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Unsaturated fatty acids based materials as auxiliaries for printing and finishing of cellulosic fabrics

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ABSTRACT

Surface-active agents were used in textile industries in all processes. Fatty acid derivatives based materials known as important auxiliaries. This research aims to develop some unsaturated fatty acids derivatives to be used as textile auxiliaries. Three unsaturated fatty acids were reacted with materials having different structure (PEG; 1000, 4000 and 6000 g/mole), polyethylenimine (PEI), stearyl alcohol and Octadecylamine). Synthesized auxiliaries were characterised by measuring FT-IR, HLB and cloud point and stability over different time period. Produced materials after characterisation were classified to be used as O/W emulsifiers or softeners. Applied these materials as softeners on cotton fabrics provide good physical and mechanical properties. Furthermore, using these materials as emulsifiers to prepare printing pastes and apply them into cotton fabrics provide good colour strength and colour fastness of printed fabrics.

Keywords: *unsaturated fatty acid, Hydrophilic – Lipophilic Balance, textile softeners and O/W emulsifiers.*

1. INTRODUCTION

The increasing awareness of surfactants effects on the environment has caused increasing needs for more environmentally friendly cleaning products. As a response, chemical industries directed towards producing more eco-friendly, which are derived from renewable resources [1-9].

The fatty acids are linear aliphatic carboxylic acids; unsaturated fatty acids are the primary natural starting materials for the production of softener, emulsifier and surfactant molecules. Surfactants derived from unsaturated fatty acids, amines show favorable physical properties, including a lower viscosity and improved handling and intended performance characteristics are maintained. These surfactants are manufactured entirely from natural, renewable resources such as plant oils [10]. They have great environmental compatibility and highly biodegradable [11-14].

In this study, we used oleic, Linoleic and Ricinoleic acid as eco-friendly materials for synthesizing a series of nonionic/cationic surfactants according to simple reactions with PEG (1000, 4000 and 6000 g/mole), Stearyl alcohol, polyethyleneimine (PEI) and Octadecylamine. The surface activities of the synthesized surfactants were determined and joined by their chemical structure.

Furthermore, the produced materials applied as emulsifier in printing paste cope industrial interest as they enhance performance benefits including higher solubility, ease of handling, water tolerance, and improved oxidative stability . High yields of branched acids are obtained from unsaturated fatty acids. all carbon atoms in the fatty acid molecule is unchanged. Produced materials will be characterized and utilize in textile sector based on their Hydrophilic Lipophilic Balance (HLB) [15-17].

2. MATERIALS AND METHODS

2.1. Materials.

Three unsaturated fatty acid; oleic acid (282.4614 g/mol), linoleic acid (280.4455 g/mol) and ricinoleic acid (298.461 g/mol). Polyethylene glycol (PEG; 1000, 4000 and 6000 g/mol), octadecylamine (269.51 g/mol), polyethyleneimine ($\cong$ 60000 g/mol) and stearyl alcohol (270.49 g/mol). Acrylate binder (ET-BASF, Egypt), chloropyrimidine pigment (Drimarine®Blue P, Clariant, Egypt). Urea and diammonium hydrogen phosphate were used.

2.2. Methods.

2.2.1. Extraction of linoleic and ricinoleic acid.

Ricinoleic acid (RA) and linoleic acid (LA) was obtained according to a slightly modified method from our previous work [18]. In typical procedure, dried castor oil for ricinoleic acid or safflower seed oil for linoleic acid (50 g) was placed in a round

flask contain alcoholic sodium hydroxide NaOH (25 g NaOH in 150 ml ethanol) and then rise the temperature to 80°C and add 20 ml water and then refluxing at 160 – 170°C for 1 h. then cool down to 80°C and the solution was acidified with HCl till pH = 1. The produced acids were extracted in ethyl acetate (600 ml) then washing with warm NaCl solution three times and then dried overnight using magnesium sulphate. The solvent was removed using vacuum distillation times. The produced acid was used for further analysis and applications.

2.2.2. Reaction of unsaturated fatty acids.

Three unsaturated fatty acid (namely oleic (OA), linoleic (LA) and ricinoleic (RA) acids) was condensate with hydroxyl or amino groups in polyethyleneimine (PEI), octadecylamine (OCTA), stearyl alcohol (SA), and/or polyethylene glycol (PEG)).

The reaction will be carried out using ultrasonic wave. Fatty acids and polymers (1: 1 mole: mole) are melted at 60°C in presence of 0.01 mole of sulphuric acid as catalyst. Then, the mixture will introduce in ultrasonic bath with 80 frequency and 100% power at 80°C for 24 h, after that the flask was cooled down to room temperature, and the product was collected.

2.2.3. Application of produced materials to cotton fabrics.

2.2.3.1. Application of produced materials as softeners. Cotton fabric was treated using pad-dry cure technique. Fabric will padded in the solution containing fatty acid derivative (10, 30 or 50 g/l), 2 g/l Hostapal®CX–ET and 2 ml/l acetic acid. Blank sample was padded in a bath containing 2 g/l Hostapal®CX–ET only. Blank and treated samples were dried at 100°C for 3 min. and cured at 140°C for 3 min.

2.2.3.2. Application of produced materials as emulsifier in printing paste. The printing paste ingredients were as following recipe presented in **Table 1** and prepared using homogeniser.

Table 1. Printing paste ingredients recipe

Colorant	2 g
Emulsifier	1.5 g
Kerosene	65 g
Water	15 g
Urea	7 g
Binder	6 g
Sodium dihydrogen phosphate	3.5g
Total	100 g

Printing was applied to fabrics via flat screen technique. The prints fabrics were dried at 100°C for 5 min. then cured at 160°C for 3 min.

