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Research Article

Organic Silicone Based Poly-Acrylate Binder Synthesis for Textile Pigment Printing

Sakil Mahmud*, Md. Ahsan Habib, Md. Nahid Pervez, and Ashraful Islam

School of Chemistry & Chemical Engineering, Wuhan Textile University, China

Abstract

This present study deals about an organic silicone based poly-acrylate binder by using Emulsion Polymerization technique because it produces high molecular weight polymers, and there is no or negligible content of volatile organic compounds (VOC) for textile pigment printing. The binder was prepared by polymerizing hard monomers, soft monomers, functional monomers, and compound emulsifying agent, organic silicone, an initiator, pH adjustor and deionized water. Then the properties like sublimation test, durability test, fastness test, yellowness and softness testing were performed. The role of acrylic acid and Methyl methacrylate on the characterization of the polymers was detected and recorded. A material has been selected based on pervious study of different research and effect of silicone amount on film was observed.

Keywords: Poly-acrylate binder; Printing Binder; Silicon Binder; Pigment Printing; Textile Printing; Polymer Synthesis
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***Correspondence to**: Sakil Mahmud, School of Chemistry and Chemical Engineering, Wuhan Textile University, China; **Email**: sakilhabib@gmail.com

1. Introduction

Pigment printing is the oldest printing strategies of textile sectors but more than 80% of the printed goods are based on this printing due to its clear compensation, as for example versatility, ease of near final prints at the printing stages itself. In pigment printing by using silicon with binder the most multitalented polymer can be achieved. Due to organic structure and super flexibility of silicon bonds, silicon offer some extraordinary properties such as thermal oxidative stability, low temperature flow ability, low viscosity change with respect to temperature, high compressibility, low surface tension, hydrophobicity, good electric properties and low fire hazard[1]. Very small amounts are required to achieve the desired properties, which offer cost effective textile operations and ensure negligible environmental impact [2-5]. On the other hand the prime characteristic of poly-acrylic coatings is their resistance to hydrolysis during extended exterior exposure as well as weathering, block resistance, hardness, gloss and high alkali and oxidation resistance [6-8]. Both outstanding properties of the binder as well as silicon addition to the pigment printing fabric contribute to crock fastness, good mechanical properties and resisting deformation of the coating on rubbing[9]. Organic silicon based textile binder, make not only fabric soft & smooth but also good elastic properties & increase the added value of the fabric[10]. The amount of silicon is explores during the preparation of binder by significantly. Observing resultant impact on polymer quality like solid content, gel ratio, polymer conversion rates, acid & alkali stability, electrolyte resistance stability etc as well as resultant impact on printed fabric quality like dry/wet rub fastness, sublimation test[11, 12]. In case of pigment binder polymer formed with the hard monomers to soft monomers with 0.6%. Acrylic binders are the most widely used and versatile binders available with various modifications. The properties of acrylic binders differ according to their derivatives and copolymers and their film in pigment print is a three-dimensional structure, the third dimension is rather less important than the other two is shown in **Figure 1**. The binder is a film-forming substance made up of long chain macromolecules, which when applied to the textile together with the pigment, produces a three-dimensionally network. The links are formed during some suitable fixing process, which usually consists of dry heat and change in pH value, bringing about either self-crosslinking or reaction with other suitable crosslinking agents[13].

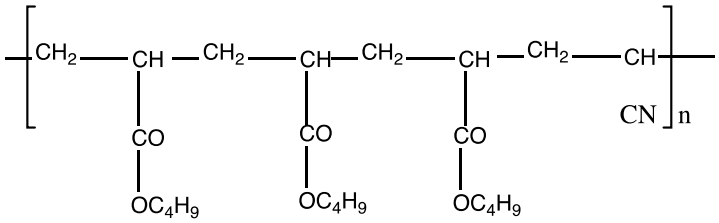

Figure 1 General structure of acrylate copolymer

Now-a-days acrylic monomer is available in wide range that can be copolymerized and provide broadly spectrum. There is a direct impact of monomers on polymer film. So, to fulfill the final product properties one must understand the overall impact of individual monomer on the copolymer. **Table 1** shows the details monomer properties on film like; physical properties of film as well as application properties of the film.

The aim of this research is to introduce silicon to improve weathering resistance of printed fabric and improving of the mechanical & physical properties of ethyl acrylate polymer which is consider as the stamina textile pigment printing binder by co-polymerization of ethyl acrylate with butyl acrylate in presence of acrylic or meth acrylic acid and applying each co-polymer as a textile pigment printing binder.

