

Organic Acrylate Binder Synthesis through Emulsion Polymerization to ensure the best Mechanical Properties on Applicable Substrates

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Abstract: Emulsions used as pigment binders in formulations have to cope with the challenge to assure an outstanding film configuration and exterior as well as good mechanical properties. One strategy to fulfil this contradictory requirement is the employment of pure poly (acrylate) resins synthesized by emulsion polymerization. For the production of Poly-Acrylate Binder, homo and copolymers were synthesized by emulsion polymerization using methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA) Acrylic Acid, and 2-Hydroxyethyl methacrylate monomers. In accordance with recipe calculation and preparation method our sample shows pretty good tensile and tear strengths, good abrasion resistance and stiffness, excellent chemical resistance and water repellence as well as air permeability.

Keywords: Emulsion, Acrylic Binder, Polymer, Crosslinking Agent, pigment.

1. Introduction

The binder film in pigment print is a three-dimensional structure, the third dimension is rather less important than the other two[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[2, 3]. 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 [4].

Binders are the mechanism used to keep the color on the fabric when using pigments for printing textiles. The choice of binders will always depend upon the final fastness requirements as well as the cost requirements of the process[5]. Choosing a binder for pigment coloration is a complex but critical step in developing a recipe which will meet very specific requirements[6, 7]. Polyacrylate is a chemical class of acrylate polymers derived from the polymerization of acrylic acid esters and salts. Each acrylate monomer contains a vinyl group: a pair of double-bonded carbon atoms attached to the carbon of a carboxyl group[8]. Due to the high reactivity of carbon double bonds, acrylates polymerize readily and are used in a variety of plastics, adhesives and chemical binder applications[9].

Pigment printing process is simple, energy saving, bright color, wide range of applications and environmental pollution, etc., have been widely used in printing and dyeing enterprises[10]. Polyacrylate binder for pigment printing most of the polymer emulsion with The emulsion adhesive in the textile printing can be divided according to their chemical structure polyacrylate, butadiene, vinyl acetate, and polyurethane, wherein the polyacrylate pressure-sensitive adhesive applications most commonly preparation conditions have a significant impact on the application performance of the adhesive, the Investigator to be a large number of trials, but is rare[11]. emulsified by most of the literature using a one-step emulsification, and theoretically, stars step the emulsion can be coated on the surface of the latex particles of sufficient emulsifier to reduce the interfacial energy between the latex particles and water, and enhance the stability of the emulsion[12]. Accordingly, in order to understand the preparation conditions on the performance of polyacrylate pressure-sensitive adhesive applications, the emulsion polymerization to prepare the Polyacrylate binder for pigment printing, and discuss the preparation of polyacrylate adhesive process conditions[13, 14].

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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[15, 16]. 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[17, 18].

2. Experimental

2.1. Materials

Hard monomers (HM): Hard monomers, characterized by high T_g values, include styrene, methyl methacrylate, ethyl acrylate and methyl acrylate. Styrene (S.T), Methyl Meth Acrylate (MMA) Supplied by Xiangcang Hongrun Co. Ltd.China. MMA Supplier: Hubei Ocean Biotech Co. Ltd China.

Soft Monomers (SM): Soft monomers, characterized by low T_g values, include n-butyl acrylate, 2-ethyl hexyl acrylate and iso-octyl acrylate. These monomers are longer chain alkyl acrylates and exhibit low water solubility (i.e., high hydrophobicity) Ethyl Acrylate (EA), Ethyl Acrylate (EA) Supplied: Changshu Jinfeng Chemical Co. Ltd China. Butyl Acrylate (BA) supplied Butyl Acrylate (EA): Hubei Ocean Biotech Co.Ltd China.

Functional/Cross-linking Monomers (FM/CM): Functional monomer with various functional groups, such as carboxyl or hydroxyl. Examples of functional monomers are acrylic acid and hydroxyethyl acrylate, which are very water-soluble[19]. Acrylic Acid, Acrylic Acid Supplied by : Zhengzhou Sino Chemical Co. Ltd China. 2-Hydroxyethyl methacrylate 2-Hydroxyethyl methacrylate Suppliers: Haihang industry (Jinan) Co.Ltd. China.

Emulsifier: Sodium Dodecyl sulfate (SDS) Emulsifier supplied by Zhengzhou Fuhong Biotech Co. Ltd. China. **Initiator:** Ammonium persulfate (APS). Deionized Water was used to emulsify the monomers. Ammonia is used to ensure the pH of water between 7-8.

