

Novel Techniques for Production of Nano Emulsion Polymers for Textile Applications

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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 butyl acrylate in presence of acrylic acid or methacrylic acid at different concentration ratios (ethyl acrylate/butyl acrylate) (100/0, 5, 10, 15, 20) respectively. 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 20% butyl acrylate/ethyl acrylate in presence of acrylic acid or methacrylic acid.

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1. Introduction

Emulsion polymerization is an important industrial method, because it produces high molecular weight polymers, and because there is no or negligible content of volatile organic compounds (VOC) ⁽¹⁾. 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 ⁽²⁾⁽³⁾ and biomaterials⁽⁴⁾. Also, they are widely used in multi-compo component polymerizations, with the final polymer products utilized as paintings, adhesives and hydrogels.^(5,6) Acrylic resins, which have an important commercial application in paint industry, are prepared through the polymerization of acrylic and methacrylic acids or their corresponding esters. The key attribute of acrylic coatings is their resistance to hydrolysis during extended exterior exposure (weathering), high block resistance, hardness, gloss and high alkali and oxidation resistance ⁽⁷⁾. Pigment textile printing is not only the oldest but also more than 80% of the printed goods are based on pigment printing to its obvious advantages, such as versatility, ease of near final print at the printing stage itself^(8,9). In pigment printing of textile fabrics, pigments with little or no chemical affinity for the fibers are bound physically to the fabric by a polymeric, film-forming adhesive. Both mechanical properties of the binder and adhesion to pigment and fabric contribute to crock fastness, good

mechanical properties being advantageous in resisting deformation of the coating on rubbing ⁽¹⁰⁾.

This work aimed to study the improving of the mechanical and physical properties of ethyl acrylate polymer which is the backbone textile pigment printing binder by co-polymerization of ethyl acrylate with butyl acrylate in presence of acrylic or methacrylic acid and applying each co-polymer as a textile pigment printing binder.

2 - Materials and Methods

2.1. Raw materials:

Ethyl acrylate monomer (EA), Butyl acrylate monomer (BA), nonyl phenyl ethoxylated (NP9), sodium lauryl sulphate (SLS), NaHCO₃, ammonia water and methacrylic acid (MAA), was supplied by Aldrich, Acrylic acid monomer (AA) was supplied by Arkema Canada, and N-methylol acrylamide monomer (NMA). Ammonium persulfate and Sodium thiosulfate were imported as fine chemical from MubyChem. Red BB & Blue 2G manufactured by Daico for Chemical Industries, Egypt. Demineralized water was used.

2.2. 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 (AA and/or MAA) is added during continuous homogenizing.

2.3. Polymerization procedure

Emulsion polymerization were carried out in a 500 ml three-necked round bottom flask equipped with a stirrer, a gas inlet system and a reflux condenser immersed in water bath. 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 under a blanket of nitrogen at 80°C followed by adding sodium acetate to adjust the pH of the reaction medium. The prepared pre-emulsion was charged into the reactor. Then, the initiator system was gradually dropped. The reaction was allowed to proceed for 4 h. The prepared emulsion cooled till 40°C and the pH adjusting using aqueous solution of ammonia till pH=8.

2.4. Pigment printing pastes

The pigment full shade printing pastes were prepared according to the following recipe:

Ingredients	By weight (%)
Binder	15
Pigment dye	4
Synthetic thickener	1.7
Distilled water	up to 100%

2.5. Characterization

(a) Morphology

The morphology of the particles was examined using cryo-TEM (Model: JEM-1230) Japan JEOL Co. Resolution till 0.2nm with Max. Magn.600Kx. the surface of the dried polymers was scanned by SEM (JEOL Model JSM-T20). The samples subjected to sputter coating (Edwards's model S 140A) of gold ions to have a conducting medium.

(b) Mechanical properties

The tensile properties of the dumbbell samples were measured according to ASTM D 412, using LLOYD tensile testing machine (The model: LRX plus), with crosshead speed of 200 mm/min, and the average value of mechanical properties was calculated using load 2.5N.

(c) Viscosity

Viscosity measurement was carried out at a shear rate of 20 rpm and 25°C using Brookfield Viscometer, Model RVF.

(d) Solid content

The solid content of prepared polymer was determined gravimetrically by drying for 2 hrs at 120°C.

(e) Fastness properties

Fastness to washing [durability], and rubbing [AATCC Standard solution of ammonia till pH=8.

Table (1): Recipes for different ratios of ethyl acrylate/butyl acrylate emulsion co-polymer containing acrylic acid.

