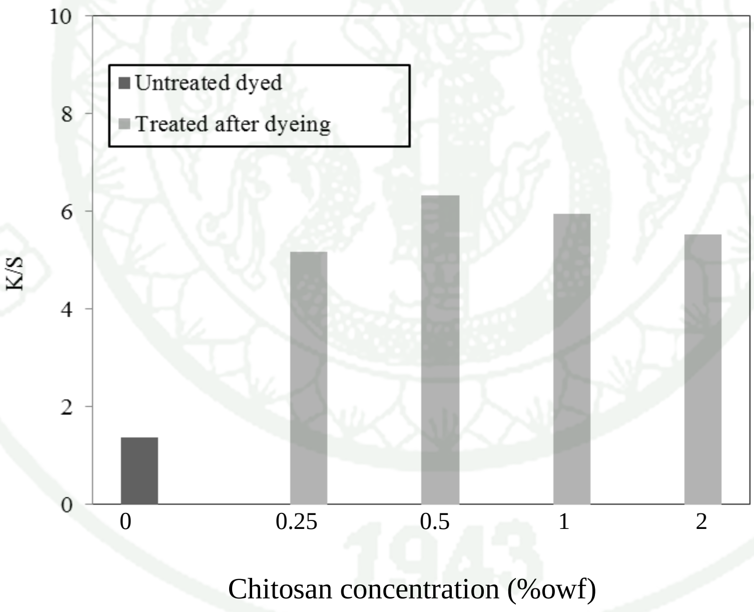


Figure 53 Effect of chitosan concentrations on color yield of turmeric dye obtained on PLA fabric dyed at 5%owf.

5.2 Effect of chitosan treatment on color fastness of turmeric-dyed on PLA fabric

As expected, chitosan brought about an improvement in color fastness properties both washing and light (Table 23). Degree of staining and fading of turmeric dye in washing and light fastness tests were lowered in the presence of chitosan. The results point out that chitosan helped improve the fastness properties of the dyed PLA fabric. Better wash fastness properties can be explained that chitosan acts as a fixing agent for the dye molecules, therefore, less dye is lost from the fabric during washing. An improvement in light fastness of turmeric is from the influence of chitosan to impart a light protection to the dye molecules.

Table 23 Color fastness to light and washing of the chitosan-treated, turmeric-dyed PLA fabrics dyed at color yield (K/S) of 10 and 15.

Fabric	**Light fastness**		**Wash fastness**			
			Staining on PET		**Staining on Nylon**	
	untreated	chitosan-treated	untreated	chitosan-treated	untreated	chitosan-treated
K/S 10	1	2	4	4	3/4	3/4
K/S 15	1	2	¾	4	2	3

This point can be concluded that treatment of the turmeric-dyed PLA fabric with chitosan affects the color and fastness properties of the dye on the fabric. A deeper shade was developed when increased chitosan concentration applied. Treating chitosan on the dyed PLA fabric gave a higher color yield than without chitosan. The color fastness to washing and light of turmeric-dyed PLA fabric were improved by chitosan.

CONCLUSTION

In the present research, the dyeing and fastness properties of the natural dyes, viz. Natural Orange, Natural Red Brown, turmeric and cassumunar, were investigated on PLA and PET fabrics.

From the water solubility study and log P analysis, it gives the information that turmeric and cassumunar dyes are hydrophobic dye with poor water solubility and high log P values whereas the commercial dyes (Natural Orange and Natural Red Brown) are highly soluble in water and have low log P values. The water solubility and log P of the dyes were found related to their dyeing properties on PLA and PET fabrics.

Turmeric and cassumunar, hydrophobic dyes, had much better dyeing properties (% exhaustion and color yield (K/S)) on PLA and PET than the highly water-soluble dyes. Turmeric exhibited very good dyeing properties on the polyester fabrics especially PLA, high color yield could be obtained.

A study on spectroscopic properties of turmeric dye in ethyl acetate and methyl benzoate, the solvents representing PLA and PET, respectively, indicates the influence of solvent media on the absorption properties of the dyes. This can be used to explain the difference in color properties of the dyes on PLA compared with PET. In addition, turmeric and cassumunar dyes also exhibited fluorescence emission properties on PLA and PET. A stronger fluorescence emission was observed for turmeric dye on PLA fabric.

The color fastness properties of turmeric-and cassumunar-dyed PLA and PET fabrics were moderate to good for washing, perspiration and rubbing fastnesses. However, the light fastness was very poor. A study to improved the light fastness properties of turmeric-dyed polyester fabrics by using chitosan was performed and it was found that chitosan could enhance the light fastness of turmeric dye on PLA and PET.