2.3. Characterization of produced materials.

Total conversion percent was determined by calculation the fatty acid amount (represented as acid value) before and after the reaction. [15, 16, 19].

$$\text{Total conversion (\%)} = \frac{(A_1 - A_2)}{(A_1 - A_c)} \times 100$$

where A_1 is the acid value before the reaction, A_2 is the acid value after the reaction, A_c is the acid value of catalyst.

Acid value was determined according the following procedure: [19] 1 g fatty acid derivatives were dissolved in 50 ml of ethanol: water (1: 1) and titrate against 0.1 N KOH using phenol phethalien as indicator, Therefore, acid value was calculated according to the following equation:

$$\text{Acid value} = \frac{VT \times 1000}{W}$$

where: V is KOH volume used in the titration of the sample, ml, T is titer of the KOH solution ($\frac{N \times eq.wt}{1000}$) g/ml, and w is sample weight g.

FT –IR spectroscopy were investigated using JASCO FT-IR spectrometer (ATR).

Hydrophilic – Lipophilic Balance (HLB) was calculated according to the following formula: [15-17, 20]

$$\text{HLB} = \frac{1}{5} \times \frac{\text{(formula weight of the compound)}}{\text{(formula weight of hydrophilic part)}} \times 100$$

Cloud point temperature was calculated as follow: 5 g of the fatty acid derivatives was added to 20 ml ethanol/water (20:80). then, 1 g paste was dispersed in 100 ml water and heated up by 1°C/min until cloudy and thee temperature was recorded (T_1). Then, the temperature was raised 5°C higher than T_1, and then cooled down with the same rate until the solution become cloudy again (T_2). Cloud point was then calculated using the following equation: [15-17, 20, 21].

$$\text{Cloud point} = \frac{(T_1 + T_2)}{2}$$

Dry crease recovery angle (CRA) was measured according to AATCC Test Method 66 – 2014 [22]. Fabric roughness was measured using Surface Roughness Measuring Instrument SE 1700 a. Fabric stiffness was determined according to ASTM Test Method D 1388 – 14E1 using the cantilever apparatus. [23]. Wettability was evaluated according to AATCC Test Method 79-(2014) [24].

Colour strength and fastness properties of the printed samples were evaluated by Hunter Lab Ultra Scan PRO (Hunter Lab Ultra Scan PRO (USA, 2007). [17, 25-37]

The colour intensity (ΔE) and the relative colour strength (*K/S*) of the printed cotton fabrics was measured and assessed by applying the Kubelka–Munk equation as follow: [38]

$$K/S = \frac{(1 - R)^2}{2R} - \frac{(1 - R_o)^2}{2R_o}$$

where *K* is the absorption coefficient, *S* is the scattering coefficient, R_o is the reflectance of uncoloured (white) sample, and *R* is the reflectance of the coloured sample.

The colourfastness to washing was determined according to the AATCC Test method 61-2013 using Launder-Ometer. [39] The colourfastness to crocking was determined according to the AATCC test method 8-2016. [40] The colourfastness to perspiration was determined according to the AATCC test method 15-2013. [41] The colourfastness to light was determined according to the AATCC test method 16.1-2014. [42] Evaluation of the fastness was established using the Gray Scale reference for colour change.

3. RESULTS

3.1. Characterisation of extracted fatty acids.

3.1.1. Characterisation of linoleic acid.

Figure 1 shows the FT-IR ATR spectra of linoleic acid. It is clear that the region 1690-1710 cm^{-1} shows a very strong peak. A strong band in this region is indicative of C=O stretch of the carboxylic acid in the linoleic acids. The sharp two peaks in region (2800-3000 cm^{-1}) are for aliphatic hydrocarbon for CH stretch containing CH$_3$ and CH$_2$ groups. The moderate peak in the region above 3000 cm^{-1} was observed to confirm the presence of the double bond in

the chemical structure. On the other hand, infrared data shows strong peaks at 988 and 948 cm^{-1} which indicates both trans-trans and trans-cis conjugated isomers are present. The weak band observed at 968 cm^{-1} (Figure 1) is indicative of some isolated trans double bonds due to the lack of complete conversion to conjugated isomers. ^{1}H NMR spectrum of linoleic acid in acetone-d6 is presented in Figure 1. The chemical shifts are: δ 10.6 ppm (1H, HA), δ 5.58- 5.12 ppm (4H, HB), δ 2.7 ppm (2H, HC), δ 2.33 ppm (2H, HD), δ 2.03 ppm (2H, HE), δ 1.6 ppm (2H, HF), δ 1.1- 1.5

ppm (18H, HG), δ 0.9 ppm (3H, HJ). In addition, the broad peak at 5.58-5.12 ppm assigned to methylene protons, supports the existence of double bonds of the linoleic acid.
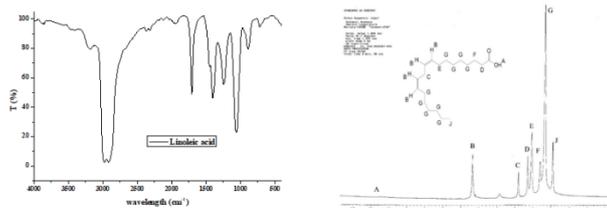

Figure 1. FT-IR and NMR spectrum of linoleic acid.

3.1.2. Characterisation of ricinoleic acid.

Figure 2 shows the FT-IR-ATR spectra of ricinoleic acid. In the IR spectral data of ricinoleic acid a strong O-H absorption band appears at 3405- 3394 cm^{-1} indicating that the hydroxyl groups of the acid remain unaffected by the alkali treatment. The strong carboxylic carbonyl absorption peak was observed at 1711 cm^{-1}. Two strong peaks at 2928 and 2856 cm^{-1} indicate the alkyl part of the acid.

