#### List of Abbreviation

SDS Sodium dodecyl sulfate

CA Cetylalcohol

AIBN 2,2'-azobisisobutyronitrile

NaPS Sodium persulfate PFR Plugflow reactors

CSTR Continuous stirred tank reactor trains

MW Molecular weight

MWD Molecular weight distribution

BuA Butyl acrylate

2-EHA 2-ethyl hexyl acrylate

HEMA Hydroxyl ethyl methacrylate

MMA Methyl methacrylate

EA Ethyl acrylate MA Methyl acrylate

MB 4-maleimidobenzanilide

MAA Methacrylicacid
BDA Butanedioldiacrylate
AMA Allylmethacrylate

EGDMA Ethylene glycol dimethacrylate

NMA N-methylolacrylamide

Vac Vinyl acetate BPO Benzoyl peroxide

DMLL N-lauroyl-N $\alpha$ ,N $\alpha$ -dimethyl-lysine LNB N,N-dimethyl-n-laurylbetaine

NP40 Nonyl phenol ethoxylated 40 units of ethoxylation

CTAs Chain transfer agent

EDTA Ethylenediaminetetraacetic acid

UV Ultra violet

TEM Transmission Electron Microscopy
SEM Scanning Electron Microscope

ASTM American Standardization Testing Material

MFFT Minimum film forming temperature

AA Acrylic acid

RPM Round per minute

Mn Average molecular weight

cps Centimeter poise AA Acrylic acid

PAC Poly urethane acrylate co-polymer

AOT Aerosol OT

SLS Sodium Lauryl Sulphate

Mostafa Mohamed Mahmoud Omar El Sheikh, Novel Techniques for Production of Nano Emulsion Polymers for Textile Applications, Chemistry Department-Faculty of Science, Ain Shams University, 2013.

**Keywords:** Ethyl acrylate, Butyl acrylate, acrylic, methacrylic, morpgology, Textile pigment printing, rubbing fastness.

#### Abstract

Ethyl acrylate is the backbone textile pigment printing binder due to its good adhesion, soft film formation, and good fastness properties. This study was designed to improve the physical and mechanical properties of ethyl acrylate polymer by co-polymerization with either butyl acrylate or 2-ethyl hexyl acrylate in presence of acrylic acid or methacrylic acid at different concentration ratios (ethyl acrylate/butyl acrylate or 2-ethyl hexyl acrylate) (100/0, 5, 10, 15, 20) respectively. The best textile pigment printing binder formulas wereprepared by different surfactant and initiation system. The prepared polymers were investigated by TEM, SEM as well as mechanical and physical tests. The prepared polymers used as textile pigment printing binder, and they were investigated by rubbing fastness, heat fastness and durability, the best results was achieved by 10% 2-ethyl hexyl acrylate/ethyl acrylate and 20% butyl acrylate/ethyl acrylate.

It was found that polymers prepared by free radical system had higher mechanical and physical properties than polymers prepared by redox system.

# <u>Acknowledgement</u>

I would like to express my deep gratitude to my **Prof. Dr. AbdElgawad M. Rabie,** Professor of Organic Chemistry, Faculty of Science, Chemistry Department,
Ain Shams University, for his consistent supervision, advice and valuable discussion.

I am cordially indebted to **Prof. Dr. Ahmed Ismael Hussein,** Professor of technology and Chemistryof Polymer, Polymer and Pigment Department, National Research Center, for suggesting the point of this thesis, planning of the experimental work, offering the technical facilities, raw materials support, carful revision and continuous encouragement through the whole work that made this thesis available in its present form.

Sincere thanks and appreciation are also due to **Dr. Iman Mohamed Ahmed Taha**, Dr. of Material Chemistry, faculty of engineering, Ain shams university, for her valuable guidance, stimulating discussion, generous help and sincere support through the mechanical testing.

Special thanks go to my friends for their kind help and really assistance. Many thanks are also forward to Mr/Amin Shosha, General Manager of Daico for Chemical Industries for his support, encouragement and the facilities provided.

Mostafa Mohamed Mahmoud Elsheikh

# Aim of work

Ethyl acrylate emulsion polymer is widely used as a textile pigment printing binder because of its good adhesion, soft film formation and good fastness properties. This thesis aimed to study the improving of the mechanical and physical properties of ethyl acrylate polymer by copolymerization of ethyl acrylate with either butyl acrylate or 2-ethyl hexyl acrylate, and applying each co-polymer as a textile pigment printing binder.

