



Synthesis, Characterization, and Application of Novel Polyacrylate Thickeners in Textile Printing

Mohamed A. Abdel-Gawad^{a, c}, Mohamed M. Eissa^{b*}, Walid S. Abdel-Wakil^c,
Ashraf M. Ashmawy^a, Hazem F. Khalil^a



^a Department of Chemistry, Faculty of Science (boys), Al-Azhar University, Cairo 11884, Egypt

^b Polymers and Pigments Department, National Research Centre, 33 El Bohouth Street,
Dokki, Giza 12622, Egypt

^c Research and Development Sector, Egyptian British Co. for Speciality Chemicals & Auxiliaries, Giza, Egypt

Abstract

In this research, novel high-molecular-weight cross-linked polyacrylate polymers have been synthesized by the inverse emulsion free radical polymerization technique. The optimal polymerization conditions were studied in terms of the initial polymerization temperature, total monomer concentration, thermal initiator type and amount, cross-linker type and amount, and co-monomer type and concentration. FTIR spectroscopy, dynamic light scattering (DLS), and transmission electron microscopy (TEM) were used to characterize the prime polymer. Then, the optimally prepared polymer was incorporated into various pigment and dye paste formulations to be tested as a rheology modifier for textile printing pastes. The prepared modified pastes were applied for printing on cotton-polyester (35:65) fabric via the flat screen printing method. More interestingly, the synthesized polymer was compared with a commercially used product, ARGOPRINT 160 (ARGON Company, China). The color strength (K/S) values and color fastness of the printed fabrics to washing and rubbing were also investigated. The results showed that the prepared acrylate polymers revealed better efficiency as a thickening and modifying agent for improving the properties of printed fabrics (e.g., handling and color fastness against washing and rubbing), as compared with the commercially used one.

Keywords: Polyacrylate; Inverse emulsion polymerization; Crosslinker; Rheology modifier; Thickener; Textile printing.

1. Introduction

Synthetic water-soluble polymers have many important applications as dispersing agents, rheology modifiers in surface coatings [1, 2, 3], textile printing [4], enhanced oil recovery [5, 6], flocculating agents in water treatments [7], controlled drug delivery [8], and other important applications. Whether homo-polymers such as polyacrylic and polyacrylate [9], [10, 11] or co-polymers with anionic [12], cationic [13], and hydrophobic monomers [14]. There are many techniques that have been used for the preparation of water-soluble polymers, such as solution [15], dispersion [16], inverse emulsion [17], and bulk-free radical polymerization [18].

According to the required application of the resultant polymers, the appropriate technique is selected. The most recommended technique for the present work is inverse emulsion polymerization, which has many

advantages, such as easy handling, fast dispersion in an aqueous medium, and no problem of by-product separation. Furthermore, polymers with high molecular weight can be synthesized while overcoming problems associated with the increase in viscosity during the polymerization process in solution, dispersion, bulk polymerization techniques, or others [19, 20]. In the inverse emulsion polymerization technique, the aqueous phase containing water-soluble monomers is dispersed in the oil phase and stabilized by a surface active agent. However, this technique has some disadvantages, such as the low percentage of active materials. The maximum concentration of water-soluble polymers prepared by inverse emulsion polymerization is 30% in the case of anionic polymers and not more than 40% for cationic polymers [21]. Increasing the concentration beyond these percentages can lead to clot formation, which affects the final products' yield

*Corresponding author e-mail: mm.eissa@nrc.sci.eg; (Mohamed M. Eissa).

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and their application. Furthermore, due to the strong exothermic behavior, there is a risk of hazardous conditions during the polymerization process. In addition, preparing the polymer with a low monomer concentration increases transportation costs and limits the product's marketing. To overcome these problems, different solutions have been discussed in many papers, such as the preparation of acrylamide-based polymers by the inverse emulsion polymerization technique with an active material percentage $\geq 50\%$ through multiple reaction steps, semi-batch monomer feeding [22] and the two-step (reaction/separation) method as described by Rivera et al. [23]. Therefore, acrylic acid-based polymers can also be produced by the same previous methods.

In the present work, the two-step (reaction/separation) synthesis method was used. In the first step, the polymer is prepared with a low monomer concentration via the inverse emulsion free radical polymerization technique, and then the concentration is increased by the distillation process. This method overcomes the previous problems of transportation costs and also lowers the application dosage. It's worth mentioning here that the stability of the emulsion is affected during both steps, which need very efficient stabilizers. Several papers have described the use of traditional surfactants, such as sorbitan fatty esters at a concentration of 10-30 wt. % based on the total weight of the organic phase, to provide adequate emulsion stability. As described by Hajjghasem et al., colloidal stability can be achieved by lowering the interfacial tension between the aqueous and oil phases [12]. The percentage of special surface active agents affects not only the stability of an inverse emulsion with a high active material concentration but also the high interfacial energy of thermodynamically unstable macroemulsions. Homogenization and particle size distribution are necessary for producing a lump-free and stable emulsion polymer during long-term storage without sedimentation or phase separation. In addition, during the distillation process, other factors should be taken into consideration to maintain the desired product stability without affecting the properties of the product for the desired applications. These factors include the type and percentage of the solvent, the solid concentration, the bulk viscosity, and others. The energy consumption and time spent during the concentration process are reduced by using a high-shear mixer. These are the basic concepts that will be relied upon during this work.

In the current work, a partially neutralized, cross-linked ammonium acrylate polymer with ionic and hydrophobic co-monomers is prepared using the inverse emulsion free radical polymerization technique. The polymerization reaction is carried out

using the two-step reaction/separation methodology. Polymerization conditions are optimized, including initial polymerization temperatures, percentage of monomers, type, and dose of initiators, etc., to get polymer dispersion with high yield, good colloidal stability, and efficient as a thickening and modifying agent for pigment and dye pastes formulations used in the textile industry.

2. Materials and Methods

2.1. Materials

Acrylic Acid (AA, 99.5%), Butyl Acrylate (BA, 99.5%), and Acrylamide (AAm, 98%) were purchased from Arkema, France. Methacrylic acid (MAA, 99%) and 2-ethylhexyl acrylate (2-EHA, 98%) were purchased from BASF, Germany. N, N'-Methylene bis-acrylamide (MBA) was purchased from Sigma Aldrich, Germany. Glycerol trimethacrylate (GTMA) was purchased from Tokyo Chemical Industry Co. (TCI), Japan. Sodium persulfate (SPS), benzoyl peroxide with 25 % H₂O (BPO), azobisisobutyronitrile (AIBN) and sodium bisulfite (SBS) were purchased from LOBA Chemie, India. Ammonium persulfate (APS), potassium persulfate (KPS) and, acetone (99.5%) were purchased from Sigma Aldrich, Germany. Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) was purchased from Ataman Chemicals, Turkey. ISOPAR M (T_b = 207.3 °C) was purchased from EXXON-MOBIL Chemical, Belgium. Span 80 (99.5%, HLB = 4.3) and Tween 80 (99.5%, HLB = 14.9) were purchased from Sigma Aldrich, Germany. Ammonium hydroxide solution 32% (Ammonia) was purchased from EMPLURA, Germany. Distilled water (DW) was used as the aqueous phase in all experiments. EBCA Print 544 binder for textile printing is a product of EBCA Company, Egypt. Printofix Red T-N (PFR) pigment and Dorospers Navy Blue K-LN (DNB) dyestuff were purchased from ARCHROMA, Switzerland. The commercial thickener ARGOPRINT 160, an inverse emulsion commonly used for textile printing with low viscosity and high electrolyte stability, pH (6-8), non-volatile matter $\leq 1\%$ and density 1.13 g/cm³, was purchased from ARGON Company, China. Textile cotton: polyester (35:65) fabric was purchased from MISR spinning and weaving, Mehalla El Kubra, Egypt.