Figure 2 illustrate the ^{1}H NMR spectrum of the ricinoleic acid. The chemical shifts are: δ 0.91 ppm (3H, HM), δ 1.2-1.6 ppm

(18H, HL), δ 1.75 ppm (2H, HK), δ 2.1 ppm (2H, HJ), δ 2.3 ppm (2H, HG), δ 2.4 ppm (2H, HF), 3.4-3.6 ppm (1H, HC), 3.8 ppm (1H, HB), 4.1 ppm (1H, HD) and δ 5.5 ppm (1H, HA). The characteristic hydroxyl proton at δ 5.5 ppm was observed. The double bond protons are distinguished as two multiplets peaks at 3.8 and 3.4-3.6 ppm.
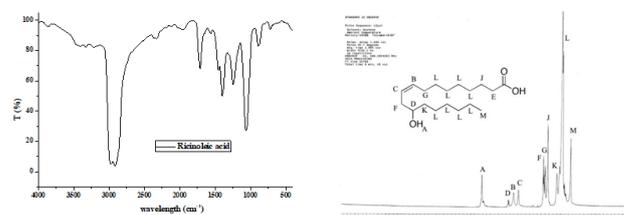

Figure 2. FT-IR and NMR spectrum of ricinoleic acid.

3.2. Characterization of produced materials.

3.2.1. Percent total conversion.

The total conversion percent for the synthesised fatty acid derivatives was presented in Table 2 and Figure 3, which give an indication for the possibility to form ester compounds through the conversion of carboxyl group to ester or amide groups.

Table 2. Percent total conversion of synthesised materials from unsaturated fatty acids and alcohol or amine compounds.

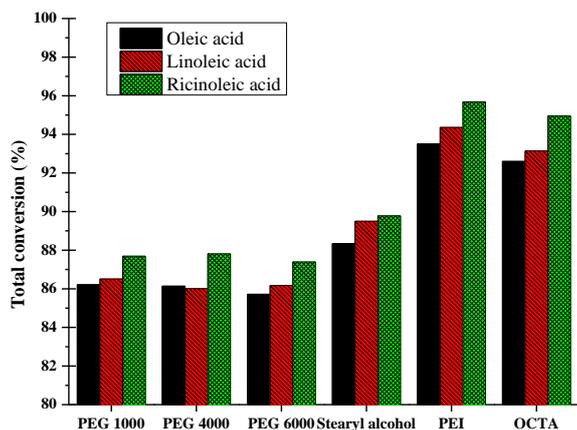| Fatty acids		Product code	Total conversion (%)
Oleic acid C$_{17}$H$_{33}$COOH CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOH (282.47)	PEG 1000	OA-1000	86.21
	PEG 4000	OA-4000	86.14
	PEG 6000	OA-6000	85.72
	Stearyl alcohol	OA-Sa	88.34
	PEI	OA-PEI	93.50
	Octadecylamine	OA-OCT	92.60
Linoleic acid C$_{17}$H$_{31}$COOH CH$_3$(CH$_2$)$_4$CH=CHCH$_2$CH=CH(CH$_2$)$_7$COOH (280.45)	PEG 1000	LA-1000	86.51
	PEG 4000	LA-4000	86.01
	PEG 6000	LA-6000	86.17
	Stearyl alcohol	LA-SA	89.50
	PEI	LA-Pei	94.36
	Octadecylamine	LA-OCT	93.14
Ricinoleic acid C$_{17}$H$_{31}$COOH CH$_3$(CH$_2$)$_5$CH(OH)CH$_2$CH=CH(CH$_2$)$_7$COOH (298.461)	PEG 1000	RA-1000	87.69
	PEG 4000	RA -4000	87.81
	PEG 6000	RA -6000	87.39
	Stearyl alcohol	RA -SA	89.78
	PEI	RA -Pei	95.68
	Octadecylamine	RA -OCT	94.95

Figure 3. Percent total conversion of unsaturated fatty acids derivatives.

The results explain that increasing the number of carbon chain number of fatty acid provide decreasing in the percent total conversion for the synthesised materials using the same alcohol or amine compound. In addition, for the unsaturated fatty acid, even the carbon chain length of investigated fatty acid are the same, the percent total conversion is changing due to the presence of double bond in the fatty acid structure. Furthermore, the presence of an additional double bond of hydroxyl group increases the percent total conversion. This increase in the percent total conversion is due to the flexibility properties of unsaturated fatty acid, which increase the reaction chance between each reactant (alcohol or amine). From another point of view, the formation of amide groups is higher than formation of ester group, so, these results

provide that, the reactivity of unsaturated fatty acid to react with PEI and OCTA is higher than hydroxyl compounds.

3.2.2. Hydrophilic – Lipophilic Balance (HLB) and cloud point values.

As the hydrophilic – lipophilic balance and cloud point give a sign for the appropriate utilization for each synthesised material, so, HLB and cloud point values for synthesised materials based on unsaturated fatty acids are listed in Table 3 and Figure 4.

From the results, it is clear that, even the carbon chain length of investigated fatty acid are the same, the HLB was decreased and cloud point was increased. Furthermore, the presence of additional double bond of hydroxyl group increases the HLB. This increase in the HLB is due to the fatty acid chain flexibility.

HLB values can recommend the appropriate uses of every material dependent on the HLB. From the information in Table 4, it can be observed that:

• Most of the synthesised materials, have HLB's lays between 8 and 18, which are inside the scope of oil – in water (o/w) emulsifiers,

• HLB's of RA– 1000 and LA–1000 are falls in the range suggested for detergents (12 – 16).