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APPENDIX

1. % Yield of extracted dyes.

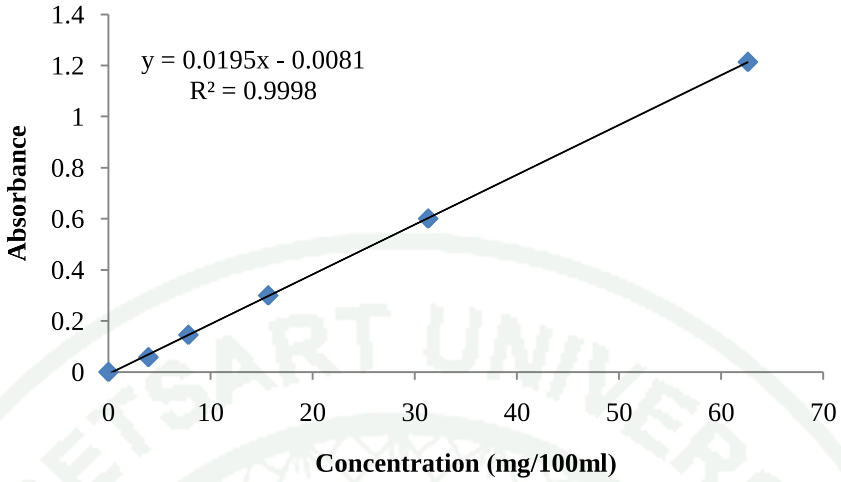
Appendix Table 1 The % yield of extracted natural dyes

No	Total weight of cassumunar (g)	Actual weight of cassumunar extract (g)	Yield of cassumunar (%)	Total weight of turmeric (g)	Actual weight of turmeric extract (g)	Yield of turmeric (%)
1	145.01	41.51	28.63	120.05	16.87	14.05
2	75.12	18.64	24.81	74.96	16.68	22.25
3	95.84	25.07	26.16	58.15	9.75	16.75
µ	-	-	26.53	-	-	17.69
S.D.	-	-	1.94	-	-	4.18

2. The calibration curve of natural dyes

Appendix Table 2 Absorbance of Natural Orange dissolved in water at various concentrations.

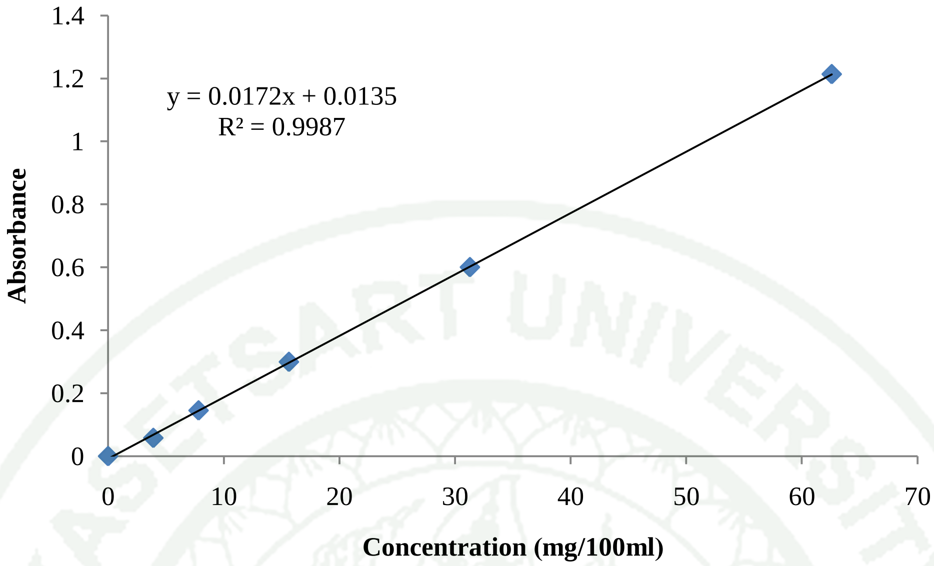
Concentration (mg/100ml)	Absorbance
62.60	1.21
31.30	0.60
15.64	0.29
7.83	0.15
3.91	0.06



Appendix Figure 1 Calibration curve of Natural Orange in water at λ_{max} 486 nm.

Appendix Table 3 Absorbance of Natural Red Brown dissolved in water at various concentrations.