The emulsion co-polymers were prepared at different concentration ratios (ethyl acrylate/2-ethyl hexyl acrylate or butyl acrylate) (100/0, 5, 10, 15, and 20) respectively in the presence of (acrylic acid or methacrylic acid).

The prepared co-polymers will be characterized using (solid content, molecular weight, coagulum, viscosity, drying time, MFFT, TEM and SEM). The mechanical properties of the prepared co-polymer samples would be also examined.

The prepared co-polymers applied as binder in textile pigment printing pastes and were examined using heat and mechanical fastness testing, such as rubbing fastness, sublimation and durability.

The effect of changing surfactant (sodium lauryl sulfate) and initiator (free radical) systems were also studied on the best formulas in the presence of acrylic acid or methacrylic acid.

# **Table of Contents**

	Acknowledgement	
	Abbreviations	I
	List of tables	II
	List of figures	IV
	Aim of work	
	Chapter I Introduction	
1.	Emulsion polymerization	1
2-	Emulsion polymerization technique	2
2.1.	Emulsion polymerization processes	3
3-	Emulsion polymerization advantages	4
3.1.	Effect of compartmentalization	5
4-	Disadvantages of emulsion polymerization	6
5-	Emulsion polymerization ingredients	6
5.1.	Monomers	6
5.1.1.	Ethyl Acrylate	6
5.1.2.	Butyl Acrylate (BuA)	7
5.1.3.	2-Ethyl Hexyl Acrylate (2-EHA)	9
5.1.4.	Functional monomers	9
5.1.5.	Crosslinker monomers	10
5.2.	Initiators	12
5.2.1.	Free radical initiator	12
5.2.2.	Redox initiator	12
5.3.	Surfactants	14
5.3.1.	Surfactant types	14
5.3.2.	Colloidal stability	17
5.4.	Other ingredients	19
6-	Pigment printing application	19

6.1.	Pigment printing paste	19
6.2.	Preparation of printing pastes	21
6.3.	Printing technique	22
6.3.1.	Hand screen printing	22
	Chapter II Materials & Experimental Techniques	
2.1.	Monomer	24
2.2.	Initiator	27
2.3.	Surfactant	28
2.4.	Other ingredients	28
2.5.	pigment paste ingredients	29
2.6.	Emulsion polymerization	31
2.7.	Testing and analysis	34
2.7.1.	Transmission electron microscopy (TEM)	34
2.7.2.	Scanning electron microscope examination (SEM)	35
2.7.3.	Mechanical properties	35
2.7.4.	Viscosity measurement	35
2.7.5.	Measuring solid content of prepared polymer	35
2.7.6.	Drying time	36
2.7.6.	Fastness properties	36
	Chapter III Results & Discussion	
3.1.	Characterizations of group (I)	40
3.1.1.	Effect of butyl acrylate on viscosity of the prepared polymer	41
3.1.2.	Solid content & coagulum	42
3.1.3.	Drying time	42
3.1.4.	Influence of group (I) on textile pigment printing binder	42
	Performance	
3.1.4.1.	Textile pigment printing paste viscosity	42
3.1.4.2.	Fastness properties	42

3.2.	Characterizations of group (II)	43
3.2.1.	Effect of 2-ethyl hexyl acrylate on viscosity of the polymer	44
3.2.2.	Solid content & coagulum	45
3.2.3.	Drying time	45
3.2.4.	Influence of group (II) on textile pigment printing binder	45
	Performance	
3.2.4.1.	Textile pigment printing paste viscosity	45
3.2.4.2.	Fastness properties	45
3.3.	Characterizations of group (III)	46
3.3.1.	Effect of butyl acrylate on viscosity of the polymer	47
3.3.2.	Solid content & coagulum	48
3.3.3.	Drying time	48
3.3.4.	Influence of group (III) on textile pigment printing binder	48
	Performance	
3.3.4.1.	Textile pigment printing paste viscosity	48
3.3.4.2.	Fastness properties	48
3.4.	Characterizations of group (IV)	49
3.4.1.	Effect of 2-ethyl hexyl acrylate on viscosity of polymer	50
3.4.2.	Solid content & coagulum	51
3.4.3.	Drying time	51
3.4.4.	Influence of group (IV) on textile pigment printing binder	51
	Performance	
3.4.4.1.	Textile pigment printing paste viscosity	51
3.4.4.2.	Fastness properties	51
3.5.	Characterizations of group (V)	52
3.5.1.	Polymer characterizations by changing surfactant and	53
	initiation systems	
3.5.1.1.	Molecular weight	53