• HLB's values of most synthesised materials are more than 16, it is known that their behaviour are similar to PEG 6000 instead of their fatty acids. [15, 16]

Table 3 and Figure 4 demonstrate the cloud points of the synthesised materials with unsaturated fatty acids under examination. Obviously, for similar unsaturated fatty acids, the cloud point increments after increasing the PEG molecular weight. This phenomenon is due to the increment in both hydrophilicity and hydrogen bonding, this increment requires high force to break the materials and separate the synthesised material in a cloudy shape. Besides, for hydroxyl or amine groups, increment the double bond or hydroxyl groups in the structure of unsaturated fatty acids prompted increment the cloud points of the synthesised materials.

Table 3: HLB-values and dependent expected function for synthesised materials from unsaturated fatty acids
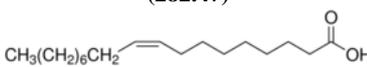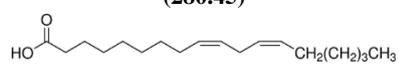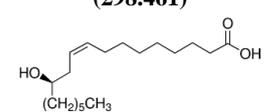
Fatty acids	Product Code	HLB value	Cloud point (°C)
Oleic acid $C_{17}H_{33}COOH$ $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ **(282.47)**	PEG 1000 — OA-1000	15.80	80.5
	PEG 4000 — OA-4000	18.75	94
	PEG 6000 — OA-6000	19.15	> 100
	Stearyl alcohol — OA-Sa	10.08	68
	PEI — OA-PEI	19.91	63
	Octadecylamine — OA-OCT	10.05	82
Linoleic acid $C_{17}H_{31}COOH$ $CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$ **(280.45)**	PEG 1000 — LA-1000	15.83	77.5
	PEG 4000 — LA-4000	18.76	91
	PEG 6000 — LA-6000	19.16	97
	Stearyl alcohol — LA-SA	10.11	65
	PEI — LA-Pei	19.91	60
	Octadecylamine — LA-OCT	10.09	79
Ricinoleic acid $C_{17}H_{31}COOH$ $CH_3(CH_2)_5CH(OH)CH_2CH=CH(CH_2)_7COOH$ **(298.461)**	PEG 1000 — RA-1000	15.60	74
	PEG 4000 — RA -4000	18.68	87.5
	PEG 6000 — RA -6000	19.10	93.5
	Stearyl alcohol — RA -SA	9.78	61.5
	PEI — RA -Pei	19.91	56.5
	Octadecylamine — RA -OCT	9.76	75.5

Table 4. HLB-value and the function expected from the product in aqueous solution.

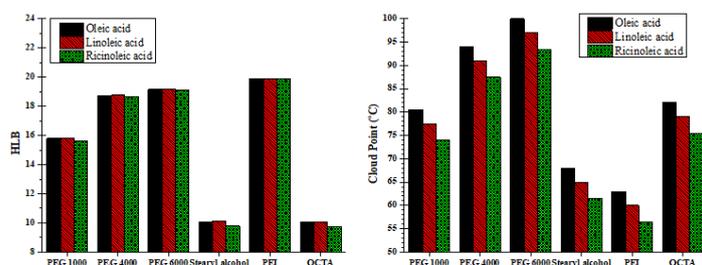| HLB value	Suitable Function	Suggested Product code		
1 to 3	Anti-foaming agent	-		
3 to 8	water in oil emulsifier	-		
7 to 9	Wetting and spreading agent	-		
13 to 16	Detergent	OA-1000	LA-1000	RA-1000
8 to 16	oil in water emulsifier	OA-OCT	LA-OCT	RA-OCT
		OA-SA	LA-SA	RA-SA
16 to 18	Solubilize or Hydrotrope	-	-	-
≥ 16	Softeners	OA-4000	LA-4000	RA-4000
		OA-6000	LA-6000	RA-6000
		OA-PEI	LA-PEI	RA-PEI

Figure 4. HLB values and Cloud point temperature of fatty acid derivatives.

3.2.3. FT-IR measurements.

FT-IR spectra of synthesised materials from unsaturated fatty acid were presented in Figure 3. Spectra of unsaturated fatty acids provide a characteristic peaks at 1110, 2850 – 2930, 2960 – 2960 and 1670 – 1710 cm^{-1} which represent the C–O–C, OH, C–H and C=O respectively [15, 16, 20, 43].

Moreover, FT-IR spectra of synthesised materials provide the presence of an ester band (–O–C=O) at 1730 – 1740 cm^{-1}. which attributed to carbonyl group in the ester group, which observed in the fatty acids spectra at 1670 – 1710 cm^{-1}. Another important peak for OH group, which presented at 3390 – 3420 cm^{-1} was found in the synthesised material spectra containing dihydroxyl groups. Therefore, there is an indication to presence the ester group in the synthesised materials.

From another point of view, spectra of synthesised materials having amine group (e.g. PEI and OCTA) provide presence of some characteristic functional groups; NH$_2$, NH and CH$_2$ (at 2850 and 2960 cm^{-1}) and two peaks appear at 1112 and 1645 cm^{-1} corresponding to C-N and NH group of PEI respectively [44-46]. Furthermore, the spectrum of synthesised materials with PEI or OCTA shows absorption peaks including (C=O, amide I and II (δ(NH); 1720, 1550 cm^{-1}) and (C-O-C, 1110 cm^{-1}), so, there is an indication to presence the amide group in the synthesised materials. [46]

3.3. Fatty acid derivatives as auxiliaries for cotton fabric

3.3.1. Fatty acid derivatives as Softeners.

Synthesised materials based on unsaturated fatty acids derivatives with both hydroxyl or amine compound have been examined as a softening agent to enhance chemical and physical properties of cotton fabrics. Mechanical and physical properties of treated cotton fabrics were listed in Table 5. The data provide that, treated fabrics with synthesised materials improve both physical and mechanical properties compared to blank fabric.