2.2. Methods

All monomers are emulsified using emulsifiers (op10, k12) 20% Req. quantity H₂O + Surfactant. (stir it thoroughly for complete dissolution of emulsifiers). Transfer this into a three neck round bottom flask and Monomers First Soft (5 min) then hard. Dissolve upto 0.5% of oxidative or reducing agent in 20 ml of water. Add remaining 80% of calculated water. Raise the temperature 75°C and 1/3rd of APS solution (Initiator) & maintain this temperature for another 20-30mins. Observation color of solution turns to light blue. Remaining 3/6th part of emulsion from step1 and 2/3rd of APS solution (Initiator) from step2 added and temperature in range of 80-85°C to starting 90mins. Observation while adding emulsion and initiator light blue color of emulsion disappears. Maintain the bath temperature to 85°C and keep stirring for another 30mins. This step monomers are converted into emulsion polymer after 30mins. Observation After complete the process we found emulsion smells like sweet taste, it indicates completion of reaction. Then cool down the bath temperature below 40°C. Neutralize with ammonia water (20%) because due to acrylate the P^H will be 3-4 so to make it's P^H 7 add ammonia. Then filter the emulsion and dry the residue left at 105°C for 1h and then weighs it.

3. Result and discussion

3.1. Gel Rate

After completion of the reaction, all gels, rinse, and baked in an oven at 120° C for 2 h, cooled to room temperature in a desiccator, weighed.

$$X\% = \frac{M}{G} \times 100\%$$

Wherein: X - The gel fraction;

M - Weight of the gel;

G - Monomer weight.

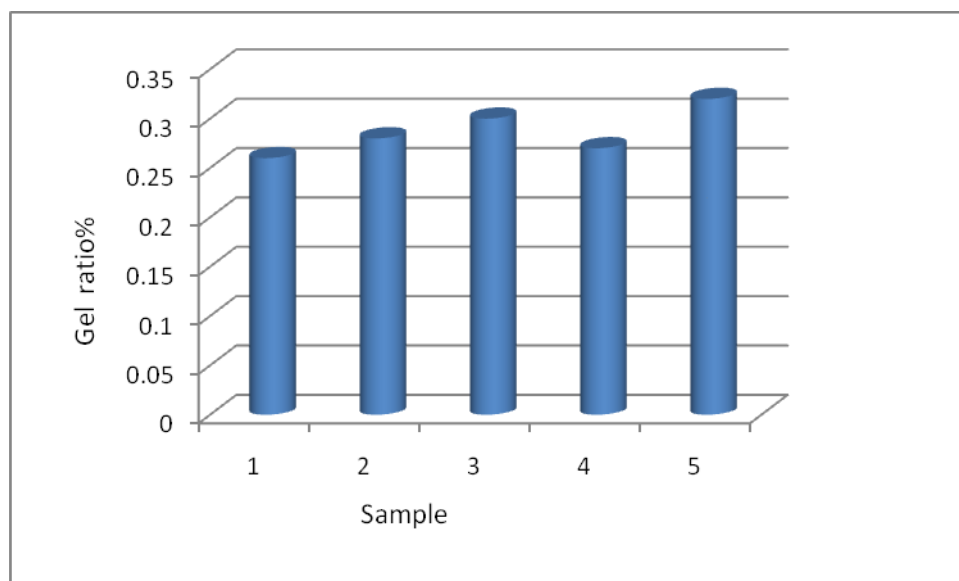


Fig. 1. Gel Ratio (%) of Prepared Binder Sample

5 samples were tested for this research where different results were found which may be due to the variation of chemical concentration as per specified chemicals in recipe. It is seen in figure-1 that Gel Ratio is maximum for sample 5 which may be due to the more concentration of Acrylate binder. Gel ratio is minimum for sample 1 where Acrylate binder is used for 1 gram per liter. The similar effect is seen for other samples too. It could be noted that less the gel ratio better the product (binder) & higher the gel ratio poorer the product quality.

3.2. Solid Content

Take approximately 5.5 gram of the sample and weigh it accurately in a glass dish. Place it in the oven for 4 hours at 110°C. After cooling in the desiccator, weigh the dish accurately.

$$\text{Solid Content (\%)} = \frac{G_1}{G_2} \times 100\%$$

G_1 = Initial weight of sample.

G_0 = Oven dry weight of the sample.

More Solid content percentage ensures that the product quality is good. Practically the % is found for 70% but 80% is considered as good binder. Normal treatment is performed at 60-80°C for 6-7 hours. Finally the solid content is found after the treatment of the polymer suspension at 140°C for 5 minutes.