3.5.1.2.	Viscosity of the polymers	54
3.5.1.3.	Solid content & coagulum	55
3.5.1.4.	Drying time	55
3.5.1.5.	MFFT	55
3.5.2.	Effect of the changing of surfactant and initiation systems on	55
	textile pigment printing binder performance	
3.5.2.1.	Textile pigment printing paste viscosity	55
3.5.2.2.	Fastness properties	56
3.6.	Effect of changing monomers concentrations on mechanical	56
	properties	
3.6.1.	Strain	56
3.6.2.	Tensile strength	59
3.7.	Morphology of the polymer	61
3.7.1.	Transmission electron microscopy (TEM)	61
3.7.2.	Scanning electron microscope (SEM)	62
	Discussion	64
	Summary	70
	Reference	73
	Arabic summary	

# **Discussion**

This work aimed to improve the physical and mechanical properties of ethyl acrylate polymer, which used as textile pigment printing binder by co-polymerization of ethyl acrylate with either butyl acrylate or 2-ethyl hexyl acrylate. The prepared co-polymers were applied as textile pigment printing binder.

This work was divided into five groups; each group was investigated to study the effect of changing monomers concentrations on the polymer performance.

# Group (I)

Group (I) results showed that there was no significant change in solid content and coagulum of the prepared butyl acrylate/ethyl acrylate co-polymers in presence of acrylic acid in all concentrations.

It was found that the prepared co-polymers improved the mechanical and physical properties of the ethyl acrylate polymer by:

- \* Increasing the viscosity of the polymer.
- \* Increasing the drying time.
- \* Improving in mechanical properties such as tensile strength, elongation and young's modulus.

Furthermore group (I) results showed that the ethyl acrylate/ butyl acrylate co-polymers in presence of acrylic acid improved the mechanical and physical properties of textile pigment printing binder by:

- \* Minimizing stiffening in the handle of the textile.
- \* Increasing the viscosity of the pigment printing paste so the consumption of thickeners would be decreased.

The heat and mechanical fastness properties investigations as shown in Table (3.2) showed no significant difference between the homo ethyl acrylate polymer and the ethyl acrylate/butyl acrylate co-polymers, as well as the color yield of co-polymers are visually higher especially at 20% concentration.

So that we can conclude that the fastness properties of co-polymer are better than ethyl acrylate homo polymer.

### Group (II)

It was clear that there wasn't any significant difference in solid content and coagulum of the prepared 2-ethyl hexyl acrylate/ethyl acrylate co-polymers in presence of acrylic acid; however they showed progressing in the mechanical and physical properties of the ethyl acrylate polymer by:

- \* Increasing the viscosity of the polymer.
- \* Increasing the drying time.
- \* Improving in mechanical properties such as tensile strength, strain.

2-ethyl hexyl acrylate/ethyl acrylate co-polymers in presence of acrylic acid improved the mechanical and physical properties of textile pigment printing binder by:

- \* Decreasing stiffening in the handle of the textile.
- \* Increasing the viscosities of the pigment printing pastes so the consumption of thickeners would be decreased.

The heat and mechanical fastness properties testing did not show any significant different between the homo ethyl acrylate polymer and the EHA/EA/AA co-polymer, in other hand visually the color yields of samples prepared by co-polymers were higher especially at 10% concentration.

So that we can conclude that the fastness properties of co-polymer is better than EA homo polymer.

# Group (III)

Table (3.6) showed that there was no significant difference in solid content and coagulum of the prepared Butyl acrylate/ethyl acrylate copolymers in presence of methacrylic acid, they also promote the mechanical and physical properties of the ethyl acrylate polymer by:

- \* Increasing the viscosity of the polymer.
- \* Increasing the drying time.
- \* Improving in mechanical properties such as tensile strength, elongation.