Component	0BA	5BA	10BA	15BA	20BA
Ethyl acrylate	132	125.4	118.8	112.3	105.6
Butyl acrylate	0	6.6	13.2	19.8	26.4
Acrylic acid	1.35	1.35	1.35	1.35	1.35
Demi. H ₂ O	132	132	132	132	132
Total	300	300	300	300	300

The above recipe contains amm.meta bisulphite (0.3), sod.meta bisulphite (0.24) as redox initiator, Datexal OS/100 (3.3), Aerosol OT (3.96) as surfactant, sodium bicarbonate (0.06) and tert. Butyl hydrogen peroxide (0.09). All ingredients weighted in grams.

Table (2): Recipes for different ratios of ethyl acrylate/butyl acrylate emulsion co-polymer containing methacrylic acid.

Component	0BM	5BM	10BM	15BM	20BM
Ethyl acrylate	132	125.4	118.8	112.3	105.6
Butyl acrylate	0	6.6	13.2	19.8	26.4
Methacrylic acid	1.35	1.35	1.35	1.35	1.35
Demi. H ₂ O	132	132	132	132	132
Total	300	300	300	300	300

The above recipe contains amm.meta bisulphite (0.3), sod.meta bisulphite (0.24) as redox initiator, Datexal OS/100 (3.3), Aerosol OT (3.96) as surfactant, sodium bicarbonate (0.06) and tert.butyl hydrogen peroxide (0.09). All ingredients weighted in grams.

3- Results & Discussion

This work was divided into two groups according to the recipe used and each group was investigated separately to study the effect of changing monomers concentrations on the polymer performance and the type of acid monomer.

3.1. Characterizations of group (I)

Table (3): Results obtained from group (I)

Test	0BA	5BA	10BA	15BA	20BA
Viscosity(spindle2) (cps) at 22°C	110	200	200	120	700
Viscosity of print paste (spindle 6) cps at 27°C	29000	30000	31000	31250	32500
Coagulum (%)	.67	.67	.5	.67	1.13
Solid content (%)	45	47.48	45.6	45.6	44.9
Drying time (sec)	75	95	120	100	115
Dry rubbing	3	3	3	3	3
Wet rubbing	(2/3)	(2/3)	(2/3)	(2/3)	(2/3)
Durability	pass	pass	Pass	Pass	pass
Sublimation test	pass	pass	Pass	Pass	pass
Adhesion to metal	pass	pass	Pass	Pass	pass
Adhesion to plastic	pass	pass	Pass	Pass	pass

3.1.1. Effect of butyl acrylate on viscosity of the prepared polymer

Figure (1) shows the relation between viscosity of the prepared samples and changing hydrophobic butyl acrylate concentrations containing acrylic acid.

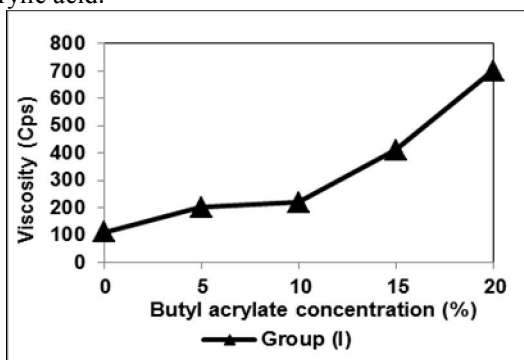


Figure (1): Effect of butyl acrylate on viscosity of ethyl acrylate polymer containing acrylic acid

From the previous figure, it is obvious that the viscosity of co-polymers increased as the concentration of butyl acrylate was increased.

3.1.2. Solid content & coagulum

The solid content and coagulum of prepared co-polymers were determined gravimetrically and recorded in Table (3), it is obvious that there is no significant difference between the prepared ethyl acrylate polymer and the prepared butyl acrylate/ethyl acrylate co-polymers.

3.1.3. Drying time

After spreading the co-polymer to a clean glass plate, drying time of the film was measured and recorded in Table (3). It is clear that, as the butyl acrylate concentration was increased, the drying time increased.

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

3.1.4.1. Textile pigment printing paste viscosity

Table (3) shows that the viscosity of the pigment printing paste was increased as butyl acrylate concentration was increased.

3.1.4.2. 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 is no significant change in the printed samples prepared by using different concentrations of prepared polymers, after exposing the samples to 180°C for 1min.

(B) Durability test

The pigment printed textile samples prepared from different concentrations of prepared polymers showed good resistance to commercial detergents, after washing all samples for 1h at 40°C.

(C) Rubbing fastness

The prepared samples achieved the same record in the grey scale in the wet/dry rubbing fastness.