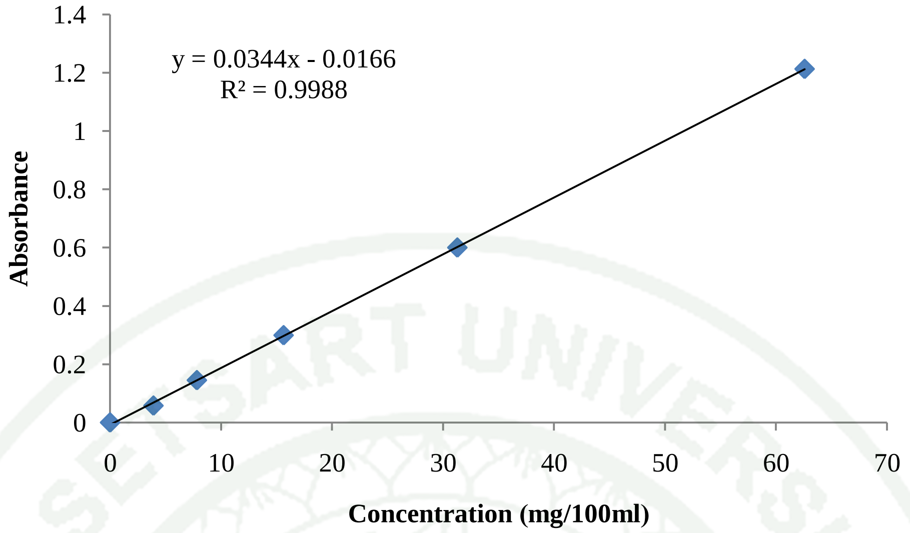
Concentration (mg/100ml)	Absorbance
99.94	1.71
50.00	0.91
25.00	0.47
12.50	0.23
6.25	0.10



Appendix Figure 2 Calibration curve of Natural Red Brown in water at λ_{max} 500 nm.

Appendix Table 4 Absorbance of turmeric dissolved in octanol at various concentrations.

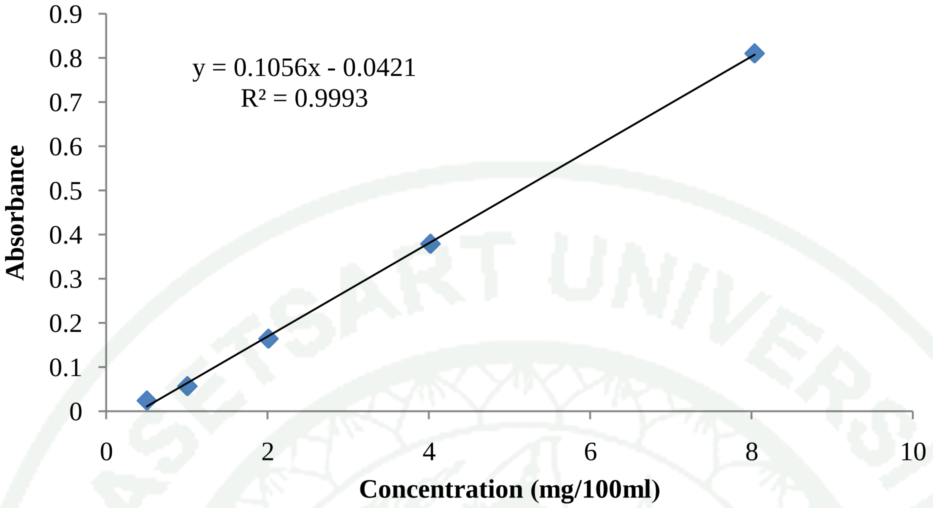
Concentration (mg/100ml)	Absorbance
25.0	0.85
12.5	4.41
6.25	0.19
3.13	0.08
1.56	0.04



Appendix Figure 3 Calibration curve of turmeric in octanol at λ_{max} 423 nm.

Appendix Table 5 Absorbance of cassumunar dissolved in octanol at various concentrations.

Concentration (mg/100ml)	**Absorbance**
8.04	0.81
4.02	0.38
2.01	0.16
1.01	0.06
0.50	0.02



Appendix Figure 4 Calibration curve of cassumunar in octanol at λ_{max} 421 nm.

3. % Water solubility of natural dyes

Appendix Table 6 The % Water solubility of the dyes.