Table 1 Properties of the monomer on the film[14]

Type of Monomer	Single body	Elasticity	Softness	Washable	Resistant to solvents Agent	Heat resistance	Dry-rub resistance	Wet-rub resistance
Hard Monomer	MMA	○	×～△	○	○	⁎	↗	↘
	S.T	↘	↘	→	↘	→	↗	↗
Soft Monomer	EA	○	○	○～△	○	⁎	↗	↘
	IOA	○～△	⁎	○	○～△	⁎	↘	↗
	BA	○～△	⁎	○	○	⁎	↘	↗
	MA	○	×～△	○～△	○	⁎	↗	↘

Here: ⁎ = Excellent; ○ = Good; △ = Moderate; × = Bad; ↗ = Increase; ↘ = Decrease and → = Unchanged

2. Experimental

2.1 Materials

100% cotton woven fabric having construction 26 ends/cm^2, 22 picks/cm^2 and an area density of 148 gm/m^2 was used for pigment printing purpose. The fabric was desized enzymatically, scoured and bleached by an exhaust method.

2.2 Chemicals

Binder and Hard Monomers: Styrene (S.T), Methyl Meth Acrylate (MMA), then Soft Monomers: Ethyl Acrylate (EA), Butyl Acrylate (BA), Functional Monomers: Acrylic Acid (AA), 2-Hydroxyethyl methacrylate, and as an organic silicone two chemicals are used for doing this experiment like Methyltrichlorosilane & Methyl-phenyl-dichlorosilane and all chemicals are supplied by BASF

2.3 Synthesis of Silicon Binder

Step-1: pre-emulsion the composition of emulsifier by Adding water (70% of solid materials) to emulsify all the monomers i.e. hard monomers 55%; soft monomers-52%; Functional/ cross-linking

Monomers-3% with 5% emulsifier (No-ionic; OP-10 and Anionic; K12 with ratio 2:1) and finally stirrer the solution well at high speed for 30min.

Step-2: Here emulsion polymerization by taking out then 15-20% of the pre-emulsion from the first step to use in next step. Increase the temperature up to 75^{O}C and add 40% of total required (5% of total monomers) initiator in to the emulsion by dropping for 20-30min. Then raised the temperature up to 80^{O}C and keep it for 30min. Before observing it under blue light, this step is finished by three segments.

Step-3: the remaining emulsion (80-85%) from step-1 and the balance initiator (60%) are added in to the solution of step-2 at a constant rate for 60-100min by keeping the temperature 80^{O}C. Solution must be continuously stirrer at medium speed. After finish the dropping keep the solution at 80^{O}C for 20min. If strong odor is found then need to be add some initiator (not more than 0.1%) and re-observe after 20min.

Step-4: Increase the temperature by 5^{O}C and keep the solution for 30min by maintaining medium stirring speed.

Step-5: Decrease the temperature below 40^{O}C and add 5-7% ammonia water to control the pH 7-8 by maintaining medium stirring speed.

Spep-6: Lower the temperature of the solution to room temperature and collect all the segments and residue by filtration.

The amount of silicon was varied between 0-18 percent of total monomer. The polymerization time has also varied to achieve optimum condition of the result.

2.4 Characterization of Binder

To evaluate the copolymer the following tests are performed; Gel Ratio, Solid content and Conversion test. Also we will apply the binder on textiles and will test the different properties like; dry and wet resistance, softness, staining etc.

2.4.1 Gel Ratio

For measuring gel ratio we have taken dry weight sample of total residue and total weight of monomer with percentage.

$$= \frac{\text{Dry Weight of Total Residue}}{\text{Total Weight of Monomer}} X\ 100 \qquad \textbf{1}$$

2.4.2 Solid Content

Take approximately 3 gram of the sample and weigh it accurately in a glass dish. Place it in the oven for 4 hours at 110^{O}C. After cooling in the desiccator, weight the dish accurately.

$$\textbf{Solid Content} = (G_1/G_0) \times 100 \qquad \textbf{2}$$

Where,
$G_1 \rightarrow$ Constant dry weight
$G_0 \rightarrow$ Sample weight,

2.4.3 Conversion Ratio

The conversion ratio measured by the following 3

$$= \frac{G_1 - G_0 W}{G_0 M \ X \ Solid \ Content} \ X \ 100 \qquad 3$$

Where,
$G_1 \rightarrow$ Constant dry weight
$G_0 \rightarrow$ Sample weight,
By getting value of W we used this 4

$$W = \frac{APS + Emulsifier}{APS + Emulsifier + Monomers} \qquad 4$$

Here, Monomers are considered in percentage.

2.4.4 Particle size and particle size distribution

The particle size and its dispersions measured by laser particle size analyzer.

