PRODUCTION OF NANO EMULSION TERPOLYMERS BINDERS FOR TEXTILE APPLICATION

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ABSTRACT

Micro emulsion polymer with a high content of ethyl acrylate soft monomer was the most used binder for textile pigment printing application. This work aimed to improve the physical and mechanical properties of pigment printing application using series of terpolymer prepared by polymerization of ethyl acrylate with methyl methacrylate and 2-ethyl hexyl acrylate at different concentration ratios of methyl methacrylate (2.5%, 5%, 7.5%, and 10%) respectively of the total monomer concentrations. The prepared terpolymers were characterized using solid content, molecular weight, coagulum, viscosity, drying time, UV, MFFT and TEM. The mechanical properties of the prepared polymers would be also examined. It was found that methyl methacrylate/ 2-ethyl hexyl acrylate/ethyl acrylate terpolymer of ratio (10:10:80) respectively showed the best heat fastness, mechanical fastness, soft handling and high color yield of pigment printed textile.

Keywords: *Pigment printing, ethyl acrylate, methyl methacrylate, 2-ethyl hexyl acrylate, characterizations, fastness properties*

INTRODUCTION

Textile printing industry is dominated by pigment printing. The on-going technology developments in the key component of the pigment printing system is one of the major reasons for such a high market share (-50 % of the textile printing market), the polymer textile “binder”. The latest developed textile binders are complex polymer mixtures impart the color fastness, durability and importantly, a soft “handle” to the textile that the final end user customer demands. (1)

Various monomers such as butadiene, acrylate, vinyl acetate and styrene etc are generally used as binders for pigment dyeing. The most common used binders are acrylate copolymers that polymerized by an emulsion polymerization technique in presence of an aqueous dispersion medium (2).

Ethyl acrylate (EA), hydroxyl ethyl acrylate (HEA), and methacrylic acid (MAA) monomers are of great importance in several commercial applications. Their polymerization products find applications in the fields of coatings (3)(4) and biomaterials(5).

Ethyl acrylate emulsion homopolymer is the most used binder for textile pigment printing application. This thesis aimed to improve the mechanical and physical properties of the binder for textile pigment printing application by copolymerization of ethyl acrylate with high mechanical resistance methyl methacrylate monomer and to balance the high Tg of it we terpolymerized with high mechanical resistance soft monomer 2-ethyl hexyl acrylate and study their effect on the polymer performance and on the pigment printing application.

MATERIAL AND METHODS

Raw materials

Ethyl acrylate monomers (EA),nonyl phenol ethoxylated (NP9), Aerosol OT 501, $NaHCO_3$were supplied as fine chemicals from Sigma Aldrich.Ammonium persulphate and N-methylol acrylamide monomer (NMA) imported from Mubychem, Acrylic acid monomer (AA) from Arkema Canada, Tert.butyl hydrogen peroxide imported as fine chemical from Dalton S.P.A., Italy.Synthetic thickener (Argoprint 160 A) was imported from Argonkimya, Turkey.Blue 2G manufactured by Daico for Chemical industries, Egypt. Bercolin Scarlet CB manufactured byBersaTekstil, Turkey.

Pre-emulsion

Distilled water, ionic surfactant, monomers were added into the flask equipped with high speed homogenizer (ultra turax homogenizer) for 30 min (in three time portions). The acid monomer (acrylic acid) is added during continuous homogenizing.

Emulsion polymerization procedure

Emulsion polymerization of ethyl acrylate crosslinked by allylglycidyl ether were carried out in a 500 mL three-necked round bottom flask immersed in water bath, equipped with a stirrer, a gas inlet system and a reflux condenser. The oxygen was removed by purging the flask by nitrogen. The 30% of used distilled water was introduced into the glass reactor with non-ionic surfactant. The mixture was stirred at 80°C followed by addingsodium acetateto adjust the pH of the reaction medium. The prepared pre-emulsion and the initiator were gradually dropped.At the end of the pre-emulsion addition, the temperature was raised to 85°C for 1h to complete the polymerization reaction. The prepared emulsion cooled till 40°C and the pH adjusting using aqueous solution of ammonia till pH=8.

Table 1. *Recipes for different ratios of methyl methacrylate/ ethyl acrylate emulsion co-polymer (Group (I)).*

Component	**blank**	**EM1**	**EM2**	**EM3**	**EM4**
Ethyl acrylate	50	48.75	47.5	46.25	45
Methyl methacrylate	0	1.25	2.5	3.75	5
N-methylol acrylamide (NMA)	0.6	0.6	0.6	0.6	0.6
acrylic acid	0.67	0.67	0.67	0.67	0.67

Table 2. *Recipes for different ratios of methyl methacrylate /2-ethyl hexyl acrylate/ ethyl acrylate emulsion terpolymers (Group (II)).*

Component	**Blank**	**EHM1**	**EHM2**	**EHM3**	**EHM4**
Ethyl acrylate	50	43.75	42.5	41.25	40
2-ethyl hexyl acrylate	0	5	5	5	5
Methyl methacrylate	0	1.25	2.5	3.75	5
N-methylol acrylamide (NMA)	0.6	0.6	0.6	0.6	0.6
acrylic acid	0.67	0.67	0.67	0.67	0.67

Characterization

The prepared polymers were characterized using solid content(6), molecular weight, coagulum, viscosity, drying time, UV, MFFT and TEM.The mechanical properties of the prepared polymers would be also examined.

RESULTS & DISCUSSION

Characterizations of group (I)

Group (I) represents studying theeffect of changing methyl methacrylate concentrations on physical and chemical properties of the methyl methacrylate/ ethyl acrylate copolymers. The results obtained and recorded in Table (3).