3.2. Characterizations of group (II)

Table (4): Results obtained from group (II)

Test	Group (II)				
	0BM	5BM	10BM	15BM	20BM
Viscosity(spindle2) (cps) at 25°C	40	70	110	110	200
Viscosity of print paste (spindle 6) cps at 27°C	30000	32000	31250	31500	33000
pH	8	7	8	8	7
Coagulum (%)	2	.33	.43	3.3	1
Solid content (%)	44.17	45.47	45.19	44.66	46
Drying time (sec)	50	75	85	95	100
Dry rubbing	3	3	3	3	3
Wet rubbing	(2/3)	(2/3)	(2/3)	(2/3)	(2/3)
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

3.2.1. Effect of butyl acrylate on viscosity of the polymer

The relation between viscosity of the prepared polymer samples and changing butyl acrylate concentrations with methacrylic acid was plotted in Figure (2). The figure shows that, the viscosity of the co-polymers was increased with increasing the concentration of butyl acrylate in presence of methacrylic acid.

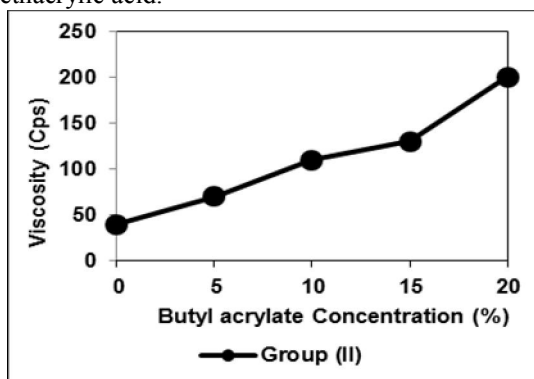


Figure (2): Effect of butyl acrylate on viscosity of ethyl acrylate polymer in presence of methacrylic acid

3.2.2. Solid content & coagulum

The solid content and coagulum of prepared co-polymers were determined gravimetrically and recorded in Table (4). It is clear that there is no significant change between the prepared ethyl acrylate polymer and butyl acrylate/ethyl acrylate co-polymers.

3.2.3. Drying time

After spreading co-polymers to clean glass plates, the drying time for the prepared films were measured and recorded in Table (4). It is clear that as the concentration of butyl acrylate was increased, the drying time of the co-polymers increased.

3.2.4. Influence of group (II) on textile pigment printing binder performance

3.2.4.1. Textile pigment printing paste viscosity

Table (4) shows that, the viscosity of the printing paste increased, as the concentration of the butyl acrylate was increased.

3.2.4.2. 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 butyl acrylate/ethyl acrylate co-polymers were carried out at 180°C for 1min, Table (4) shows that all prepared samples achieved the same record in the grey scale.

(B) Durability test

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

(C) Rubbing Fastness

Both the ethyl acrylate polymer and the butyl acrylate/ethyl acrylate co-polymers prepared samples show good resistance to wet/dry rubbing and achieved the same record in the grey scale.

3.3. Molecular weight

Figure (3), shows the molecular weight of the co-polymer prepared by redox system and the co-polymer prepared by free radical system respectively.

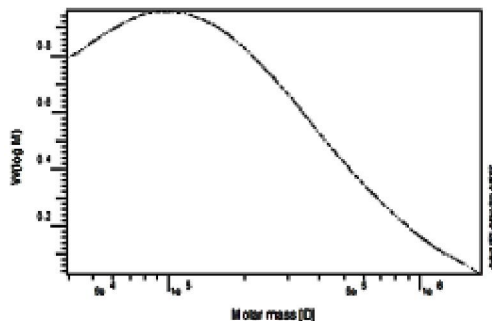


Figure (3): The molecular weight of the co-polymer prepared by redox system

The molecular weight of (20% butyl acrylate/ethyl acrylate) co-polymer prepared by redox system was measured and give (M.wt. = 2.29e5, Mn=1.12e5).

3.4. MFFT

MFFT of the prepared co polymers (ethyl acrylate, 20% butyl acrylate/ethyl acrylate) was recorded in the following table.

Sample	EA	20BA
MFFT (°C)	.3	1.2

3.5. Effect of changing monomers concentrations on mechanical properties

The bulk properties of a polymer are those most often of end-use interest. These are the properties that dictate how the polymer actually behaves on a macroscopic scale

3.5.1. Strain

The co-polymer samples prepared by redox system were tested in four groups and plotted in Fig (4).

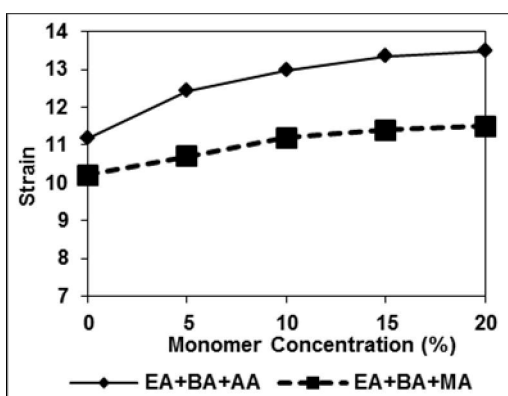


Figure (4): Strain of the prepared samples with changing monomers concentrations

The previous Fig. shows the strain behavior of every co polymers through different monomers

concentrations. From the above Fig. it was found that the strain of copolymers prepared from butyl acrylate/ethyl acrylate was increased, as the concentration of butyl acrylate increased. Furthermore the above Fig. show that the co-polymers prepared from butyl acrylate/ethyl acrylate had higher strain in the presence of acrylic acid than the co-polymers prepared from butyl acrylate/ethyl acrylate in the presence of methacrylic acid.