2.2. Methods

2.2.1. Polymerization technique

In the present study, the acrylate polymers were prepared via inverse emulsion free radical polymerization of the aqueous phase-containing acrylic monomers, which dispersed in the oil phase with the aid of a low HLB emulsifier. The startup

formula, as designed by Inchausti et al. [24], was used. The synthesis process passes through the following steps:

2.2.1.1. Preparation of the aqueous and oil phases

For the preparation of the aqueous phase, acrylic acid (AA) monomer was dissolved in a certain amount of distilled water (DW), and then the pH of the solution was adjusted to 4–5 by ammonia under stirring while the temperature was controlled by a water bath at 25 °C. Furthermore, 0.17 and 0.5 wt. % of MBA and EDTA-2Na, respectively (based on the total weight of the monomers) were added as a water-soluble cross-linker and a complexing agent, respectively, to the aqueous solution. On the other hand, the oil phase was prepared by dissolving Span 80 stabilizer (a low-HLB emulsifier) and solvent-base cross-linker(s) in ISOPAR M as the oil phase [22, 25].

2.2.1.2. Preparation of the water-in-oil (w/o) pre-emulsion

The oil phase was transferred to a 500-mL four-necked flat-bottomed glass flask designed in a cooling/heating water bath and equipped with a mechanical stirrer, a nitrogen inlet, a condenser, and a thermometer. The aqueous phase was then added drop-wise to the oil phase under continuous vigorous stirring (at 1500 rpm) for 30 minutes to form a water-in-oil emulsion (w/o) with a constant aqueous-to-oil weight ratio of 70:30, as described by Inchausti et al. [23]. The temperature was raised to 45 °C with a low stirring rate (200 rpm) under an inert nitrogen atmosphere. Then, the whole dual redox initiator (APS: SBS = 300:137 ppm) with an equimolar ratio (1:1), based on the total weight of the monomers, was added to the flask in the form of an aqueous solution, and then the polymerization reaction started spontaneously. The reaction was monitored by the rise in temperature to a maximum peak, due to the exothermic nature of the reaction, followed by cooling down again to the starting reaction temperature (45°C), indicating the completion of the reaction. Then, the reaction product was left at room temperature for one hour under continuous stirring, followed by a pH adjustment of 6-7 with ammonia solution. The formation of the water-in-oil (w/o) emulsion is shown in Fig. 1.

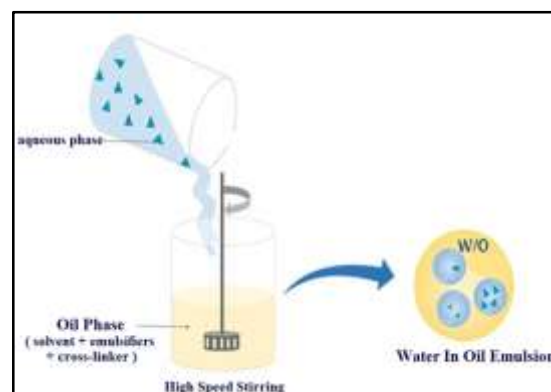


Fig. 1 Formation of the water-in-oil (w/o) emulsion

2.2.1.3. Inversion to oil-in-water (o/w) emulsion

The water-soluble nonionic surfactant Tween 80 was added stepwise to the prepared water-in-oil (w/o) emulsion under gentle continuous stirring (300 rpm), to invert the emulsion from w/o to o/w and to speed up the swelling rate of the prepared polymers in the aqueous medium.

2.2.1.4. Synthesis of different (o/w) polymer emulsions at various parameters

The inverse emulsion polymerization reaction was studied in terms of the initial polymerization temperature, acrylic acid percentage, type of redox initiator used and its percentage, and co-monomer type and its dose. All other parameters (ISOPAR M amount, emulsifier concentration, EDTA-2Na percentage, and aqueous/oil ratio) were held constant to optimize the maximum product efficiency as a rheological modifier in the aqueous solutions and different textile printing paste formulations. Here, it is worth mentioning that the startup formula was designed according to Inchausti, et al. [23].

2.2.1.5. Water separation

One of the disadvantages of the produced polymer emulsion is its low active matter percentages (i.e., low polymer content). To overcome that problem, the prepared polymer emulsion was subjected to vacuum distillation (500 mbar pressures) at 85°C and kept under continuous and vigorous mechanical stirring at 1500 rpm for 3 hours to reduce the energy consumption and increase the stability of the polymer during the distillation process.

2.2.1.6. Preparation of the pigment and dye printing pastes

For the preparation of the pigment paste formulation, 4 g of the synthesized polymer emulsion (after distillation) was dissolved first in 200g of distilled water under high shear mixing (1500 rpm), and then the pH was adjusted to 7-8 by using ammonia solution. Subsequently, 24 g of the EBCA Print 544 binder and 6 g of the PFR pigment were introduced to

the above solution under continuous stirring at 500 rpm. Then, the resultant paste was homogenized at 1500 rpm for 10 minutes. The dye printing paste formulation was prepared by dissolving 8 g of the synthesized polymer emulsion (after distillation) in 200 g of distilled water with high shear stirring at 1500 rpm, followed by pH adjustment to 7-8 by using ammonia solution. Then, 6 g of the DNB dyestuff was added under continuous stirring at 500 rpm, followed by homogenization for 10 min. at 1500 rpm.

2.2.1.7. Printing fabric and fixation techniques

The pigment and dye printing pastes were applied on the cotton/polyester (35/65) fabric by using the flat screen printing technique, and then the printed fabrics were thermo-fixed at 150–160 °C for 4 min.