Table 3. *Results obtained from group (I)*

Test	**Group (I)**				
	Blank	**EM1**	**EM2**	**EM3**	**EM4**
Viscosity(spindle2) (cps) at 24°C	35	75	115	170	195
Coagulum (%)	1.2	.5	.56	.85	.5
Solid content (%)	49.76	50.51	49.85	51.20	50.16
Drying time (sec)	42	110	100	103	92

Effect of changing methyl methacrylate concentrations on viscosity of the prepared copolymers

Effect of changing methyl methacrylate concentrations on viscosity of the prepared methyl methacrylate/ ethyl acrylate copolymers was plotted in Fig (1).

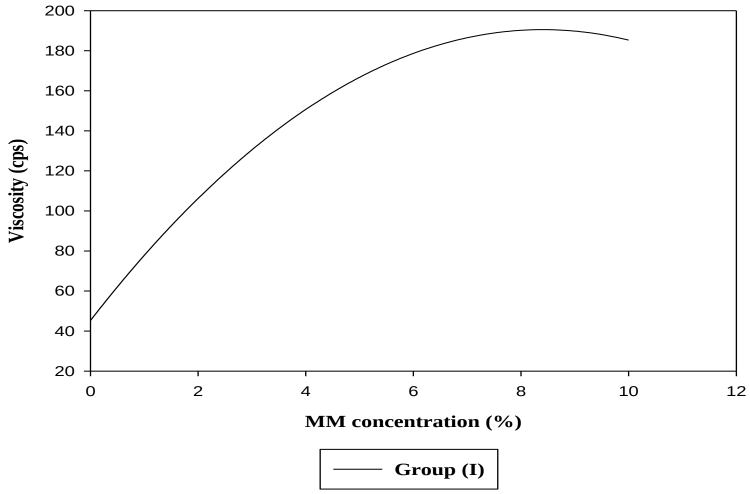

Figure 1. *Effect of changing methyl methacrylate concentrations (group(I)) on viscosity of methyl methacrylate/ ethyl acrylate copolymer*

The above figure shows that, the viscosities of the methyl methacrylate/ ethyl acrylateco-polymers were increased with increasing the concentrations of methyl methacrylate. That may be from the high hydrophobicity of methyl methacrylate.

Solid content & coagulum

Table (3) shows the solid content and coagulum of prepared co-polymers.It is clear that there wasn't any significant change between the prepared ethyl acrylate polymer and methyl methacrylate/ ethyl acrylate co-polymers that mean methyl methacrylate didn't adversely affect on the polymerization process.

Drying time

The effect of changing methyl methacrylate concentration on drying time for the prepared methyl methacrylate/ ethyl acrylate copolymer films was plotted in Fig (2).

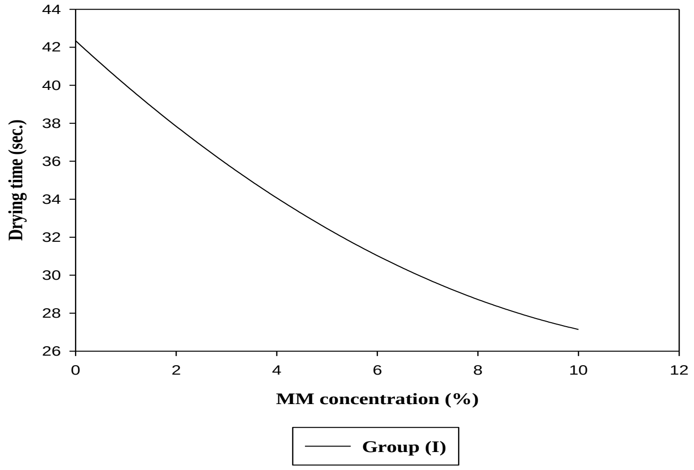

Figure 2. *Effect of methyl methacrylateconcentrations (group(I))on drying time ofmethyl methacrylate/ethyl acrylate copolymer*

It is clear from Fig (2) that, as the concentration of methyl methacrylate was increased, the drying time of the methyl methacrylate/ ethyl acrylateco-polymers decreased. It may be due to high Tg of methyl methacrylate.

Minimum film forming temperature (MFFT)

Rhopoint 60 instrument was used to measure MFFT of the prepared samples and it was found that methyl methacrylate/ ethyl acrylate copolymer (group (I)) (MFFT around -1.2°C) had the same MFFT of ethyl acrylate homopolymer (blank) (MFFT = -1.2°C).

Mechanical properties

Methyl methacrylate/ ethyl acrylate copolymers tensile strength and elongation at break were measured according to ASTM standards with stretching speed of 100 mm min^{-1}.

Tensile strength

Figure (3) shows the effect of changing methyl methacrylate concentrations on tensile strength of methyl methacrylate/ ethyl acrylate copolymer.

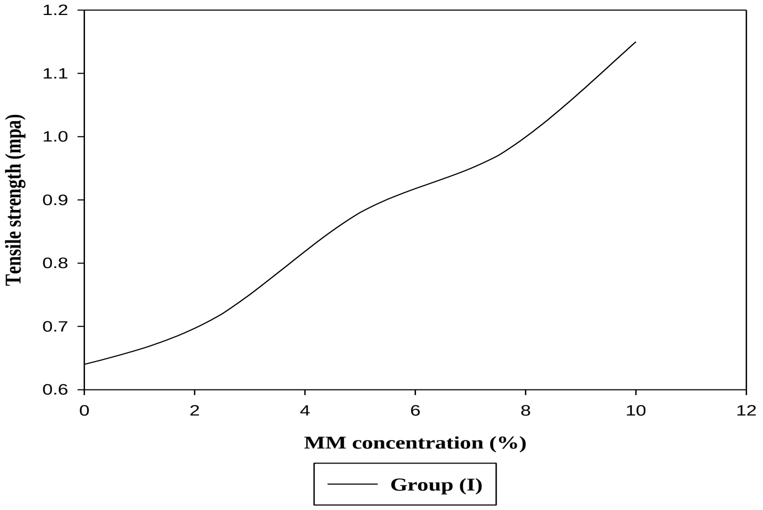

Figure 3. *Effect of changing methyl methacrylate concentrations (group (I)) on tensile strength of methyl methacrylate/ ethyl acrylate copolymer*

It is obvious that tensile strength of methyl methacrylate/ ethyl acrylate copolymers increased by increasing the concentration of methyl methacrylate. This may be because of methyl methacrylate is harder than ethyl acrylate.