2.4.5 Emulsion stability test

We have done the entire test for individual sample according to following procedure:

- **Dilution Stability:** The emulsion was diluted to a solid content of 3%, then the emulsion was poured into 30ml tubes after dilution, the liquid column height of 20cm, is placed 72h, measuring the volume of supernatant and precipitate upper portion.
- **Acid and Alkali Stability:** In two test tubes were charged emulsion 5g sample tested, the two tubes were then added drop wise 1ml (1mol / L) hydrochloric acid and 1ml (1mol / L) solution of KOH. After shaking, the P^H test and observe the emulsion is stable. Then the two tubes placed at room temperature for 24h, and then observe the stability of the emulsion.
- **Electrolyte Resistance Stability:** Added 16ml polymer emulsion sample into the test tube, then add 4ml of 0.5% $CaCl_2$ solution, shake and let stand 48h, the emulsion changes observed.

2.5 Application of Si-binder on Cotton Fabric

All prepared polymers sample were applied as binder for textile pigment printing according to general industrial printing process. We were prepared full shade pigment printing pastes according to the following recipe shown in **Table 2.** The physical and mechanical tests were carried out on the printed samples.

Table 2 Pigment Printing Recipe

Materials	Weight %
Binder	13-16
Pigments Dyes	3-4
Synthetic Thickener	1.5-18
Distilled Water	Up to 100%

2.6 Performance Testing of Binder

2.6.1 Sublimation Test: For conducting sublimation test the printed samples prepared by using different concentrations of prepared polymers, after exposing the samples at 180^{O}C for 1min. and no significant changes are observed.

2.6.2 Durability Test: The pigment printed textile samples prepared from different concentrations of prepared polymers and observed resistance to commercial detergents, after washing all samples for 1h at 40^{O}C.

2.6.3 Dry Rubbing Fastness and Wet Rubbing Fastness:
According to For AATCC 116-1995 methods by using standard crock meter cloth, maintain uniform pressure for applying rubbing strokes and number of strokes. Degree of staining and color changing are assessed by Grey scale

In the case of wet rubbing, % moisture on the crock-cloth has to be kept to uniform level and rubbing cloth that has been wetted with water, has to be squeezed to contain its own weight of water. Wet pick up is to be maintained between 65±5 % by squeezing the wet crock meter cloth using a AATCC blotting paper.

3. Result & Discussion

3.1 Effect of amount of silicon on binder

The properties of prepared binder are either directly or indirectly proportional to the amount & quality of silicon. With the better quality and performance of binder, improves the various properties of printed fabric. The quality parameters with respect to conversion rate, gel ratio & solid content of the prepared binder are shown in the Figure 2. When influences of amount of silicon were measured, of course other synthesized conditions like time & temperature were kept same.

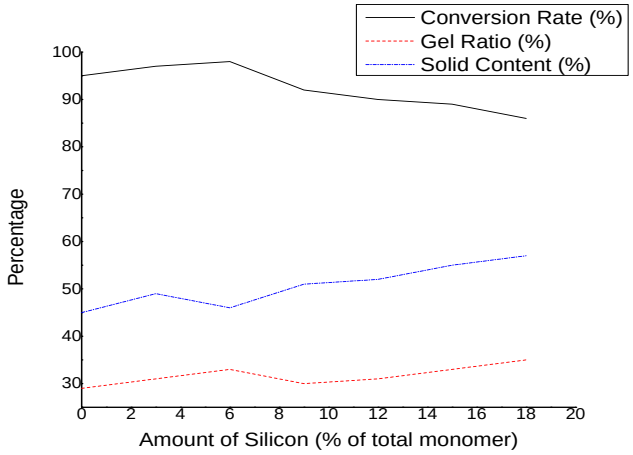

Figure 2. Influence of amount of silicon on binder

The **Figure 2** illustrates that, with increasing the amount of silicon percentage of the monomer conversion decreases but the gel quality & solid content increase slightly. When the amount of silicon was 6% of total monomer; the performance of the binder decreases with respect to conversion rate & gel ratio. This is may be due to number of Si-OR cross-linking structure and subjected to improve the water resistance on the surface. The Si-OH, those are remaining un-react in polymerization, able to create H-bond or other bonds due to cohesive force.

3.2 Effect of polymerization time on binder

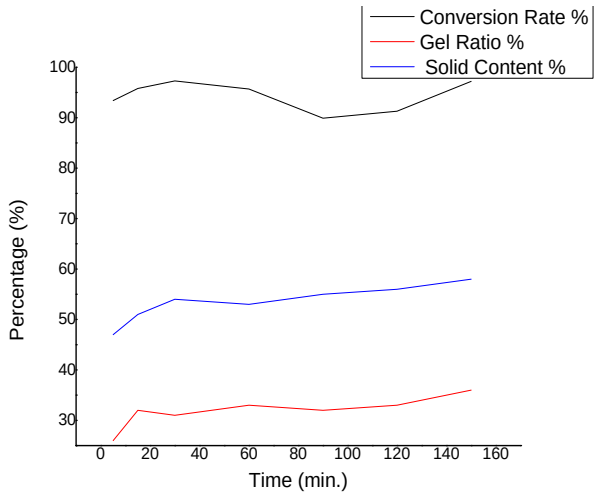

Figure 3. Influence of polymerization time on binder

The **Figure 3** described that, long polymerization demonstrates better adhesive performance but it goes down at after 150 min. The reason found that, when more time allowed for polymerization reaction, the larger particle turns to smaller latex progressively. The further increasing time, the smaller particle formation resulting viscosity decreases & enhancing staining resistance. So it can be suggested that the polymerization should not be exceed 150 min.