2.3. Characterization

2.3.1. Solids content and polymer conversion (%)

Non-volatile content (solid content) in weight % of the prepared polymer emulsions before distillation was determined gravimetrically by drying them for 2 hours in a well-aerated oven at 130°C using the standard test method ISO 3251:2019. The practical (PSC) and theoretical (TSC) solid contents are expressed in the following equations:

$$PSC (\%) = (Wd/Wb) \times 100 \quad (1)$$

$$TSC (\%) = (Wt - Wv/Wt) \times 100 \quad (2)$$

Where Wd and Wb are the weights of the prepared polymer emulsions after and before drying, respectively, while, Wt and Wv represent the theoretical total weights of the starting polymerization recipe and its volatiles, respectively. From equations 1 and 2, the overall polymer conversion % for the synthesized polymers is calculated according to the following equation:

$$Polymer\ Conversion (\%) = (PSC/TSC) \times 100 \quad (3)$$

2.3.2. Viscosity measurement

Viscosity of the prepared polymer emulsions (after distillation) being dispersed in aqueous solutions, pigment, and dye printing pastes was measured using a Brookfield DVE viscometer at pH 7-8 and 25 ± 1 °C according to the standard test method ISO 2555:2018.

2.3.3. FT-IR Spectroscopy

Chemical composition of the synthesized polymer emulsions and the commercial product ARGOPRINT 160 was elucidated by FT-IR spectroscopy (INVENIO-S, Bruker Company, Germany) with an

ATR unit within the spectral range of 4000–400 cm^{-1} . Before being tested by FTIR, the polymer sample was precipitated and washed several times with acetone (99.5%), then dried at 130°C for 15 minutes.

2.3.4. Particle size and size distribution measurements

Particle size and size distribution of the prepared polymer lattices and the commercial ARGOPRINT 160 product were determined by dynamic light scattering (DLS) (NICOMP 380 ZLS, PSS, Santa Barbara, CA, USA).

2.3.5. Transmission electron microscopy (TEM)

Morphology of the selected optimal polymer emulsion (after the distillation process) and the commercial product ARGOPRINT 160 were examined by transmission electron microscopy (TEM, JEOL Co., JEM-2100; Japan) at 200 kV. A drop of the appropriately diluted sample was deposited onto a carbon-coated copper grid, negatively stained with 1% phosphotungstic acid, and left to dry at ambient temperature before being examined at suitable magnifications.

2.3.6. Color strength measurement

Color strength of the pigment- and dye-printed fabrics (cotton/polyester = 35/65), expressed as K/S values, was determined by reflection measurements using a data color international model (SF 500, USA). The K and S symbols refer to absorption and scattering coefficients, respectively.

2.3.7. Color fastness properties

Color fastness of the pigment- and dye-printed fabrics to washing, rubbing, and light were evaluated according to the rubbing standard test method BS EN ISO 105-X12:2016 and crocking standard test method AATCC 8:2016 [26].

3. Results and Discussion

3.1. Optimization of the polymerization conditions

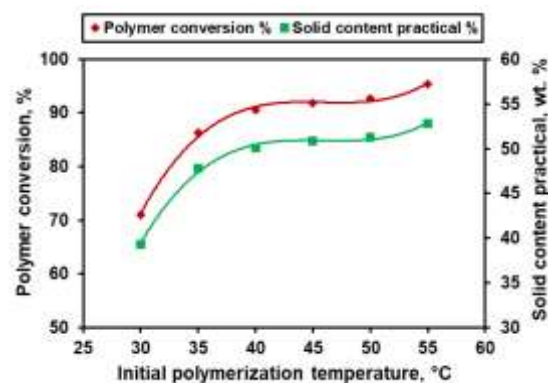
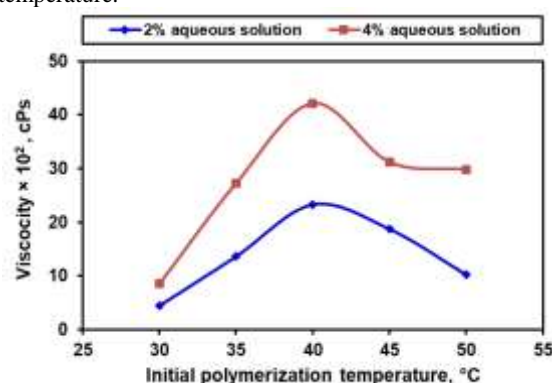
The polymerization parameters affecting the properties of the resultant polymer emulsions in terms of their solid content, polymer conversion, formation of precipitate and/or coagulum, emulsion stability, viscosities of their 2% aqueous solution and pigment pastes, and viscosities of their 4% aqueous solution and dye pastes were studied. These parameters include the initial polymerization temperature, AA monomer percentage, redox initiator type and percentage, and co-monomer type and dose. The main polymerization recipe is shown in **Table 1**.

Table 1 The main polymerization recipe

Phase	Raw Material	Weight (g)
Aqueous phase	Monomer(s)	100
	DW	152.24
	Ammonia	25
	EDTA-2Na	0.5
	MBA	0.175
Oil phase	ISOPAR-M	108
	Span 80	12
Initiator solution	APS	0.03
	DW	1
Reducing agent solution	SBS	0.0137
	DW	1
pH modifier	Ammonia	22.7
High HLB emulsifier	Tween 80	12
Total weight (g)		434.66

3.1.1. Effect of initial polymerization temperature (SPT₂₅₋₅₅)

Polymerization of acrylic acid (AA) monomer at different initial polymerization temperatures (25–55°C) was carried out, keeping all other parameters constant during the reaction. At the initial polymerization temperature of 40°C, the experimental studies demonstrated the production of polymer emulsions with high polymer conversion (%) and excellent colloidal stability with no signs of agglomeration or precipitation, as shown in **Table 2** and **Fig. 2**. Below that temperature, for instance, at 25°C (SPT₂₅), no reaction happened, while at 30 °C (SPT₃₀) the polymerization conversion was very low (71%), and the product has the odor of free monomers. At 35°C (SPT₃₅), the polymer conversion % increased but the polymer yield was still low, as shown in **Table 2**. However, at higher initial temperatures of more than 40 °C (SPT₄₅₋₅₅), the stability of the products was negatively affected, and precipitation or coagulation started to form. That behavior may be attributed to the formation of more free radicals and consequently more active sites, which led to the formation of low molecular-weight polymers. In addition, this reaction is exothermic, so when the initiation process takes place at high temperatures, the high exothermic reaction inversely affects the emulsion stability, causing precipitation and/or coagulation of the emulsion. Consequently, the efficiency of the polymer emulsion obtained as a rheology modifier was reduced, as shown in **Fig. 3**. Accordingly, the initial polymerization temperature of 40 °C was selected for the other polymerization reactions in the next steps.

**Fig. 2** Polymer conversion (%) and solid content (wt.%) of the poly (AA) as a function of the initial polymerization temperature.**Fig. 3** Effect of the initial polymerization temperature on the viscosity of the poly(AA) emulsion in its 2% and 4% aqueous solutions.