Elongation

Figure (4) shows the relation between elongation ofmethyl methacrylate/ ethyl acrylate copolymer and changing methyl methacrylate (MM) concentrations.

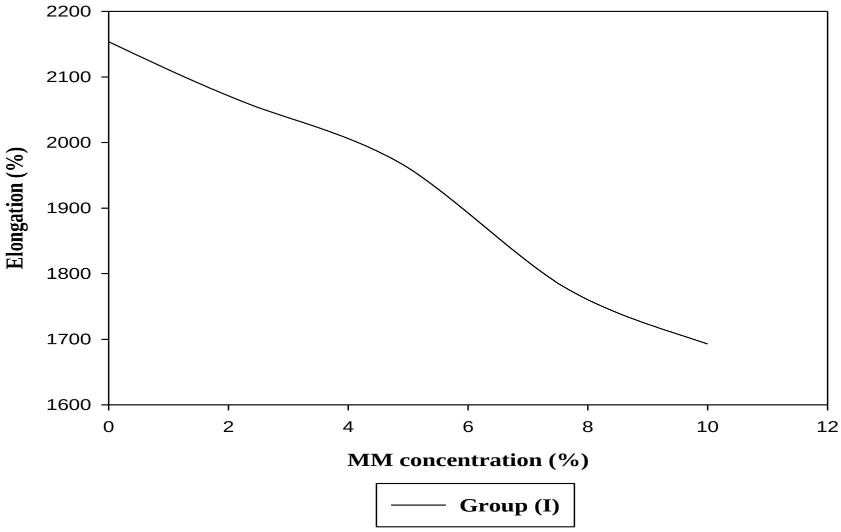

Figure 4. *Effect of changing methyl methacrylate concentrations (group (I)) on elongation of methyl methacrylate/ ethyl acrylate copolymer*

Figure (4) shows that as the concentration of methyl methacrylate increased as the elongation of the prepared methyl methacrylate/ ethyl acrylate copolymers decreased. For the same reasonthis may be because of methyl methacrylate is harder than ethyl acrylate.[6]

Molecular weight analysis (M.wt)

The molecular weight and its distribution of group (I) were measured by GPC and listed in Table (4).

Table 4. *Molecular weight results of group (I)*

Sample	**M_n**	**M_w**	**M_D**	**D**
Blank	$1.07e^{6}$	$1.854e^{6}$	$1.7e^{6}$	1.7
Group (I)	$6.4077e^{4}$	$4.7129e^{5}$	$1.3895e^{5}$	2.3551

Table (4) shows that ethyl acrylate homopolymer (blank) had higher weight average molecular weight M_w and number average molecular weight (M_n) than methyl methacrylate/ ethyl acrylate copolymers (group (I)) and even though molecular weight distribution was narrower (D).

Ultra violet (UV) analysis

The following figures show the effect of methyl methacrylate on absorbance and transmittance spectra of ethyl acrylate polymer.

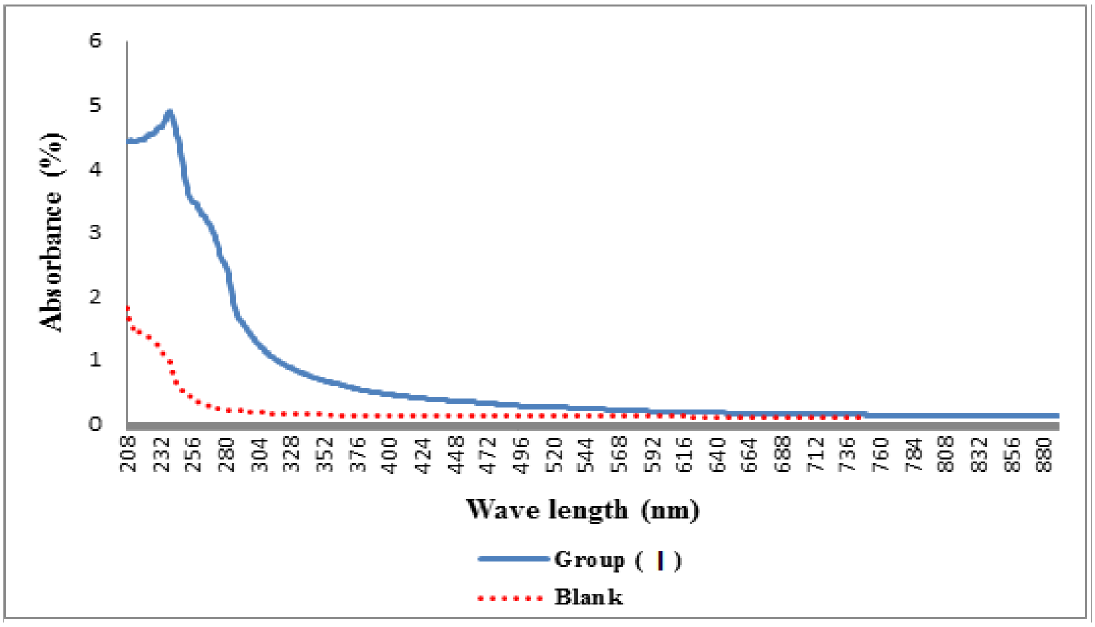

Figure 5. *UV absorbance chart of methyl methacrylate/ ethyl acrylate copolymer (group (I))*

Methyl methacrylate/ ethyl acrylate copolymer (group(I)) showed higher absorbance than ethyl acrylate homopolymer (blank) and that was clear in the previous Fig (5).