3.5.2. Tensile strength

The tensile strength of a material quantifies how much stress the material will endure before suffering permanent deformation.⁽¹¹⁾ When tensile strength measured for the prepared co-polymers, the records are observed as follows:

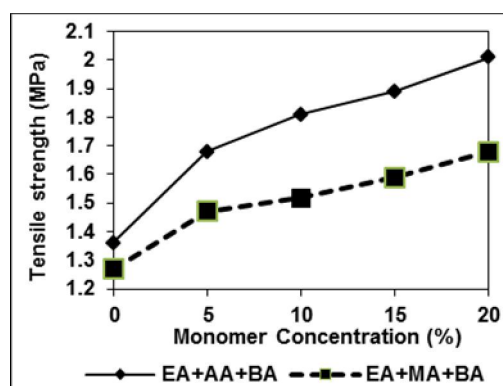


Figure (5): Tensile strength of the prepared samples with changing monomer concentration

Figure (5) shows the tensile strength of the prepared co- polymers through different monomers concentrations.

From the above Fig. it was found that the tensile strength of copolymers prepared from butyl acrylate/ethyl acrylate was increased, as the concentration of butyl acrylate increased.

Furthermore the above Fig. shows that the co-polymers prepared from butyl acrylate/ethyl acrylate in the presence of acrylic acid had higher tensile strength than the co-polymers prepared from butyl acrylate/ethyl acrylate in the presence of methacrylic acid.

3.6 Morphology of the polymer

3.6.1. Transmission electron microscopy (TEM)

Figure (6) refer to the TEM graph of 20% butyl acrylate/ethyl acrylate nano-particles co-polymer. By investigating the TEM graphs, the average particle size of the nano-particles was 38:50 nm; the dispersion of the co-polymer nano- particles was spherical-like in shape, had good homogeneity and dispersability. The black shadows observed in the graph due to the excess of dye that used in sample preparation.

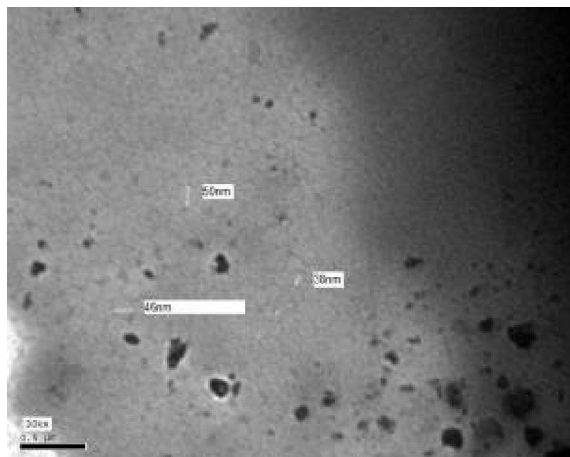


Figure (6): The TEM of the butyl acrylate/ethyl acrylate co-polymer in nano sized particles.

3.6.2. Scanning electron microscope (SEM)

The SEM micrograph of butyl acrylate/ethyl acrylate co-polymer is shown in Fig (7). It is clear that the surface of the co-polymer was very smooth and didn't have any cracks and this may be referred to the good film forming of the co-polymer. This result confirmed by the good mechanical properties obtained from the co-polymer as shown in Figs. (4, 5).

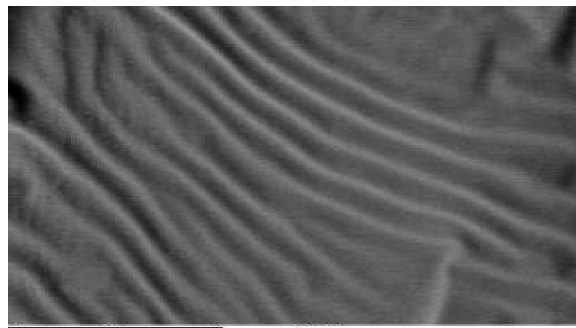


Figure (7): The SEM micrograph of the surface of butyl acrylate/ethyl acrylate co-polymer

Conclusion

So from the above data, it is clear that co-polymerization of ethyl acrylate with butyl acrylate improved the physical and mechanical properties of the polymer, The role of acrylic acid and methacrylic acid on the Characterization of the polymers was detected and recorded⁽¹²⁾.

In other hand when applying the co-polymer of 20% butyl 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.

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