3.1.2. Optimization of acrylic acid (AA) monomer percentage (SPA₁₉₋₃₁)

In this series (SPA₁₉₋₃₁), different concentrations of AA monomer (19, 21, 23, 25, 27, 29, and 31 wt. %), based on the total amount of inverse pre-emulsion, were polymerized at 40°C, keeping the other reaction parameters constant. As shown in **Fig. 4**, the AA monomer conversion (%) decreased with increasing AA content. Conversely, the solid content of the prepared polymers increased. On the other hand, the application of the prepared polymers as rheology modifiers (in terms of their viscosities of 2% in aqueous solution and pigment pastes, and viscosities of 4% in aqueous solution and dye pastes) showed a gradual increase in the viscosity along with increasing AA concentration up to 27 wt.% as shown in **Figs. 5** and **6**. Then the viscosities decreased by further addition of AA and the stability of the emulsions was inversely affected since precipitates and coagulation were formed at concentrations of 29, 31 wt. %. Since the polymerization reaction is exothermic, the high monomer concentration causes the elevation of the reaction temperature, which adversely affects the emulsion stability.

Table 2 Physical properties of series 1 “Polymerization of AA monomer at different initial temperatures”

Exp. Code	Viscosity of 2% aqueous solution (cPs) ^(a)	Viscosity of 2% pigment paste (cPs) ^(b)	Viscosity of 4% aqueous solution (cPs) ^(a)	Viscosity of 4% dye paste (cPs) ^(b)	Solid content theoretical (%)	Solid content practical (%)	Polymer conversion (%)	Coagulum formation	PPT formation
SPT ₂₅	-	-	-	-	55.35	ND*	ND*	-	-
SPT ₃₀	450	ND*	850	ND*	55.35	39.30	71	-	-
SPT ₃₅	1365	ND*	2723	100	55.35	47.77	86.3	-	-
SPT ₄₀	2325	154	4210	230	55.35	50.09	90.5	-	-
SPT ₄₅	1870	127	3115	190	55.35	50.81	91.8	-	Traces
SPT ₅₀	1025	108	2980	150	55.35	51.31	92.7	Partial	Traces
SPT ₅₅	ND*	ND*	ND*	ND*	55.35	52.80	95.4	Complete	-

(a) At 24 °C, pH=7 and spindle/speed = 4/50, (b) At 24 °C, pH=7 and spindle/speed = 2/100 and ND* = not determined

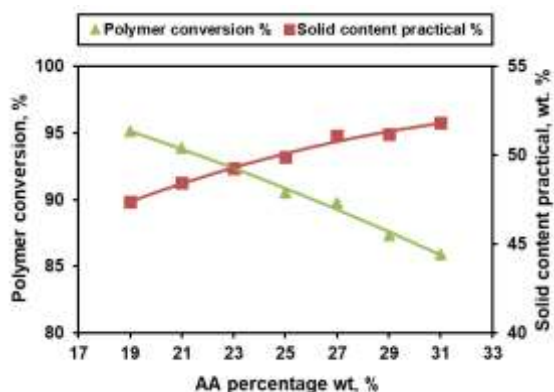


Fig. 4 Polymer conversion (%) and solid content (wt.%) of the poly(AA) emulsion as a function of AA monomer concentration.

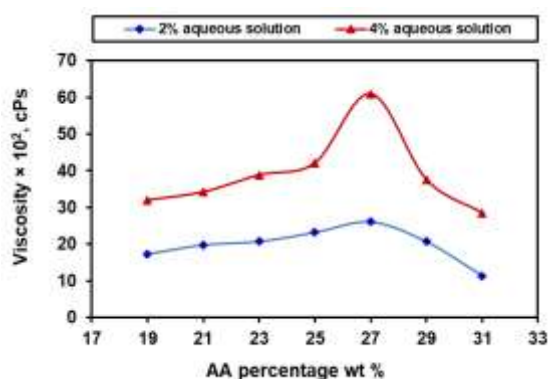


Fig. 5 Viscosity of the poly (AA) emulsion in aqueous solution at different concentrations (2 wt.% and 4 wt.%) as a function of AA monomer concentration.

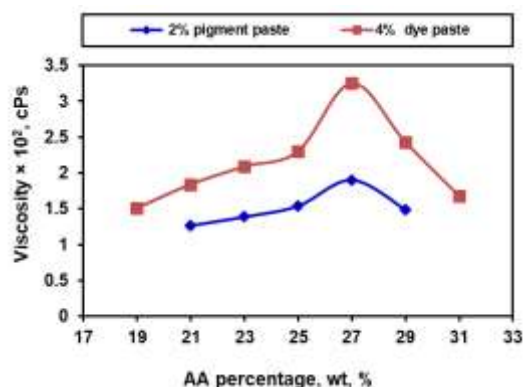


Fig. 6 Viscosity of the poly(AA) emulsion (2 wt.% in pigment paste and 4 wt.% in dye paste) as a function of AA monomer concentration.

3.1.3. Optimizing the type of the redox initiation system

The effect of different types of redox thermal initiation systems on the characteristics of the prepared polymer emulsions was studied at an equivalent molar ratio. Sodium bisulfite (SBS) reducing agent was used at a fixed concentration (159.5 ppm) in all preparations, and APS, SPS, and KPS were used with amounts of 350, 365, and 414.6 ppm, respectively, as water-soluble oxidizing agents. On the other hand, the oil-soluble initiators AIBN and BPO were utilized at concentrations of 251.8 and 371.5 ppm, respectively (all calculations were based on the total weight of the monomer).

As shown in **Fig. 7**, in the case of oil-soluble initiators (AIBN/SBS and BPO/SBS), the polymer conversion (%) and solid content (wt. %) are low, and the emulsion stability was affected by the

coagulate formation. On the other hand, for all water-soluble initiators investigated, the polymer conversion (%), polymer solids (wt. %), and emulsion stability are high. More specifically, ammonium persulfate (APS/SBS) exhibited the optimum features; this may be due to its highest solubility compared to the other initiators investigated, which positively reflected the highest rate of collision **Fig. 7**. Furthermore, the polymer obtained using the APS/SBS system possessed the highest thickening effect in its aqueous, pigment, and dye paste formulations **Fig. 8**.

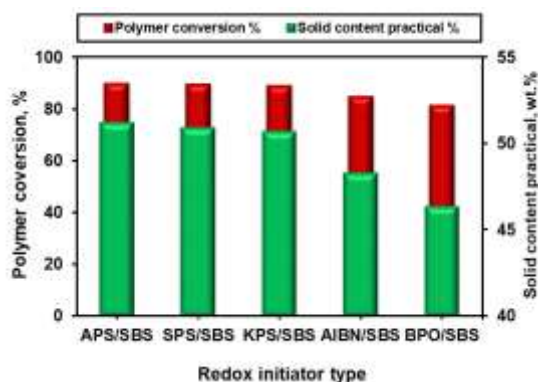


Fig. 7 Polymer conversion (%) and solid content (wt. %) as a function of the redox initiator type.