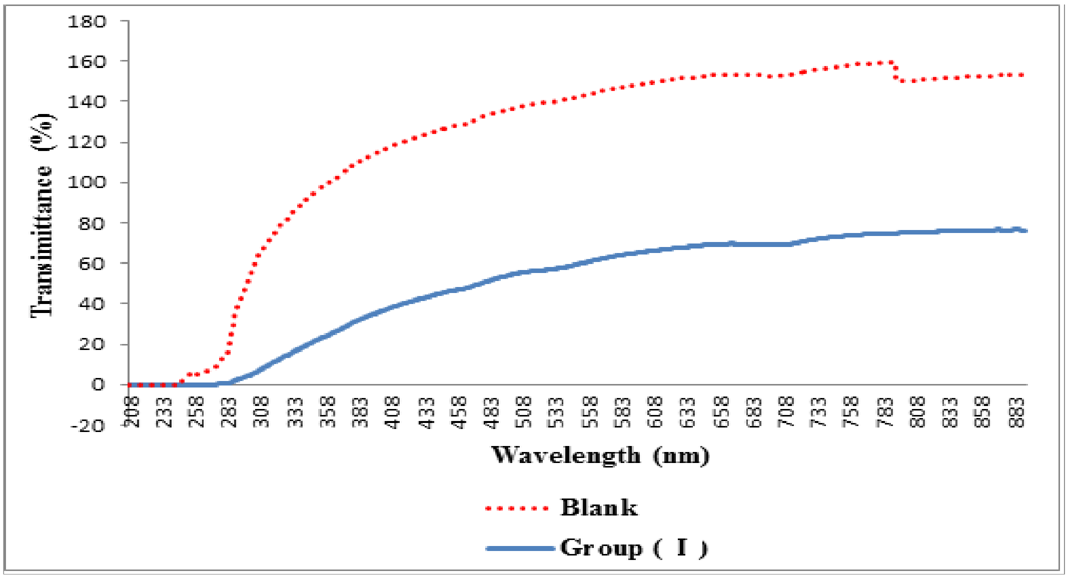

Figure 6. *UV transmittance chart ofmethyl methacrylate/ ethyl acrylate copolymer (group (I))*

In the other site Fig (6) showed that methyl methacrylate/ethyl acrylate copolymer has lower transmittance than ethyl acrylate homopolymer(blank).

Transmission Electron Microscope (TEM)

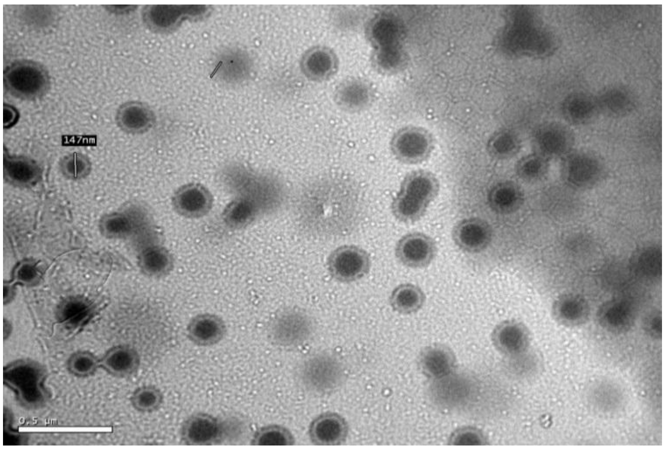

Figure 7. *TEM of methyl methacrylate/ ethyl acrylate copolymer (group (I))*

The above TEM figure shows that the particle size of the prepared methyl methacrylate/ ethyl acrylate copolymers (group (I)) was about 147 nm and all particles were in the same size (homo-dispersed), and the particles had uniform core shell.

Influence of group (I) on textile pigment printing binder performance

Theprinting results obtained from ethyl acrylate copolymerized by different concentrations of methyl methacrylate (group (I)) were recorded in Table (5).

Table 5. *Printing results obtained from group (I)*

Test	**Group (I)**				
	Blank	**EM1**	**EM2**	**EM3**	**EM4**
Viscosity of print paste (spindle 6) cps at 24°C	28100	27800	29100	28000	30210
Dry rubbing	4/5	4/5	4/5	5	5
Wet rubbing	2/3	2/3	3	3	¾
Sublimation test	pass	pass	pass	pass	pass
Durability	pass	pass	pass	pass	pass
Adhesion to plastic	pass	pass	pass	pass	pass
Adhesion to metal	pass	pass	pass	pass	pass

Textile pigment printingpaste viscosity

Table (5) shows that, the viscosity of the printing paste increased, as the concentration of the methyl methacrylatewas increased. Meanwhile no significant difference in viscosity of the pigment printing paste with blank.

Printing color yield

A paste consisted of pigment, thickener, water and different binders to investigate the effect of changing binders in printing color yield.