Dyes	**1**	**2**	**3**	**µ**	**S.D.**
Natural Orange	87.82	98.55	90.87	92.41	5.53
Natural Red Brown	99.61	97.85	95.17	97.55	2.24
Turmeric	0.63	3.84	0.77	1.75	1.48
Cassumunar	6.49	2.09	2.23	3.60	2.50

3.1 The % solubility of Natural Orange in 50 ml of water

Calculation (measurement 1)

$$\%\ \text{Water solubility} = \frac{\text{Weight of dye dissolved} \times 100}{\text{Total weight of dye}}$$

$$\%\ \text{Water solubility} = \frac{8.89\ \text{mg} \times 100}{10.12\ \text{g}}$$

$$\%\ \text{Water solubility} = 87.82$$

3.2 The % solubility of Natural Red Brown in 50 ml of water

Calculation (measurement 1)

$$\%\ \text{Water solubility} = \frac{\text{Weight of dye dissolved}}{\text{Total weight of dye}} \times 100$$

$$\%\ \text{Water solubility} = \frac{6.86\ \text{mg}}{6.89\ \text{mg}} \times 100$$

$$\%\ \text{Water solubility} = 99.61$$

3.3 The % solubility of turmeric in 50 ml of water

Calculation (measurement 1)

$$\%\ \text{Water solubility} = \frac{\text{Weight of dye dissolved}}{\text{Total weight of dye}} \times 100$$

$$\%\ \text{Water solubility} = \frac{0.04\ \text{mg}}{6.38\ \text{mg}} \times 100$$

$$\%\ \text{Water solubility} = 0.63$$

3.4 The % solubility of cassumunar in 50 ml of water

Calculation (measurement 1)

$$\%\ \text{Water solubility} = \frac{\text{Weight of dye dissolved}}{\text{Total weight of dye}} \times 100$$

$$\%\ \text{Water solubility} = \frac{0.11\ \text{mg}}{5.06\ \text{mg}} \times 100$$

$$\%\ \text{Water solubility} = 2.09$$

4. % Exhaustion of dyes

Appendix Table 7 % Exhaustion of Natural Orange on PLA fabric at 2%owf.

Times	**Absorbance before dyeing**	**Wavelength (nm)**	**Absorbance after dyeing**	**Wavelength (nm)**	**%Exhaustion**
1	1.50	484	1.48	485	1.26
2	1.41	485	1.39	484	1.18
3	1.51	485	1.50	483	0.34
µ	1.47		1.46		0.93
S.D	0.06		0.06		0.51

Example (Measurement 1): natural orange 2% owf and L:R = 1 : 1 0

$$\% \text{ Exhaustion} = \frac{[A_1 - A_2] \times 100}{A_1}$$

where A_1 is the absorbance of the dye solution before dyeing

A_2 is the absorbance of the dye solution after dyeing.

$$\% \text{ Exhaustion} = \frac{[1.50 - 1.48] \times 100}{1.50}$$

$$\% \text{ Exhaustion} = 1.26$$

Appendix Table 8 % Exhaustion of Natural Orange on PET fabric at 2% owf.

Times	**Absorbance before dyeing**	**Wavelength (nm)**	**Absorbance after dyeing**	**Wavelength (nm)**	**% Exhaustion**
1	0.66	484	0.6	485	1.77
2	0.66	485	0.64	484	2.55
3	0.70	485	0.68	483	2.20
µ	0.67		0. 65		2.17
S.D	0.02		0.02		0.39

Appendix Table 9 % Exhaustion of Natural Red Brown on PLA fabrics at 2% owf.

Times	Absorbance before dyeing	Wavelength (nm)	Absorbance after dyeing	Wavelength (nm)	% Exhaustion
1	0.20	500	0.20	500	1.98
2	0.19	500	0.19	500	3.57
3	0.20	500	0.20	500	1.51
µ	0.20		0.19		2.36
S.D	0.05		0.00		1.07

Appendix Table 10 % Exhaustion of Natural Red Brown on PET fabric at 2% owf.

Times	Absorbance before dyeing	Wavelength (nm)	Absorbance after dyeing	Wavelength (nm)	% Exhaustion
1	5.12	500	4.97	500	2.96
2	5.48	500	5.14	500	6.14
3	5.06	540	4.95	504	2.15
µ	5.22		5.012		3.75
S.D	0.23		0.11		2.11

Appendix Table 11 % Exhaustion of cassumunar on PLA fabric at 2 % owf.

Times	Absorbance before dyeing	Wavelength (nm)	Absorbance after dyeing	Wavelength (nm)	% Exhaustion
1	4.13	338	1.47	338	57.26
2	3.01	339	0.92	339	69.34
3	3.31	339	1.29	339	61.08
µ	3.48		1.23		62.56
S.D	0.58		0.28		6.18

Appendix Table 12 % Exhaustion of cassumunar on PET fabric at 2% owf.