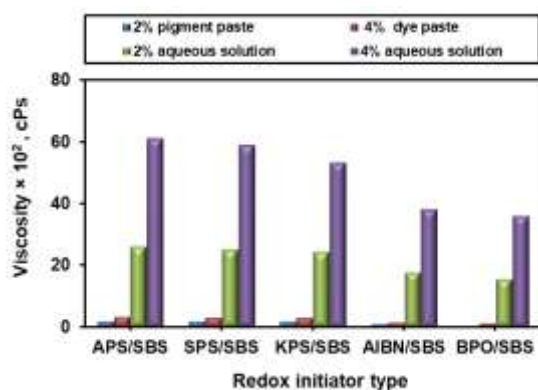


Fig. 8 Effect of redox initiator type on the viscosity of the poly(AA) emulsion in: aqueous solution (2 wt.%), pigment printing paste (2 wt.%), and in dye printing paste (4 wt.%).

3.1.4. Optimization of the APS/SBS redox initiator system concentration (SPAS 250-450)

In the present series, the polymerization reaction of 27 wt. % AA was carried out at 40 °C using the APS/SBS redox initiator system at a fixed molar ratio (APS: SBS, 1:1) with different concentrations (250/114, 300/136.8, 350/159.6, 400/182.5, 450/205.3 ppm, based on the total weight of monomers). It is well known that the rate of polymerization and the molecular weight are affected by the amount of initiator. The polymer's molecular weight decreases as the amount of initiator increases due to the formation of more active sites and more

propagated fragments. However, there is an optimum initiator dose to start the reaction at a specific temperature; below that amount, the rate of polymerization decreases. As shown in **Fig. 9**, at a low APS/SBS dose (250/114 ppm), the polymer conversion (%) and solid content (wt.%) are very low, and they are increased by increasing the amount of APS/SBS initiator system up to 350/159.6 ppm, where the polymer obtained has high conversion (92.7%) and high solid content (52.84 %), as well as the highest efficiency as a rheology modifier (**Fig. 10**). Increasing the initiator system concentration more than (350/159.6 ppm) led to a successive increase in the polymer conversion (%) but with less colloidal stability and lower efficiency as a rheology modifier.

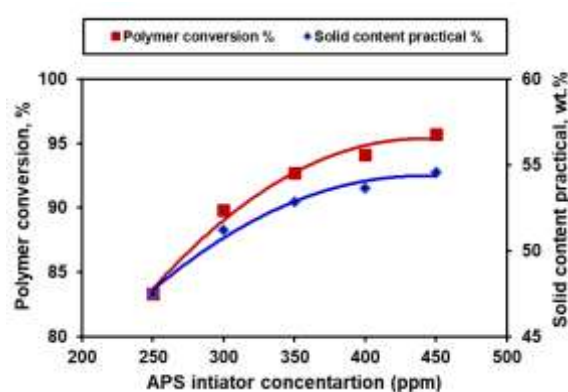


Fig. 9 Polymer conversion (%) and solid content (wt.%) of the poly(AA) emulsion as a function of the redox initiator APS/SBS concentration.

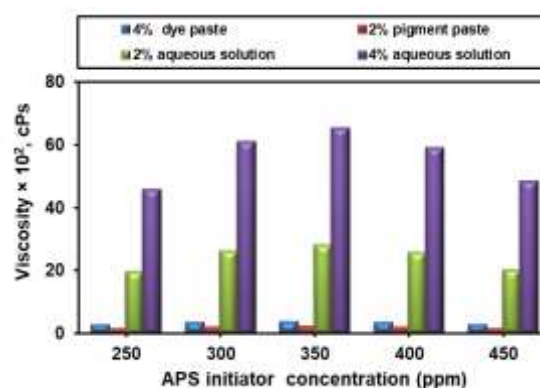


Fig. 10 Effect of the redox initiator APS/SBS concentration on the viscosity of the poly(AA) emulsions in aqueous solution at different concentrations (2 wt.% and 4 wt.%), and in pigment and dye pastes with concentrations of 2 wt.% and 4 wt.%, respectively.

3.1.5. Optimization of the cross-linker type

One of the most important factors affecting the efficiency of polymers as rheology modifiers or synthetic thickeners is the cross-linker. Cross-linked polymers appear in the form of three-dimensional

networks, which are required for polymer swelling at high shear rates and their ability to carry water or aqueous solutions, increasing the rheology of the solution. Therefore, in the present series, a difunctional cross-linker, MBA, and a trifunctional cross-linker, GTMA, with amounts of 0.175 and 0.363 wt.%, respectively, based on the amount of monomers, were studied. The polymerization reaction of 27 wt.% AA was carried out at an initial temperature of 40 °C using the redox initiator APS: SBS at a 1:1 molar ratio (350:159.6 ppm, based on the total amount of the monomers). The other polymerization parameters were kept constant. The type of cross-linker remarkably affects the swelling power of the resultant polymers in terms of the viscosities of their aqueous solutions, pigment pastes, and dye paste formulations. It is obvious that the trifunctional cross-linker (GTMA) has a higher significant impact on the polymer conversion % (Fig. 11) and the viscosities of their polymer solutions are higher than those of the difunctional cross-linker (Fig. 12). This may be attributed to the fact that the network formed by the difunctional cross-linker MBA is shorter than that obtained by GTMA (Scheme 1). Additionally, the GTMA cross-linker includes methacrylate ester groups (Scheme 2), which could expand the network during the swelling process and, as a result, increase the swelling capacity and viscosity of its corresponding printing paste formulations.

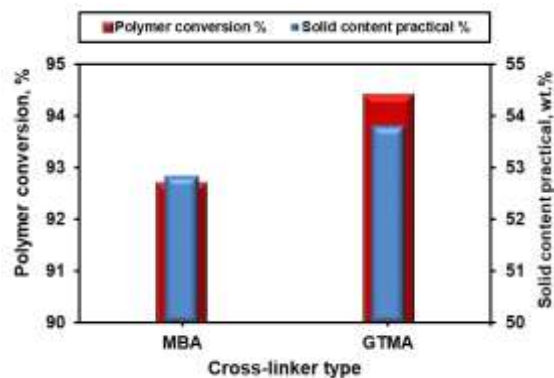


Fig. 11 Polymer conversion (%) and solid content (wt.%) as a function of the cross-linker type.