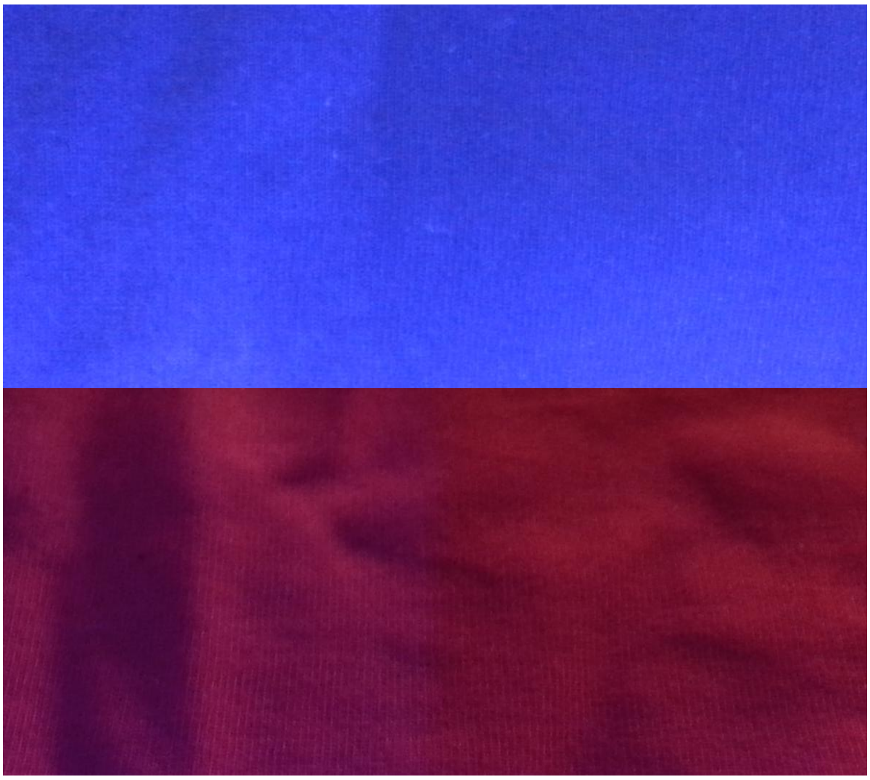

Figure 8. *Textile printed by pigment printing paste using methyl methacrylate / ethyl acrylate copolymer (group (I))*

The textile printed by the pigment printing paste using methyl methacrylate/ ethyl acrylate copolymer (group (I)) has higher color yield and stiff handling than using ethyl acrylate homopolymer (blank) as shown in previous Fig (8). This may be due to the high absorbance and low transmittance of methyl methacrylate/ ethyl acrylate copolymers (group (I)) as shown in pervious UV analysis. Stiff handling may be due to the hardness of methyl methacrylate is higher than ethyl acrylate.

Fastness properties

After printing the prepared samples and curing them at 150°C for 5min, the prepared samples were physically and mechanically tested.

(A) Sublimation test

The sublimation test for both the ethyl acrylate polymer and the methyl methacrylate/ethyl acrylate co-polymers were carried out at 180°C for 1min, Table (5) shows that all prepared samples achieved the same record in the grey scale.

(B) Durability test

All printed samples prepared by ethyl acrylate homopolymer and the methyl methacrylate/ethyl acrylate co-polymers achieved the same record in the grey scale.

(C) Rubbing fastness

Methyl methacrylate/ethyl acrylate co-polymers showed higher resistance to wet/dry rubbing than ethyl acrylate homopolymeras shown in Table (5). It can be explained by the presence of hard methyl methacrylate.

It was found that the methyl methacrylate/ethyl acrylate copolymer maximize stiffening in the handle of the printed textile and decrease the elongation of the copolymer.

So in group (II) we balance the elongation and Tg of the copolymer in addition to the harsh feeling (stiffening in the handle) of the copolymer by addition of 2-ethyl hexyl acrylate to methyl methacrylate/ ethyl acrylate copolymer.(7)

Characterizations of group (II)

Group (II) represents studying the effect of changing methyl methacrylate concentrations on physical and chemical properties of the methyl methacrylate/ 2-ethyl hexyl acrylate/ ethyl acrylate terpolymers.Table (6) represents the results obtained from group (II).

Table 6. *Results obtained from group(II)*

Test	**Group (II)**				
	blank	**EHM1**	**EHM2**	**EHM3**	**EHM4**
Viscosity(spindle2) (cps) at 24°C	35	165	200	231	245
Coagulum (%)	1.2	1.5	.5	.4	1.2
Solid content (%)	49.76	49.25	49.7	50.33	50.63
Drying time (sec)	42	116	85	70	65

Effect of methyl methacylate on viscosityofthe preparedterpolymer

Figure (9) shows the relation between viscosity of the prepared terpolymers and changing methyl methacrylate concentrations.

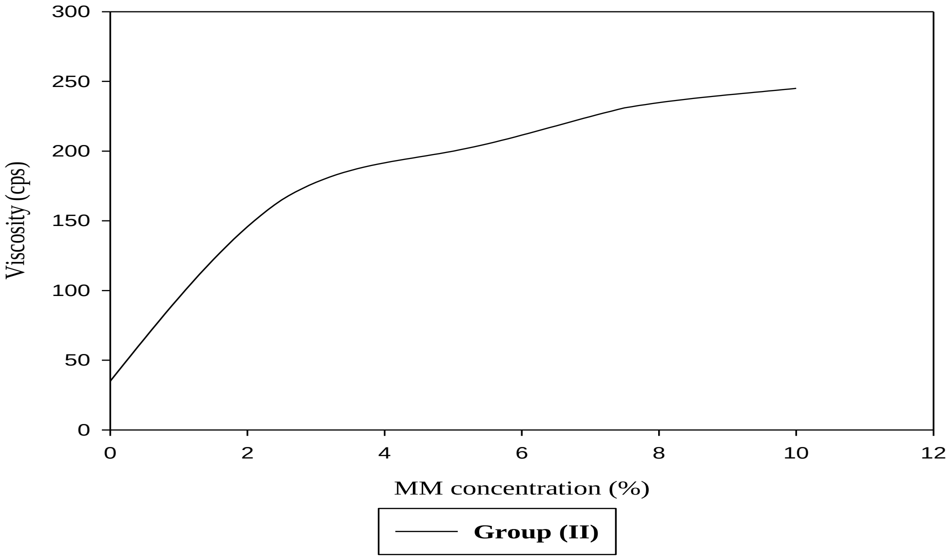

Figure 9. *Effect of methyl methacrylate concentration on viscosity of methyl methacylate/2-ethyl hexyl acrylate/ethylacrylateterpolymers (group (II)).*

Figure (9) shows that, the viscosity of the prepared terpolymers increased as the concentration of methyl methacrylate was increased.

Solid content & coagulum

The solid content andcoagulum of the prepared terpolymerswere determined gravimetrically and recorded in Table (6), it is clear that there wasn't any significant difference between the ethyl acrylate polymer and methyl methacylate/ 2-ethyl hexyl acrylate/ethyl acrylate terpolymers that means adding methyl methacylate or 2-ethyl hexyl acrylate didn’t adversely affect on the polymerization process.

Drying time

Table (6) shows the recorded drying times for methyl methacrylate/ 2-ethyl hexyl acrylate/ ethyl acrylate terpolymers. Fig (10) shows the relation between drying time of the prepared terpolymer samples and Methyl metacrylate concentration.