Times	Absorbance before dyeing	Wavelength (nm)	Absorbance after dyeing	Wavelength (nm)	% Exhaustion
1	2.35	335	1.50	335	36.05
2	2.23	335	1.54	335	31.07
3	2.30	335	1.59	335	30.91
µ	2.29		1.54		32.68
S.D.	0.96		0.05		2.92

Appendix Table 13 % Exhaustion of turmeric on PLA fabric at 2% owf

Times	Absorbance before dyeing	Wavelength (nm)	Absorbance after dyeing	Wavelength (nm)	% Exhaustion
1	2.76	343	0.78	341	71.69
2	2.48	343	0.63	341	74.52
3	2.66	343	0.77	341	71.03
µ	2.63		0.73		71.42
S.D	0.15		0.08		1.86

Appendix Table 14 % Exhaustion of turmeric on PET fabric at 2% owf.

Times	Absorbance before dyeing	Wavelength (nm)	Absorbance after dyeing	Wavelength (nm)	% Exhaustion
1	5.08	340	2.18	339	57.03
2	5.14	341	2.25	338	56.20
3	5.14	341	2.26	338	55.98
µ	5.12		2.23		56.44
S.D.	0.04		0.04		0.55

5. The color properties of the natural dyes on PLA and PET fabrics

Appendix Table 15 Color properties of Natural Orange on PLA fabric.

% owf	L*	a*	b*	C	H	K/S
0.5	73.44	7.846	13.006	15.206	58.843	0.753
1	72.223	8.673	12.7	15.38	55.663	0.813
2	71.196	9.873	14.216	17.31	55.236	0.823
3	70.593	10.503	15.613	18.816	56.08	0.866
5	69.8236	11.28	17.371	20.713	56.926	0.986

Appendix Table 16 Color properties of Natural Orange on PET fabric.

% owf	L*	a*	b*	C	H	K/S
0.5	76.969	5.26	9.376	10.75	60.716	0.84
1	71.716	6.366	10.286	12.096	58.253	1.083
2	70.943	7.923	11.876	14.273	56.293	1.113
3	69.793	9.006	12.776	15.633	54.826	1.173
5	69.016	10.786	15.08	18.546	54.423	1.243

Appendix Table 17 Color properties of Natural Red Brown on PLA fabric.

% owf	L*	a*	b*	C	H	K/S
0.5	74.156	6.9	10.093	12.256	55.473	0.73
1	72.753	7.956	11.393	13.66	55.063	0.83
2	71.973	9.03	11.43	14.58	51.573	0.843
3	71	9.74	11.4743	15.033	49.613	0.866
5	71.276	9.196	11.483	14.71	51.306	0.856

Appendix Table 18 Color properties of Natural Red Brown on PET fabric.

% owf	L*	a*	b*	C	H	K/S
0.5	72.51	4.8	9.673	10.796	63.613	1.103
1	71.096	5.29	10.056	11.393	62.253	1.176
2	72.273	5.933	10.923	12.43	61.476	1.113
3	72.15	6.033	10.856	12.42	60.93	1.106
5	72.31	6.376	11.883	13.483	61.793	1.123

Appendix Table 19 Color properties of cassumunar on PLA fabric**.**

% owf	L*	a*	b*	C	H	K/S
0.5	88.79	-2.21	10.98	11.2	101.36	0.7
1	87.45	-2.63	17.15	17.35	98.76	1.22
2	83.65	-3.88	27.94	28.21	97.96	2.56
3	82.75	-3.17	39.52	39.66	94.59	3.76
5	79.91	-2.45	51.32	51.38	92.73	6.22

Appendix Table 20 Color properties of cassumunar on PET fabric.

% owf	L*	a*	b*	C	H	K/S
0.5	89.26	-0.46	10.77	10.78	92.52	0.83
1	88.33	-0.19	14.9	14.9	90.69	1.06
2	86.95	-0.58	18.59	13.6	91.8	1.41
3	84.4	-1.06	27.44	27.46	92.25	2.29
5	81.6	-3.54	43.61	43.76	94.64	3.99

Appendix Table 21 Color properties of turmeric on PLA fabric.

% owf	L*	a*	b*	C	H	K/S
0.5	85.95	-2.79	23.3	23.46	96.83	0.9
1	92.49	-3.47	33.18	33.36	95.98	1.95
2	79.86	-3.41	47.97	48.09	94.07	4.88
3	75.12	-1.48	54	54.014	91.57	9.18
5	73.15	1.03	66.3	66.31	89.11	20.55

Appendix Table 22 Color properties of turmeric on PET fabric.

% owf	L*	a*	b*	C	H	K/S
0.5	86.2	-4.39	23.17	23.58	100.68	0.92
1	83	-8.04	38.42	39.25	101.76	1.84
2	79.16	-8.06	51.23	51.87	98.94	4.41
3	77.18	-7.98	59.51	60.04	97.64	7.52
5	73.91	-5.92	69.36	69.54	94.06	14.42

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