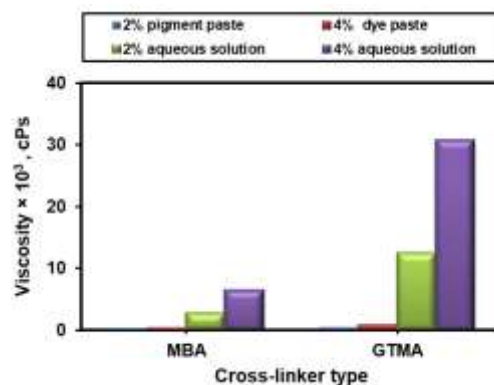
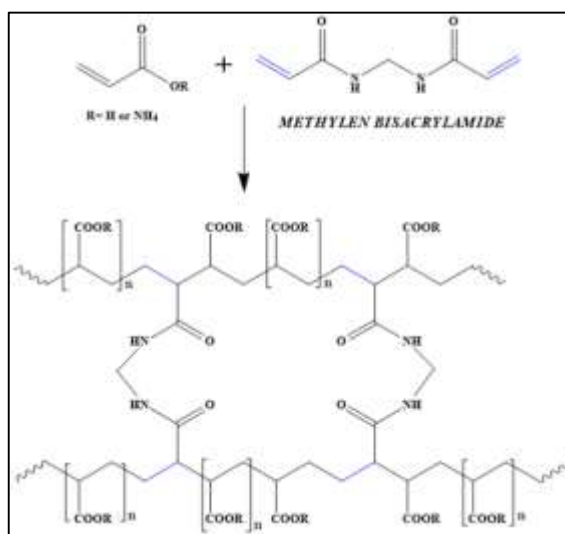
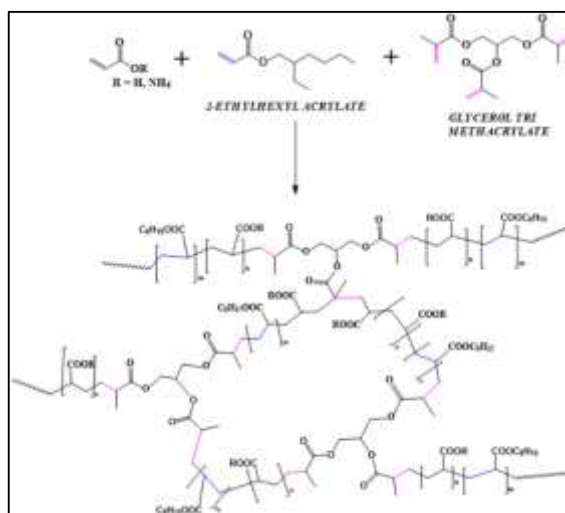


Fig. 12 Effect of the crosslinker type on the viscosity of the poly(AA) emulsion in aqueous solution at different concentrations (2 wt.% and 4 wt.%), and in pigment and dye pastes with 2 wt.% and 4 wt.%, respectively.



Scheme 1 Structure of the partially neutralized poly (AA) cross-linked by MBA



Scheme 2 Structure of the partially neutralized poly (AA) cross-linked by GTMA

3.1.6. Optimization of the cross-linker GTMA dose

The effect of the GTMA cross-linker dose (0.21, 0.43, 0.65, 0.86, 1.08, 1.3, 1.5, and 1.7 wt. %, based on the total amount of the monomer) on the properties of the produced polymers was investigated. The other polymerization reaction parameters were kept constant (initial polymerization temperature 40°C, AA 27 wt.%, and APS/SBS 350:159.6 ppm based on the total amount of the monomers). As clearly seen from Fig. 13, the polymer conversion (%) and colloidal stability of the polymer emulsions were not significantly affected by GTMA cross-linker content. On the other hand, increasing the amount of GTMA cross-linker enhanced the thickening effect of the obtained polymers in their aqueous solutions, pigment, and dye paste formulations up to ≈ 1.3 wt. %, as shown in Fig. 14. Beyond that concentration, the stability of the obtained emulsion product was adversely affected, and coagulation was formed, where, at 1.5 and 1.7 wt.%, partial and complete, respectively, coagulation happened.

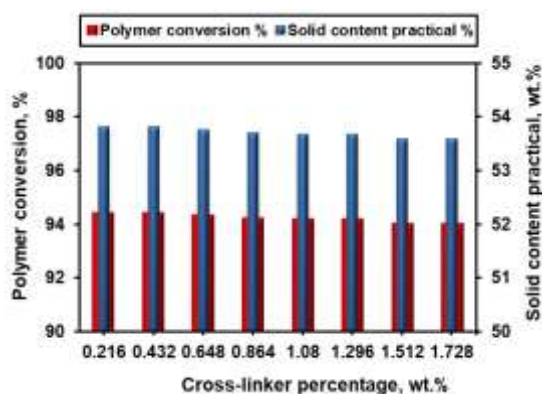


Fig. 13 Polymer conversion (%) and solid content (wt. %) of the partially neutralized poly(AA) cross-linked by GTMA.

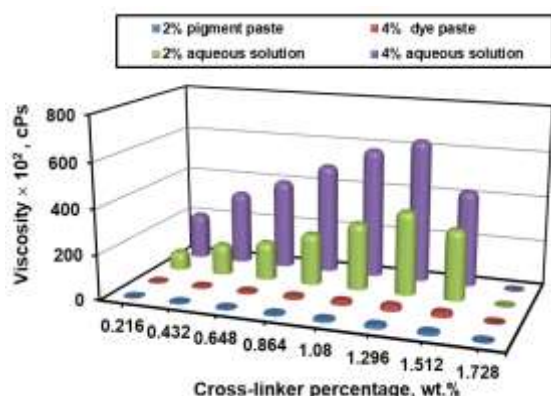


Fig. 14 Viscosity of the the poly(AA) emulsion in aqueous solutions at different concentrations (2% and 4%) as a function of GTMA crosslinker content.

3.1.7. Co-polymerization of AA monomer: optimization of the co-monomer type

To investigate the influence of co-polymerization of AA with other monomers on the properties of the produced polymer emulsions, various monomers, namely acrylamide (AAM), Methacrylic acid (MAA), butyl acrylate (BA), and 2-ethylhexyl acrylate (2-EHA), were used with constant 5 wt. % of total monomers concentration. It was found that the copolymerization had no significant negative effect on the polymer conversion and solid content of the prepared emulsions (Fig. 15). In addition, there was no precipitation or coagulation observed at the end of the polymerization reaction. More interestingly, the prepared copolymer emulsions significantly enhanced the viscosity of their aqueous solutions as compared to the AA homopolymer (Fig. 16). Additionally, the AAM-based copolymer emulsion exhibited the highest efficiency in its aqueous solution. However, the 2-EHA based copolymer emulsion possessed the highest efficiency as a rheology modifier in its pigment and dye paste formulations (Fig. 16). This could be attributed to the hydrophobic components of BA and 2-EHA, which improve the polymer's resistance to pigment and dye particles while also preserving the molecules' swelling ability and capability to carry aqueous solutions. This was confirmed by viscosity measurements, notably for 2-EHA. As a result, 2-EHA was chosen for further examination in the next steps.

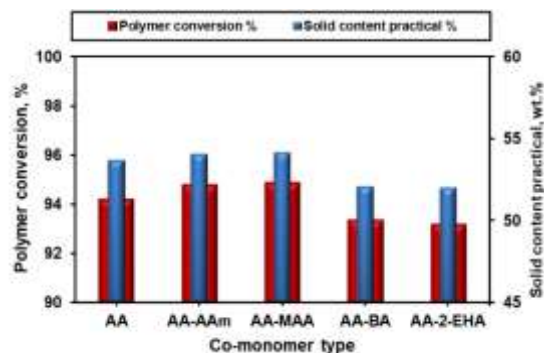


Fig. 15 Polymer conversion (%) and solid content (wt. %) as a function of the comonomer type.