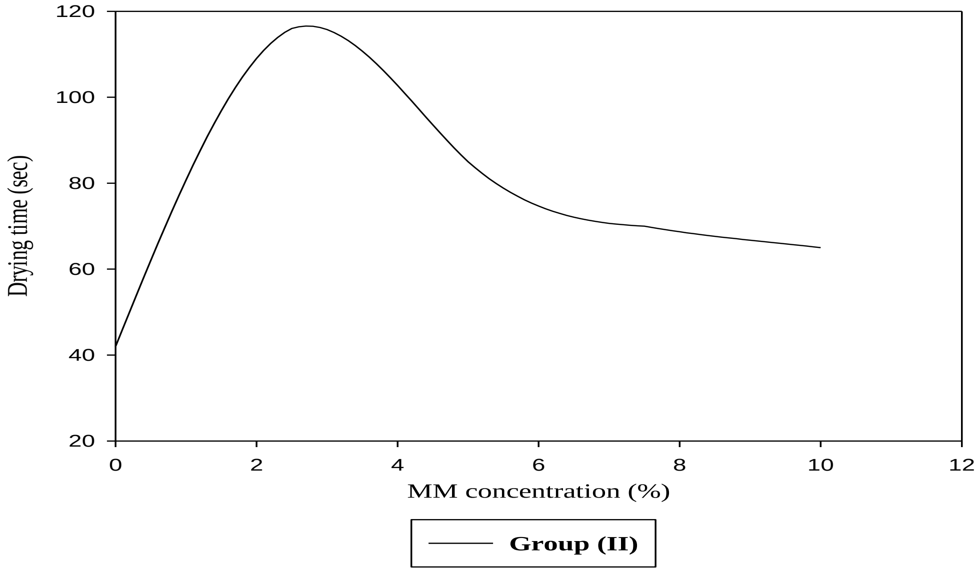

Figure 10. *Effect of methyl methacrylateconcentrations on drying time of methyl methacylate/2-ethyl hexyl acrylate/ethylacrylateterpolymers (group(II))*

It is obvious that as the concentration of methyl methacrylate was increased, the drying time of the terpolymers decreased. It may be due to high Tg of methyl methacrylate but the sudden raise of drying time may be due to presence of low Tg 2-ethyl hexyl acrylate. (8)

Minimum film forming temperature (MFFT)

MFFT had been measured and detected by rhopoint 60 instrument and it was found thatthere wasn’t any significant difference between methyl methacrylate/ 2-ethyl hexyl acrylate/ ethyl acrylate terpolymers(group (II)) (MFFT around -1.1°C) and MFFT of ethyl acrylate homopolymer (blank) (MFFT = -1.2°C).

Mechanical properties

Tensile strength and elongation at break of the prepared emulsion terpolymers of group (II) were measured according to ASTM standards with stretching speed of 100 mm min−1.

Tensile strength

Figure (11) shows the effect of changing methyl methacrylate concentrations on tensile strength of methyl methacrylate/ 2-ethyl hexyl acrylate/ ethyl acrylate terpolymer.

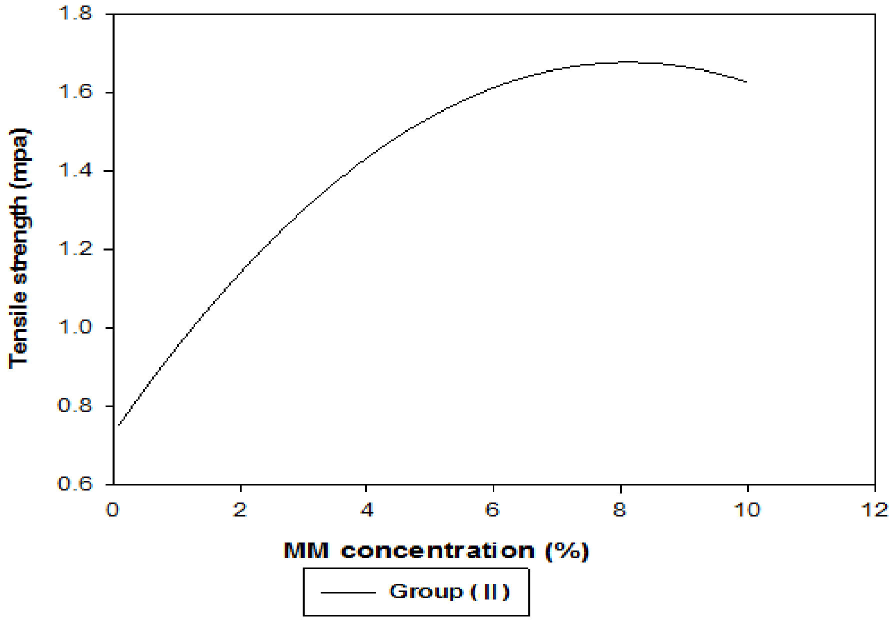

Figure 11. *Effect of methyl methacrylate (MM)concentrations on the tensile strength of methyl methacrylate/ 2- ethyl hexyl acrylate/ ethyl acrylate terpolymer (group(II))*

It is obvious that tensile strength of methyl methacrylate/ 2- ethyl hexyl acrylate/ ethyl acrylate terpolymer increased by increasing the concentration of methyl methacrylate. This may be because of methyl methacrylate is harder than ethyl acrylate.

Elongation

Figure (12) shows the relation between elongation ofmethyl methacrylate/ 2-ethyl hexyl acrylate/ethyl acrylate terpolymer and changing methyl methacrylate (MM) concentrations.