In addition, increasing the concentration of synthesised materials led to increasing in the softening effect on the treated fabrics. Moreover, hydrophilicity (expressed as wettability) of treated fabrics decreased after treatment especially with material based on PEG compounds. From the other view, presence of double bond or hydroxyl group in the synthesised materials improve the hydrophilicity properties of treated fabrics, which attributed to the flexibility of fatty acid, which noticeable provided by increasing the concentration from 10 to 60 g/l.

Furthermore, for the same unsaturated fatty acid, increasing the PEG molecular weight shows increasing in roughness and

decreasing in both stiffness and wettability. In addition, synthesised materials containing amine groups (PEI) provide increasing in both roughness and wettability properties with decreasing in stiffness property of the treated fabrics.

One of the important properties of cotton fabrics, which need to enhance, is crease recovery angle (CRA). The examination of CRA for all treated fabrics with synthesised materials based on unsaturated fatty acids derivatives with polyalcohol or amine provides enhancement comparing to the untreated one.
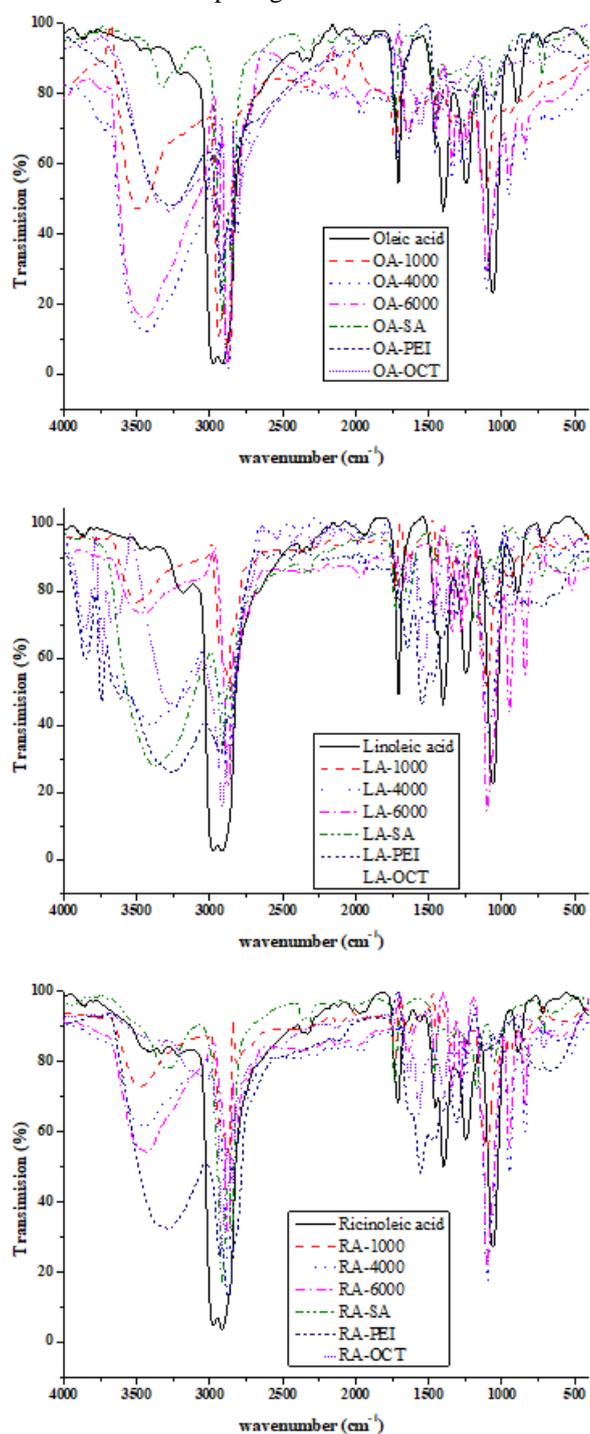

Figure 5. FT-IR spectra of unsaturated fatty acid and its derivatives.

3.3.2. Fatty acid derivatives as emulsifier for printing paste.

Prepared printing paste in the presence of commercial emulsifier or unsaturated fatty acid based materials as emulsifiers has been utilised in the printing of cotton fabrics. Colour strength (K/S) and fastness properties to washing, perspiration, rubbing and

light of printed cotton fabrics have been investigated and the result was listed in **Table 6**. The results of printed fabrics with using unsaturated fatty acid based materials as emulsifiers shows increasing of washing, perspiration and light fastness more than printed fabrics using commercial emulsifier. In addition, rubbing fastness (wet and dry) of printed fabrics using either commercial or synthesised emulsifier in printing paste are moderate.

Table 5. Mechanical and physical properties of treated cotton fabrics

Unsaturated Fatty acid derivatives	concentration of unsaturated fatty acid derivatives (g/l)											
	10				30				60			
	R (µm)	S (mg.cm)	CRA (W+F°)	W (sec)	R (µm)	S (mg.cm)	CRA (W+F°)	W (sec)	R (µm)	S (mg.cm)	CRA (W+F°)	W (sec)
Blank	20.3	26497	181	4	20.3	26497	181	4	20.3	26497	181	4
OA-4000	15.95	15667	256	29	14.15	13667	261	49	12.45	12540	275	69
OA-6000	17.05	14433	250	5	15.65	12433	256	29	14.15	11022	273	49
OA-PEI	20.05	24295	273	3	18.45	21127	279	3	16.65	18892	294	3
LA-4000	16.25	13655	275	38	14.65	12531	290	58	12.65	11990	292	77
LA-6000	16.65	12533	268	8	15.35	11647	274	16	14.35	11422	284	25
LA-PEI	21.25	24056	294	3	19.65	22489	305	2	18.35	22091	311	2
RA-4000	17.15	12518	275	38	16.15	12542	290	53	15.35	10757	299	56
RA-6000	17.85	11778	270	10	16.95	11420	276	17	16.05	10218	291	20
RA-PEI	22.85	23856	295	2	21.75	23194	307	1	20.65	20972	318	1

R: Roughness (µm), S: Stiffness (mg.cm), CRA: Crease Recovery Angle (warp + weft) (W+F°), W wettability (sec)

Table 6. Colour strength and fastness properties of printed cotton fabrics.