As shown in Figures 8, 10, 12, 14, and 16, there is a remarkable decrease in the viscosity with the addition of pigment and dye pastes to the prepared thickener solution. This behavior was noticed by Chang-E Zhou et al. [27]. This could be attributed to the ionic nature of the emulsifier in the EBCA Print 544 binder and the dye molecules, which affect the hydrogen bonding between the negatively charged associative thickener and water molecules in the aqueous medium, leading to viscosity reduction. The same behavior was also noticed in the case of the commercial product (ARGOPRINT 160).

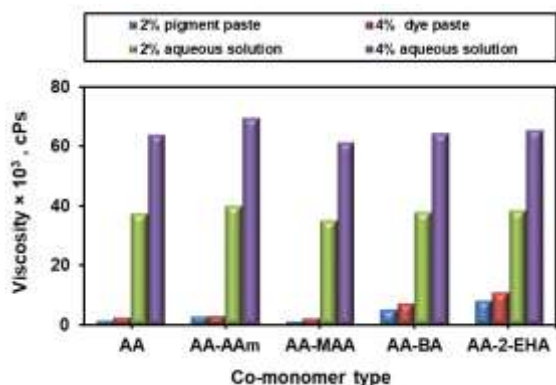


Fig 16 Effect of comonomer type on the viscosity of the polymer emulsions in: aqueous solutions at different concentrations (2 wt.% and 4 wt.%), pigment paste (2 wt.%), and dye paste (4 wt.%).

3.1.8. Optimization of 2-EHA co-monomer concentration

Effect of the 2-EHA co-monomer content (2.5, 5, 7.5, and 10 wt. % based on the total amounts of the monomers) on the properties of the final products, as rheology modifiers, was investigated. As shown in **Fig. 17**, it is evident that the co-monomer 2-EHA content has no significant impact on the conversion (%) and solid content (wt. %) of the polymers obtained. On the other hand, the co-polymer emulsion 2-EHA co-monomer (7.5 wt.%) demonstrated superior thickening as a rheology modifier in its 2% and 4% aqueous solutions, pigment paste, and dye paste formulations (**Fig. 18**). Beyond that concentration, the viscosity started to decrease. This may be attributed to increasing the hydrophobicity of the copolymer upon increasing the 2-EHA content, which consequently leads to a reduction in the solubility and swelling behavior of the product in its aqueous medium.

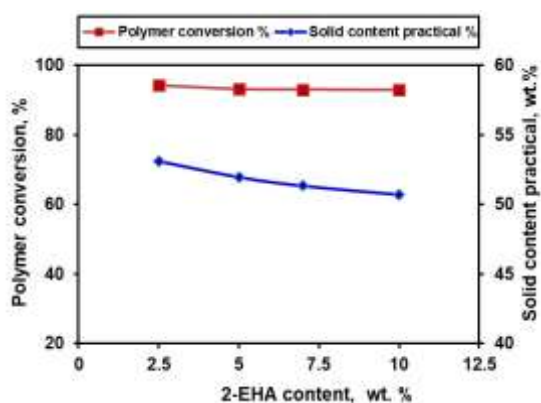


Fig. 17 Polymer conversion (%) and solid content (wt. %) as a function of 2-EHA co-monomer content.

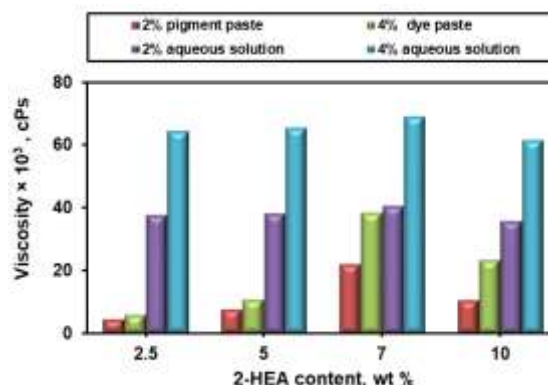


Fig. 18 Effect of 2-EHA co-monomer content on the viscosity of the polymer emulsions in: aqueous solutions at different concentrations (2 wt.% and 4 wt.%), pigment paste (2 wt.%), and dye paste (4 wt.%).

3.1.9. Comparison between the best-formed polymer (SPEHA7.5) and ARGOPRINT 160

Based on the previous results, it is interesting to make a comparison between the optimal synthesized polymer SPEHA7.5 after the vacuum distillation process and the commercial product ARGOPRINT 160 as rheology modifiers. As shown in **Fig. 19**, the prepared SPEHA7.5 emulsion exhibits better rheological performance than ARGOPRINT 160 in its 2% aqueous solution and pigmented pastes, and its 4% aqueous solution and dyed pastes.

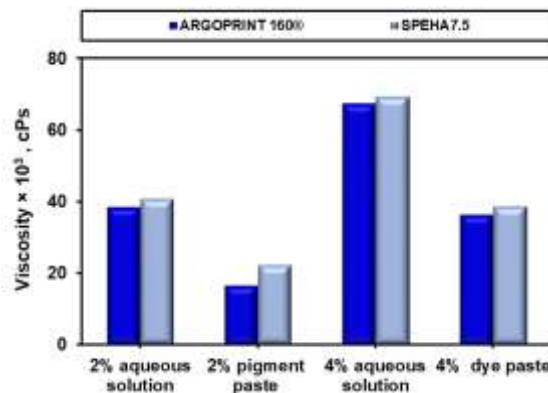


Fig. 19 Comparison between viscosity of the prepared optimal polymer emulsion SPEHA7.5 and the commercial ARGOPRINT 160 in their 2 wt.% aqueous solution and pigmented pastes, and 4 wt.% aqueous solution and dyed pastes.

3.1.10. FT-IR spectroscopy

Chemical structure of the prepared SPEHA7.5 and the commercial product ARGOPRINT 160 was investigated using FTIR spectroscopy. As clearly seen from **Fig. 20**, both polymers have similar spectra, and their characteristic bands are shown in **Table 3**. The characteristic CH_2 absorption peak of the prepared polymer SPEHA7.5 appeared at 2925 cm^{-1} while the peak at 3188 cm^{-1} is attributed to the

stretching vibrations of O–H bonds. Furthermore, the characteristic C=O stretching (carbonyl bond) absorption peaks appeared at 1692 cm^{-1} and the peak at 1171 cm^{-1} is related to the C–O ester groups of the network structure.