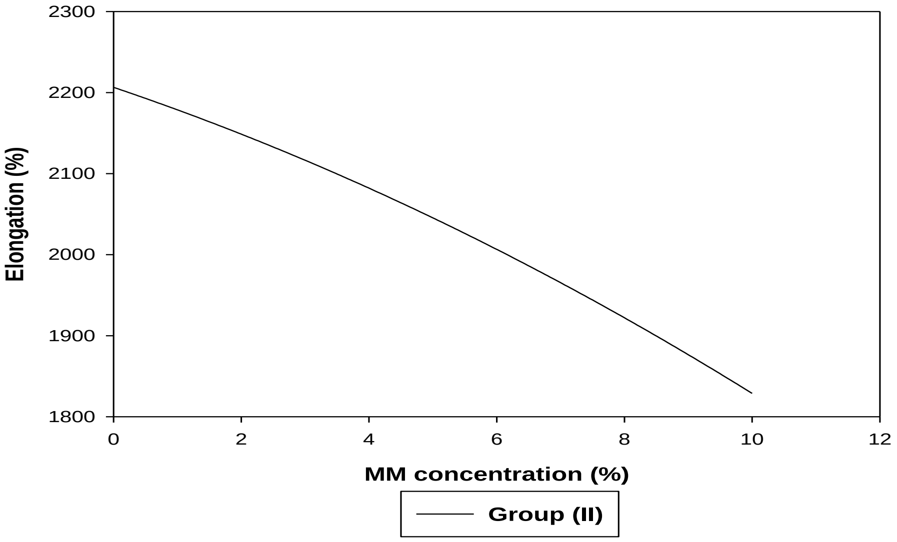

Figure 12. *Effect of methyl methacrylate (MM)concentrations on elongation of methyl methacrylate/ 2- ethyl hexyl acrylate/ ethyl acrylate terpolymer(group(II))*

The above figure shows that as the concentration of methyl methacrylate increased the elongation of the prepared terpolymer decreased.For the same reasonthis may be because of methyl methacrylate is harder than ethyl acrylate.(8)

Molecular weight analysis (M.wt)

After dissolvingthe samples in THF the molecular weight and its distribution are listed in Table (7).

Table 7. Molecular weight results of group (II)

Sample	**M_n**	**M_w**	**M_D**	**D**
Blank	$1.07e^6$	$1.854e^6$	$1.7e^6$	1.7
Group (II)	$4.1084e^5$	$1.9991e^5$	$8.0664e^5$	2.865

It is clear that ethyl acrylate homopolymer (blank) had higher weightaverage molecular weightM_w and number average molecular weight(M_n) than methacrylate/ 2-ethyl hexyl acrylate/ ethyl acrylate emulsion terpolymer (group (II)) and even though molecular weight distribution was narrower (D).

Ultra violet (UV) analysis

The following figures show the effect of methacrylate/ 2-ethyl hexyl acrylate/ ethyl acrylate emulsion terpolymer (group (II)) on the absorbance and transmittance spectra of ethyl acrylate homopolymer.

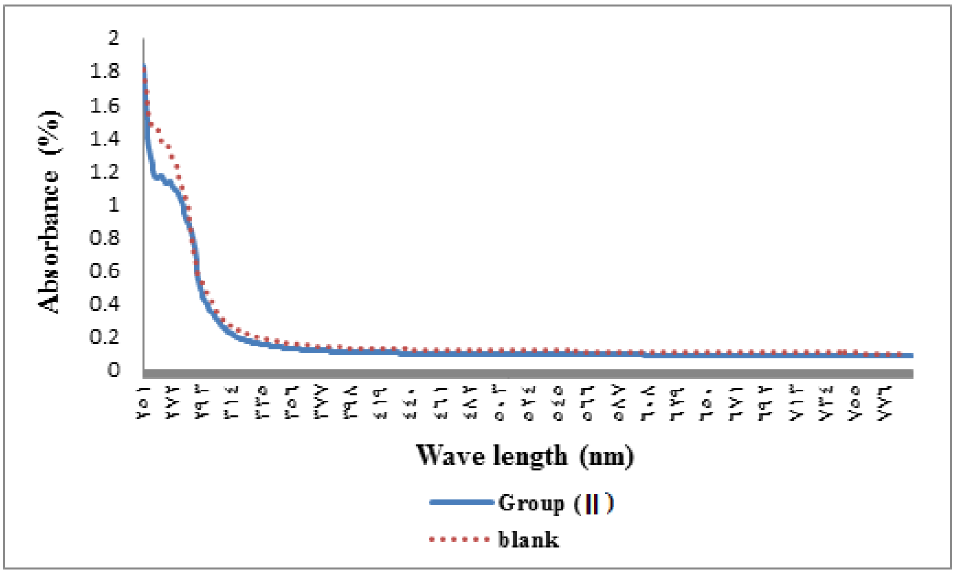

Figure 14. *UV absorbance chart ofmethyl methacrylate/ 2ethyl hexyl acrylate/ ethyl acrylateterpolymer(group (II))*

The UV analysis confirmed that there isn't significant difference between methyl methacrylate/ 2-ethyl hexyl acrylate/ ethyl acrylate terpolymer (group(II)) and ethyl acrylate homopolymer (blank) and that was clear in the previous Fig (14).

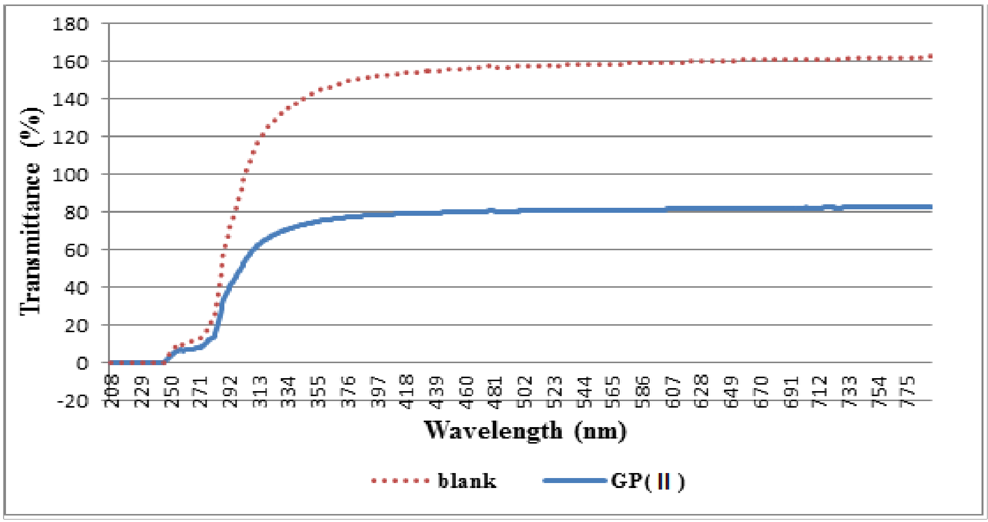

Figure 15. *UV transmittance chart of methyl methacrylate/ 2ethyl hexyl acrylate/ ethyl acrylateterpolymer (group (II))*