Unsaturated Fatty acid derivatives	K/S	Fastness properties								
		Washing		Rubbing		Perspiration				Light
		St.	Alt.	Wet	Dry	Alkaline		Acidic		
						St.	Alt.	St.	Alt.	
Commercial emulsifier	3.75	3	4	2	2	4	4	4	4	5
OA-SA	4.83	4	4	2-3	2-3	4-5	4-5	4-5	4-5	5
OA-OCT	4.95	4	4	2-3	2-3	4-5	4-5	4-5	4-5	5
LA-SA	4.42	4	4	2-3	2-3	4-5	4-5	4-5	4-5	5
LA-OCT	4.81	4	4	2-3	2-3	4-5	4-5	4-5	4-5	5
RA-SA	3.86	4	4	2-3	2-3	4-5	4-5	4-5	4-5	5
RA-OCT	4.77	4	4	2-3	2-3	4-5	4-5	4-5	4-5	5

St.: Staining   Alt.: Alternation

3.3.3. *Stability of the paste upon Storing.*

Assessment of the printing paste stability against time was investigated by estimating the printing paste viscosity on the various shear rate at various storing time. Table 7 recorded the viscosity for printing paste upon various storing time (0, 7 and 30 days) at various shear rate. From the results listed in Table 7, all printing pastes under the examined storing time are stable without any separation. Despite shear rate, the printing pastes have good viscosity even by storing; by implying that, increasing storing time provide a higher viscosity which in the same line with known phenomena for polymeric printing paste as a result of good solubility and swelling behaviour [15, 17]. Furthermore, increasing the viscosity of printing paste upon storing time is attributed to changing in the printing paste internal structure. These changing is attributed to the hydrogen bonding between hydroxyl and amino groups of the fatty acid derivatives and water (external phases). In this way, the authoritative between two phases was increments with storing and prompting more protection from the flow [15, 17].

Table 7. Effect of storing time on the viscosity of printing paste.

Storing time	Shear rate (S⁻¹)	Apparent Viscosity (poise)						
		Commercial emulsifier	OA-SA	OA-OCT	LA-SA	LA-OCT	RA-SA	RA-OCT
Freshly Prepared	2	144.6	110.6	103.15	106.15	104.65	105.45	105.05
	20	43.8	34.74	33.84	34.24	34.04	34.14	34.04
	50	18.3	9.44	8.64	9.04	8.84	8.94	8.84
	100	11.4	4.54	4.74	4.64	4.64	4.64	4.64
After 7 days	2	190.6	167.2	165.05	165.45	165.25	165.35	165.35
	20	57.7	52.94	54.14	53.54	53.84	53.64	53.74
	50	24.1	16.54	16.44	16.44	16.44	16.44	16.44
	100	15.0	9.74	10.74	10.24	10.54	10.34	10.44
After 1 month	2	232.0	205.1	201.25	202.45	201.85	202.15	201.95
	20	70.3	64.94	65.94	65.44	65.64	65.54	65.64
	50	29.4	21.34	21.04	21.14	21.04	21.14	21.14
	100	18.3	13.14	14.24	13.64	13.94	13.84	13.84

4. CONCLUSIONS

Oleic, linoleic and ricinoleic acids were chosen as model for unsaturated fatty acids to react with different materials having different functional groups e.g. octadecylamine having mono amino group, stearyl alcohol having mono hydroxyl group, polyethylene glycol (1000, 4000 and 6000 g/mole) having di hydroxyl groups and polyethyleneimine (PEI) having poly-amino groups at 180°C for 8 h. Percent total conversion provides a good preparation of suggested compounds. FT-IR spectra confirmed presence of ester or amide groups in the id derivatives. Calculated HLB suggesting that, some compounds can be used as O/W emulsifier and most of them can be used softeners. Applied these materials in a suitable field based on HLB values as emulsifier in O/W emulsion have succeeded. Furthermore, using these materials as finishing agents provide good physical and mechanical properties for treated cotton fabrics.

5. REFERENCES

1. Britton, L.N. Surfactants and the environment. *Journal of Surfactants Detergents* **1998**, *1*, 109-117, https://doi.org/10.1007/s11743-998-0014-6.

2. Nada, A.A.; Hassabo, A.G.; Mohamed, A.L.; Mounier, M.M.; Abou Zeid, N.Y. Liposomal Microencapsulation of Rodent-Repelling Agents onto Jute Burlaps: Assessment of Cytotoxicity and Rat Behavioral Test. *Journal of Applied Pharmaceutical Science*, **2016**, *6*, 142-150

3. Mohamed, A.L.; Hassabo, A.G.; Nada, A.A.; Abou-Zeid, N.Y. Properties of Cellulosic Fabrics Treated by Water-Repellent Emulsions. *Indian Journal of Fibre & Textile Research* **2017**, *42*, 223-229

4. Mohamed, A.L.; Hassabo, A.G.; Shaarawy, S.; Hebeish, A. Benign Development of Cotton with Antibacterial Activity and Metal Sorpability through Introduction Amino Triazole Moieties and Agnps in Cotton Structure Pre-Treated with Periodate. *Carbohydrate Polymers*, **2017**, *178*, 251-259