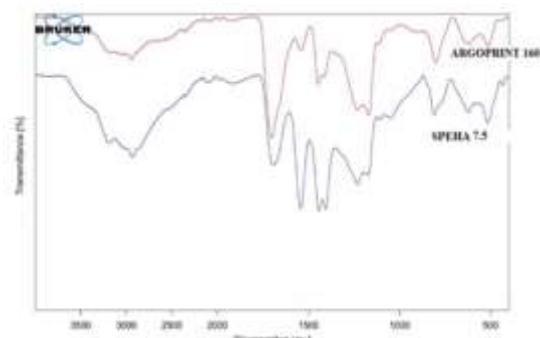


Fig. 20 FTIR spectra of the prepared SPEHA7.5 and the commercial thickener ARGOPRINT 160

Table 3 FTIR characteristic bands of the prepared SPEHA7.5 and the commercial thickener ARGOPRINT 160

Characteristic bands	Band assignments (cm^{-1})	
	ARGOPRINT 160	SPEHA7.5
CH ₂ stretching	2939	2925
C=O stretching	1702	1692
O-H stretching	3188	3188
C-O stretching	1169	1171
C-H bending	1447	1447

3.1.11. Particle size and size distribution

The colloidal particle size is critical for the stability of the developed emulsions. The size and particle size distributions of SPEHA7.5 and ARGOPRINT 160 polymer emulsions are depicted in **Fig. 21**. It is clear that the mean particle diameter (size) for SPEHA7.5 with a confined size distribution is 323.6 nm, ARGOPRINT 160 exhibits a broad size distribution of 1022 nm.

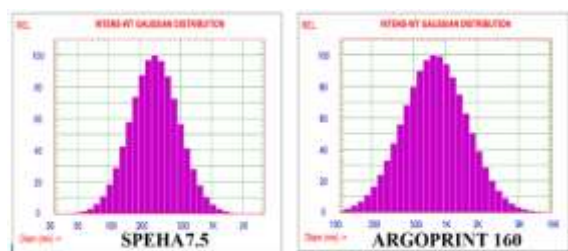


Fig. 21 Particle size and size distribution of SPEHA7.5 and ARGOPRINT 160 emulsions.

3.1.12. Transmission electron microscope (TEM)

The morphology of the polymeric colloidal particles of both SPEHA7.5 and ARGOPRINT 160 emulsions was examined by TEM analysis, as illustrated in **Fig. 22**. As clearly seen, both polymer colloidal particles displayed spherical morphology with core-shell structure. In addition, the particle size observations

showed that the SPEHA7.5 colloidal particles have smaller hydrodynamic size, and consequently more specific surface area than ARGOPRINT 160, as confirmed by particle size measurements.

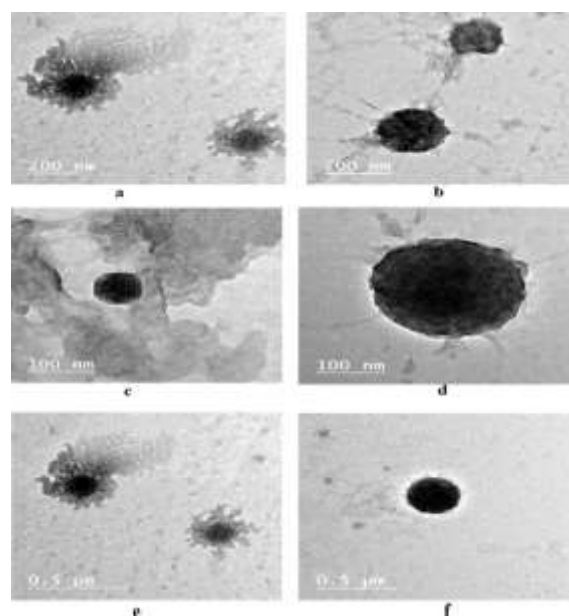


Fig. 22 TEM photos of SPEHA7.5 (a, c and e), and ARGOPRINT 160 (b, d and f).

3.1.13. Textile printing application

Cotton: polyester (35:65%) fabric was printed by the blue dye printing pastes containing ARGOPRINT 160 and SPEHA7.5 as rheology modifiers, as shown in **Fig. 23** (a and b), respectively. While, the fabric printed by the red pigment printing paste containing ARGOPRINT 160 and SPEHA7.5, is represented in **Fig. 23** (c and d), respectively. It's clear that the prepared SPEHA7.5 has comparable results to the commercial ARGOPRINT 160 product, as shown in **Table 4**. Advantageously, from the economic point of view, prepared SPEHA7.5 polymer emulsion is cheaper than the imported ARGOPRINT 160 product.

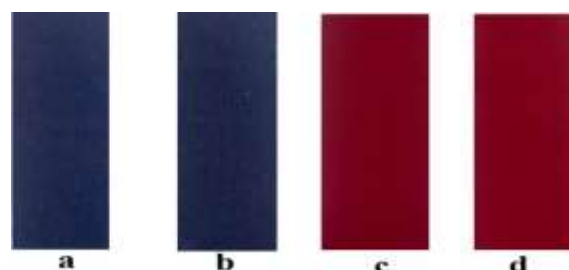


Fig. 23 Application of SPEHA7.5 polymer and ARGOPRINT 160 product, as thickeners and modifying agents for printing of cotton: polyester (35:65%) fabric. Printed (cotton: polyester, 35:65) fabric by DOROSPERS NAVY BLUE K-LN (DNB) dye printing paste thickened by (a) ARGOPRINT 160, and (b) SPEHA7.5.

Printed (cotton: polyester, 35:65) fabric by PRINTOFIX ARGOPRINT 160, and (d) SPEHA7.5. RED T-N (PFR) pigment printing paste thickened by (c)

Table 4 Color strength and color fastness of the pigment- and dye-printed fabrics

Sample code	Color strength (K/S) measured at 580 nm	Washing fastness	Perspiration		Rubbing fastness		Light fastness
			Acid	Base	Wet	Dry	
A	12.45	3	3	3	1	1	7
B	12.22	3	3	3	1	1	7
C	12.74	4	4	4	2-3	3	7
D	12.73	3-4	3-4	3-4	2-3	3	7

Printed (cotton: polyester, 35:65) fabric by DOROSPERS NAVY BLUE K-LN (DNB) dye printing paste thickened by (A) ARGOPRINT 160, and (B) SPEHA7.5.

Printed (cotton: polyester, 35:65) fabric by PRINTOFIX RED T-N (PFR) pigment printing paste thickened by (C) ARGOPRINT 160, and (D) SPEHA7.5.

4. Conclusion

In conclusion, novel partially neutralized ammonium acrylate water-soluble polymers were successfully prepared using the inverse emulsion polymerization technique at a constant aqueous/oil ratio of 70/30. The ideal prepared polymer was selected after optimizing the polymerization conditions, including the initial polymerization temperature of 40 °C, the acrylic acid percentage of 27 wt. %, the type of redox initiator (APS/SBS) and its dose (350:159.6), the cross-linker GTMA and its dose of 1.3 wt. %, the comonomer type (2-EHA) and its dose (7.5 wt. % of the total monomers). At these optimum conditions, the prepared polymer emulsion (SPEHA7.5) has the highest polymerization conversion, solid content, and colloidal stability. In addition, it exhibited better rheological performance in its aqueous solutions, pigment, and dye paste formulations as compared to the commercially used product ARGOPRINT 160. Moreover, the newly prepared polymer emulsion could be used as an efficient thickening and modifying agent for the pigment and dye printed fabrics at lower cost compared to the imported ARGOPRINT 160 commercial product.

5. Conflict of interest:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence this work.

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