In the other site the Fig (15) showed thatmethyl methacrylate/ 2ethyl hexyl acrylate/ ethyl acrylate terpolymer(group(II))has lower transmittance than ethyl acrylate homopolymer (blank).This advantage appeared in printing process by producing high color yield printed textile.

Transmission Electron Microscope (TEM)

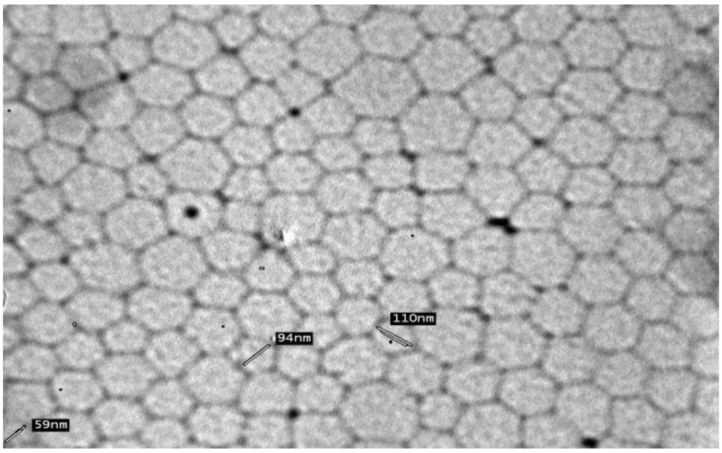

Figure 13. *TEM of methyl methacrylate/ 2ethyl hexyl acrylate/ ethyl acrylateterpolymers*

From the above TEM figure it is clear that the particle size of the prepared methyl methacrylate/ 2-ethyl hexyl acrylate/ ethyl acrylate emulsion terpolymer (group (II)) was about 60 - 110 nm and all particles were in the same size (homo-dispersed), and the particles had uniform core shell.

Influence of group (II) on textile pigment printing binderperformance

The printing results obtained from methyl methacrylate/ 2-ethyl hexyl acrylate/ ethyl acrylate terpolymer (group (II)) was recorded in Table (8).

Table 8. *Printing results obtained from group (II)*

Test	Group (II)				
	blank	EHM1	EHM2	EHM3	EHM4
Viscosity of print paste (spindle 6) cps at 24°C	28100	28600	29100	29200	30000
Dry rubbing	4/5	5	5	5	5
Wet rubbing	2/3	2/3	3	3	3
Sublimation test	pass	pass	pass	pass	pass
Durability	pass	pass	pass	pass	pass
Adhesion to plastic	pass	pass	pass	pass	pass
Adhesion to metal	pass	pass	pass	pass	pass

Textile pigment printingpaste viscosity

Table (8) shows that, the viscosity of the printing paste using methyl methacrylate/ 2-ethyl hexyl acrylate/ ethyl acrylate terpolymerwas increased, as the concentration of the methyl methacrylate was increased.

Printing color yield

Ethyl acrylate polymer was used as pigment printing binder. A paste consisted of pigment, thickener, water and different binders to investigate the effect of changing binders in printing color yield.

Figure 16. *Textile printed by pigment printing paste using methyl methacrylate/ 2ethyl hexyl acrylate/ ethyl acrylateterpolymer (group(II))*

The previous Fig (16) shows that the textile printed by red and blue pigment printing paste using methyl methacrylate/ 2-ethyl hexyl acrylate/ ethyl acrylate terpolymer (group (II)) has higher color yield and soft handing than pigment printing textile using ethyl acrylate polymer crosslinked by NMA (blank). This may be due to the hydrophobicity of soft 2-ethyl hexyl acrylate which balances the hardness ofmethyl methacrylate.

Fastness properties

The prepared samples were used as a binder in textile printing paste, the physical and mechanical tests were carried out on the printed samples.

(A) Sublimation test

There wasn't any significant difference between the printed samples prepared by using different concentrations of methyl methacrylate in the prepared terpolymers and blank after exposing the printed samples to 180°C for 1min.

(B) Durability test

Both of the ethyl acrylate homopolymer and methyl methacrylate/ 2-ethyl hexyl acrylate/ ethyl acrylate terpolymers achieved the same record in the grey scale after washing for 1h with a commercial detergent.

(C) Rubbing fastness

The printed samples of methyl methacrylate/ 2-ethyl hexyl acrylate/ ethyl acrylate terpolymers achieved higher records in the grey scale in the wet/dry rubbing fastness thanethyl acrylate homopolymer. This can be explained by presence of hard methyl methacrylate that increases the mechanical resistance as well as the high hydrophobicity of 2-ethyl hexyl acrylate.

CONCLUSIONS

The heat and mechanical fastness properties showed that methyl methacrylate/ ethyl acrylate copolymer had higher durability, sublimation and rubbing fastness than the ethyl acrylate homopolymer, althoughmethyl methacrylate/ ethyl acrylate copolymer maximize stiffening in the handle of the printed textile.

So to balance the elongation and Tg of copolymer in addition to the harsh feeling (stiffening in the handle) of the copolymer by addition of soft monomer 2-ethyl hexyl acrylate to methyl methacrylate/ ethyl acrylate copolymer.

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