5. Salama, M.; Hassabo, A.G.; El-Sayed, A.A.; Salem, T.; Popescu, C. Reinforcement of Polypropylene Composites Based on Recycled Wool or Cotton Powders. *Journal of Natural Fibers*, **2017**, 1-14

6. Hassabo, A.G.; Mohamed, A.L.; Shaarawy, S.; Hebeish, A. Novel Micro-Composites Based on Phosphorylated biopolymer/Polyethyleneimine/Clay Mixture for Cotton Multi-Functionalities Performance. *Bioscience Research*, **2018**, *15*, 2568-2582

7. Ibrahim, N.A.; Nada, A.A.; Eid, B.M.; Al-Moghazy, M.; Hassabo, A.G.; Abou-Zeid, N.Y. Nano-Structured Metal Oxides: Synthesis, Characterization and Application for Multifunctional Cotton Fabric. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, **2018**, *9*, 035014 (2018)

8. Mohamed, A.L.; Hassabo, A.G. Composite Material Based on Pullulan/Silane/ZnO-Nps as Ph, Thermo-Sensitive and Antibacterial Agent for Cellulosic Fabrics. *Advances in Natural Science: Nanoscience and Nanotechnolgy*, **2018**, *9*, 1-9

9. Hassabo, A.G.; El-Naggar, M.E.; Mohamed, A.L.; Hebeish, A.A. Development of Multifunctional Modified Cotton Fabric with Tri-Component Nanoparticles of Silver, Copper and Zinc Oxide. *Carbohydrate Polymers*, **2019**, *210*, 144-156

10. Zhao, F.; Clarens, A.; Murphree, A.; Hayes, K.; Skerlos, S.J. Structural Aspects of Surfactant Selection for the Design of Vegetable Oil Semi-Synthetic Metalworking Fluids. *Environmental Science & Technology* **2006**, *40*, 7930-7937, https://doi.org/10.1021/es061418l.

11. Lisi, R.D.; Perron, G.; Paquette, J.; Desnoyers, J.E. Thermodynamics of micellar systems: activity and entropy of sodium decanoate and n-alkylamine hydrobromides in water. *Canadian Journal of Chemistry* **1981**, *59*, 1865-1871, https://doi.org/10.1139/v81-278.

12. Negm, N.A.; Mohamed, A.S. Synthesis, Characterization and Biological Activity of Sugar-Based Gemini Cationic Amphiphiles. *Journal of Surfactants Detergents* **2008**, *11*, 215-221, https://doi.org/10.1007/s11743-008-1071-9.

13. Negm, N.A.; Zaki, M.F. Corrosion inhibition efficiency of nonionic Schiff base amphiphiles of p-aminobenzoic acid for aluminum in 4N HCL. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2008**, *322*, 97-102, https://doi.org/10.1016/j.colsurfa.2008.02.027.

14. Jurado, E.; Vicaria, J.M.; Fernandez-Arteaga, A.; Chachalis, P.; García-Martín, J.F. Wetting Power in Aqueous Mixtures of Alkylpolyglucosides and Ethoxylated Fatty Alcohols. *Journal of Surfactants Detergents* **2010**, *13*, 497-501, http://dx.doi.org/10.1007/s11743-010-1228-1.

15. Hassabo, A.G. *Preparation, Characterisation and utilization of some textile auxiliaries*. El-Azhar University: Cairo, Egypt, 2005.

16. Abo-Shosha, M.H.; Nassar, F.A.; El-Sayed, Z.; Hassabo, A.G. Preparation and Characterizations of Some Fatty Acid/Polyethylene Glycol Condensates and Utilization as Softeners for Cotton Fabric. *Research Journal of Textile and Apparel* **2009**, *13*, 46-60, http://dx.doi.org/10.1108/RJTA-13-02-2009-B006.

17. Abo-Shosha, M.H.; Nassar, F.A.; Haggag, K.; El-Sayed, Z.; Hassabo, A.G. Utilization of Some Fatty Acid/PEG Condensates as Emulsifiers in Kerosene Paste Pigment Printing. *Research Journal of Textile and Apparel* **2009**, *13*, 65-77, https://doi.org/10.1108/RJTA-13-01-2009-B007.

18. Nada, A.A.; Hassabo, A.G.; Awad, H.M.; Fayad, W.; Shaffie, N.M.; Sleem, A.A.; Zeid, N.Y.A. (2015) Biomaterials Based on Essential Fatty Acids and Carbohydrates for Chronic Wounds. *Journal of Applied Pharmaceutical Science* **2015**, *5*, 13-21.

19. ASTM Standard Test Method (ASTM D-1980 – 87 (Reapproved 1998)), *Standard Test Method for Acid Value of Fatty acids and Polymerized Fatty acids*. ASTM International: West Conshohocken, PA, 1998, pp. 227.

20. Abo-Shosha, M.H.; Nassar, F.A.; El-Sayed, Z.; Hassabo, A.G. Preparation and Characterizations of Some Fatty Acid/Polyethylene Glycol Condensates, in Egyptian First International Conference in Chemistry: Chemistry for Human Needs In Developing Countries: Sharm El-Sheikh, Egypt, 2006.

21. ASTM Standard Test Method (D2024 − 09 (Reapproved 2017)), *Standard Test Method for Cloud Point of Nonionic*

Surfactant. ASTM International: West Conshohocken. 2017; pp. 204.

22. AATCC Test Method (66-2014), *Wrinkle Recovery of Fabric: Recovery Angle Method, in Technical Manual Method American Association of Textile Chemists and Colorists*. 2017; pp. 113-116.

23. ASTM Standard Test Method (ASTM D1388 − 14e1), *Standard Test Methods for Stiffness of Fabrics*. ASTM International: West Conshohocken, PA, 2016.