3.3 Particle size & its distribution analysis by laser particle size analyzer

Figure 4 shows the particle size and their distribution in emulsion. Here, the minimum particle size in the emulsion was around 40nm and the maximum particle size was 280 nm. Particles in the aqueous emulsion were finally distributed, and the average particle size was 120 nm.

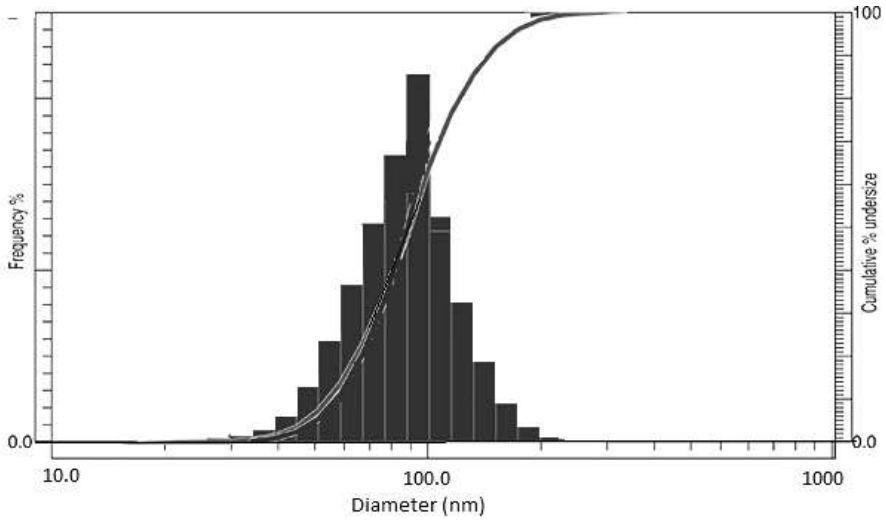

Figure 4. Particle size & its distribution analysis by laser particle size analyzer

3.4 Polymer Stability Test:

We have done the entire test for individual sample according to following procedure is shown in Table 3**:**

- **Dilution Stability:** No change found in the emulsion.
- **Acid and Alkali Stability:** No change found, Emulsion is resistant to both acid and alkali.
- **Electrolyte Resistance Stability:** No change found, Emulsion is resistant to electrolyte.
- **Thermal Stability:** no change found up to 150^0C

Table 3 Emulsion Durability Testing Result

Electrolyte Resistance Stability	Dimensional Stability	Emulsion Stability	Acid & Alkali Stability					Thermal Stability
			PH-6	PH-7	PH-8	PH-9	PH-10	25-150^{O}C
Resistant	Stable	Stable	Good	Excellent	Average	Fair	Poor	No change*

*****Every after 10min raise the temp & thermal stability of the polymer was tested & recorded.

From **Table 3** it was observed that the dilution stability and electrolyte resistance of polymer emulsion were good in any condition and there was no precipitation. It was also found that, acid and alkali stability of the emulsion improves gradually up to pH 7.

3.5 Application on Cotton Fabric

After developed standard method & condition, binders were applied in a white plain woven cotton fabric in rotary screen printing method. Assessment of the sublimation test, durability test, rubbing fastness test, Staining Resistance and others performance test of a printed fabric & recorded in the **Table 4**.

Table 4 Application Performance Test

Sublimation test	Durability test	Wet Rubbing	Dry Rubbing	Staining Resistance	Yellowing	Softness (cm)
Pass	Pass	2/3	3	2.5	13.9	6.5

After testing the result we observed pass signal for sublimation and durability test. Then comparatively dry rubbing fastness value is high and yellowness and softness is comparatively satisfied.

4. Conclusion

After experimental data analysis we can conclude that, hard monomers, soft monomers and function monomers to get the film, having pretty good elasticity, very soft hand feel washable, heat resistant and obviously pretty good wet & dry resistance. Organic silicones are added to increase the mechanical properties, air permeability, water resistant and good stain resistant. High speed stirring during pre-emulsion process and double dosing ensured the good conversion rate of monomers & low solid content into the copolymer and pH would be 7-8 and would have excellent film forming ability.

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