It was obvious that the butyl acrylate/ethyl acrylate co-polymers in presence of methacrylic acid improved the mechanical and physical properties of textile pigment printing binder by:

- \* Minimizing stiffening in the handle of the textile.
- \* Increasing the viscosity of the pigment printing paste so the consumption of thickeners would be decreased.

The heat and mechanical fastness properties investigations in Table (3.6) did not show any significant difference between the homo ethyl acrylate polymer and the co-polymers, visually it was observed that the color yield of group (III) co-polymers is higher than the homo polymer especially at 20% BA concentration.

So that we can conclude that the fastness properties of co-polymers are better than ethyl acrylate homo polymer.

## Group (IV)

Group (IV) showed that there was no change in solid content and coagulum of the 2-ethyl hexyl acrylate/ethyl acrylate co-polymers in presence of methacrylic acid, as well as they improved the mechanical and physical properties of the ethyl acrylate polymer by:

- \* Increasing the viscosity of the polymer.
- \* Increasing the drying time.
- \* Improving in mechanical properties such as tensile strength, elongation.

Table (3.8) showed that the butyl acrylate/ethyl acrylate copolymers in presence of methacrylic acid improve the mechanical and physical properties of textile pigment printing binder by:

- \* Minimizing stiffening in the handle of the textile.
- \* Increasing the viscosity of the pigment printing paste so the consumption of thickeners would be decreased..

Table (3.8) showed that the heat and mechanical fastness tests did not show any difference between the homo ethyl acrylate polymer and the EHA/EA/AA co-polymer, in addition the color yield of EHA/EA/AA co-polymer is higher than the homo polymer especially at **10% EHA** concentration,.

So that we can conclude that the fastness properties of the copolymers are better than EA homo polymer.

## Group (V)

The best formula concentrations of the textile pigment printing binder (20% butyl acrylate/ethyl acrylate co-polymer & 10% 2-ethyl hexyl acrylate/ethyl acrylate copolymer) were studied by changing the surfactant and initiation systems using SLS/cetyl alcohol as surfactant and ammonium persulphate as free radical initiator.

# (a) Characterizations of prepared polymers with changing surfactant and initiation systems

- \* As shown from Table (3.10), the physical properties such as viscosity& drying time of polymers prepared by free radical system are higher than the polymers prepared by redox system in presence of acrylic acid, beside both solid content and coagulum of all the prepared samples didn't show any significant difference.
- \* The mechanical properties of polymers prepared by free radical system are higher than the polymers prepared by redox system.
- \* The molecular weights of the polymers prepared by free radical system were higher than polymers prepared by redox system, as well as the polymer molecules prepared by free radical system had poly dispersibility of the molecular weight (Mn) lesser than polymer molecules prepared by redox system.
- \* TEM graphs of butyl acrylate/ethyl acrylate nano-particles as shown in Fig (3.1-a, b) and 2-ethyl hexyl acrylate nano-particles as shown in Fig (3.2-a, b) confirm that the average particle size of the nano-particle were 30:75 nm and 10:20 nm respectively. The dispersion of both co-polymers nano-particles were well spherical-like in shape.
- \* MFFT test showed that the addition of the hydrophobic monomer increase the MFFT.

# (b) Characterizations of the prepared textile pigment printing binder with changing surfactant and initiation systems

\* The viscosities of the textile pigment printing pastes prepared by free radical system were slightly higher than the pigment printing pastes prepared by the polymers with redox system, this means that the increasing in M.wt. of the polymer increases the viscosity of the polymer itself and so increases the viscosity of the textile pigment

printing paste.

- \* Neither the sublimation test nor rubbing fastness properties showed any significant difference between the textile pigment printing binders prepared by the polymers of different systems.
- \* There is no significant difference in the color yield even at 20% butyl acrylate/ethyl acrylate co-polymer & 10% 2-ethyl hexyl acrylate/ethyl acrylate copolymer.

#### **Conclusion**

So from the above data, it is clear that co-polymerization of ethyl acrylate with either butyl acrylate or 2-ethyl hexyl acrylate improved the physical and mechanical properties of the polymer.

In other hand when applying the co-polymer of 20% butyl acrylate/ethyl acrylate and 10% 2-ethyl hexyl acrylate/ethyl acrylate as textile pigment printing binder, They showed obvious improving in color yield, minimal stiffening in handle of the textile, heat and mechanical fastness.

# INTRODUCTION