24. AATCC Test Method (79-2014), *Absorbency of Textiles. Technical Manual Method of the American Association of Textile Chemists and Colorists*: USA, 2017.

25. Kubelka, P.; Munk, F. Ein Beitrag zur Optik der Farbanstriche. *Z. Tech. Phys*. **1931**, *12*, pp. 593.

26. Mehta, K.T.; Bhavsar, M.C.; Vora, P.M.; Shah, H.S. Estimation of the Kubelka--Munk scattering coefficient from single particle scattering parameters. *Dyes and Pigments* **1984**, *5*, 329-340, https://doi.org/10.1016/0143-7208(84)80027-3.

27. Waly, A.; Marie, M.M.; Abou-Zeid, N.Y.; El-Sheikh, M.A.; Mohamed, A.L. Process of Single – Bath Dyeing, Finishing and Flam – Retarding of Cellulosic Textiles in Presence of Reactive Tertiary Amines. In 3rd International Conference of Textile Research Division, NRC; Textile Processing: State of the Art & Future Developments. 2006; Cairo, Egypt.

28. Waly, A.; Marie, M.M.; Abou-Zeid, N.Y.; El-Sheikh, M.A.; Mohamed, A.L. Flame Retarding, Easy Care Finishing and Dyeing of Cellulosic Textiles in One Bath. *Egyptian Journal of Textile Polymer Science and Technology* **2008**, *12*, 101-131.

29. Waly, A.I.; Marie, M.M.; Abou-Zeid, N.Y.; El-Sheikh, M.A.; Mohamed, A.L. Processes of Dyeing, Finishing and Flame Retardancy of Cellulosic Textiles in the Presence of Reactive Tertiary Amines. *Research Journal of Textile and Apparel* **2012**, *16*, 66–84, http://dx.doi.org/10.1108/RJTA-16-03-2012-B007.

30. Hassabo, A.G. *Preparation, Characterisation and utilization of some textile auxiliaries*. El-Azhar University: Cairo, Egypt, 2005.

31. Hassabo, A.G. *Synthesis and Deposition of Functional Nano-Materials on Natural Fibres*. RWTH Aachen University, Germany. 2011; pp. 154.

32. Hassabo, A.G.; Mendrek, A.; Popescu, C.; Keul, H.; Möller, M. Deposition of Functionalized Polyethylenimine-Dye onto Cotton and Wool Fibres. *Research Journal of Textile and Apparel* **2014**, *18*, 36-49, https://doi.org/10.1108/RJTA-18-01-2014-B006.

33. Hassabo, A.G.; Erberich, M.; Popescu, C.; Keul, H. Functional polyethers for fixing pigments on cotton and wool fibres. *Research & Reviews in Polymer* **2015**, *6*, 118-131.

34. AATCC Test Method (61-*2007), Colorfastness to Laundering: Accelerated, in American Association of Textile Chemists and Colorists,* Technical Manual Method American Association of Textile Chemists and Colorists. 2008; pp. 88-90.

35. AATCC Test Method (8-2007), *Colorfastness to Crocking. Crockmeter Method,* in Technical Manual Method American Association of Textile Chemists and Colorists, 2008; pp. 17-19.

36. AATCC Test Method (15-2013), *Colour Fastness to Perspiration,* in Technical Manual Method American Association of Textile Chemists and Colorists, 2013; pp. 30-32.

37. AATCC Test Method (16-2004), *Colour Fastness to Light: outdoor*, in Technical Manual Method American Association of Textile Chemists and Colorists, 2005; pp. 23-25.

38. Cai, Y.; Pailthrope, M.T.; David, S.K. A New Method for Improving the Dyeability of Cotton with Reactive Dyes. *Textile Research Journal* **1999**, *69*, 440–446, https://doi.org/10.1177/004051759906900608.

39. AATCC Test Method (61-2013), *Color Fastness to Laundering: Accelerated*, in Technical Manual Method American Association of Textile Chemists and Colorists, 2017; pp. 108.

40. AATCC Test Method (8-2016), *Colorfastness to Crocking. Crockmeter Method,* in Technical Manual Method American Association of Textile Chemists and Colorists, 2017; pp. 17-19.

41. AATCC Test Method (15-2013), *Colour Fastness to Perspiration,* in Technical Manual Method American Association of Textile Chemists and Colorists, 2017; [p. 30-32.

42. AATCC Test Method (16.1-2014), *Colour Fastness to Light: Outdoor,* in Technical Manual Method American Association of Textile Chemists and Colorists, 1993; pp. 33-48.

43. Silverstein, R.M.; Basster, G.C.; Morrill, T.C. *Spectrometric Identification of Organic Compounds*. Vol. Fifth Edition, New York, USA: John Wily & Sons, Inc. 1991.

44. Kurecic, M.; Sfiligoj-Smole, M.; Stana-Kleinschek, K. UV Polymerization of Poly (N-Isopropylacrylamide) Hydrogel. *Materials and Technology* **2012**, *46*, 87-91.

45. Yang, T.; Hussain, A.; Bai, S.; Khalil, I.A.; Harashima, H.; Ahsan, F. Positively Charged Polyethylenimines Enhance Nasal Absorption of the Negatively Charged Drug, Low Molecular Weight Heparin. *Journal of controlled release : official journal of the Controlled Release Society* **2006**, *115*, 289-297, https://doi.org/10.1016/j.jconrel.2006.08.015.

46. Hassabo, A.G.; Sharaawy, S.; Mohamed, A.L. Saturated Fatty Acids Derivatives as Assistants Materials for Textile Processes. *Journal of Textile Science & Fashion Technology* **2018**, *1*, 516, https://doi.org/10.33552/JTSFT.2018.01.000516.

6. ACKNOWLEDGEMENTS