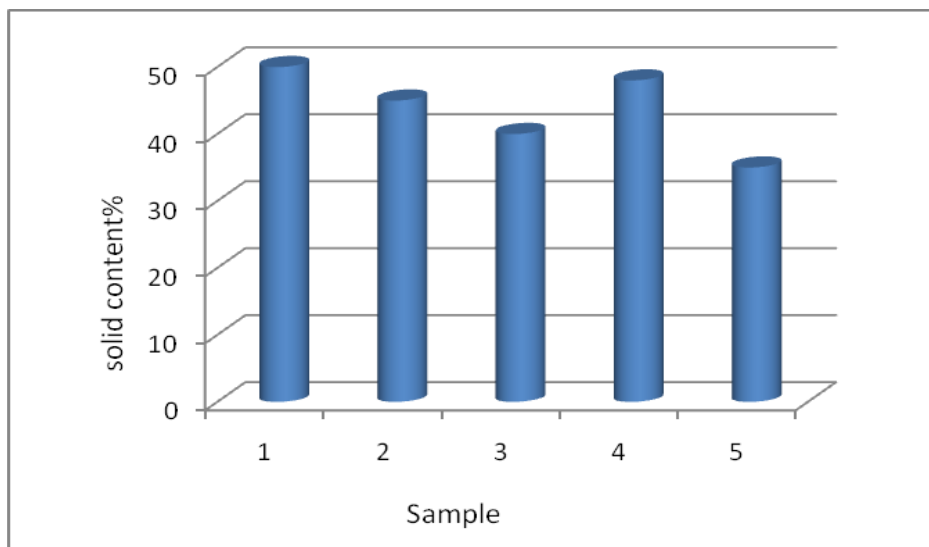


Fig. 2. Solid content (%) of Prepared Binder Sample

3.3. Monomer conversion rate

Draw 1 to 2 g emulsion to clean the weighing bottle, add 1 to 2 drops of a solution of hydroquinone, and baked in an oven at 120°C for 2h, cooled to room temperature in a desiccator.

$$C\% = [W(W_2 - W_1) / G_1 - Y] / G \times 100\%$$

Wherein: C- monomer conversion;

W₁ - Empty weighing bottle;

W₂ - Dried weighing bottle;

W - Weight of the material;

Y - The weight of non-volatile matter in the emulsion;

G₁- To learn the weight of the emulsion;

G - The total weight of the monomer.

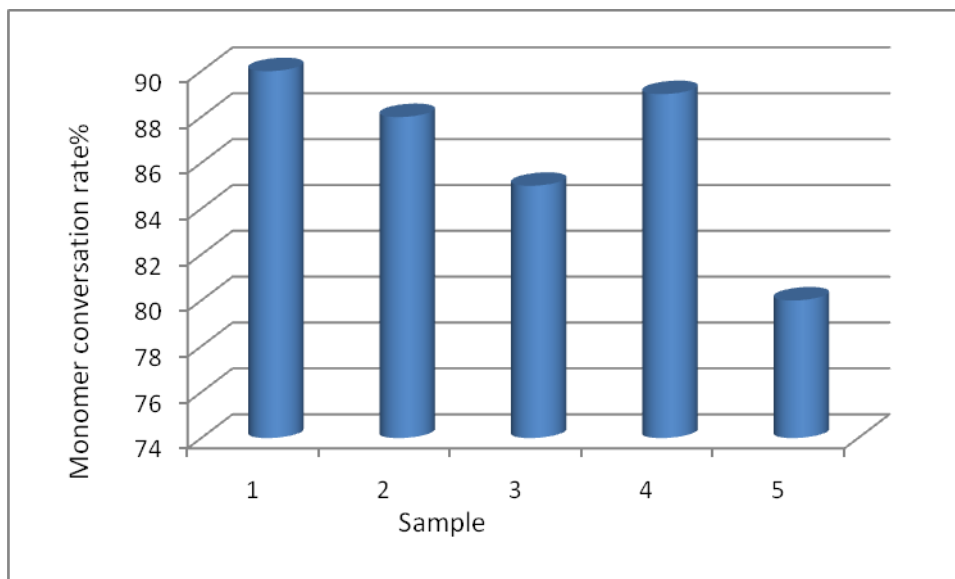


Fig. 3. Monomer Conversion Rate (%) of Prepared Binder Sample

More the monomer conversion rate the better the polymer product quality. The average monomer conversion rate found is more than 83% which ensures that the binder quality is good.

3.4. Surface Tension Test

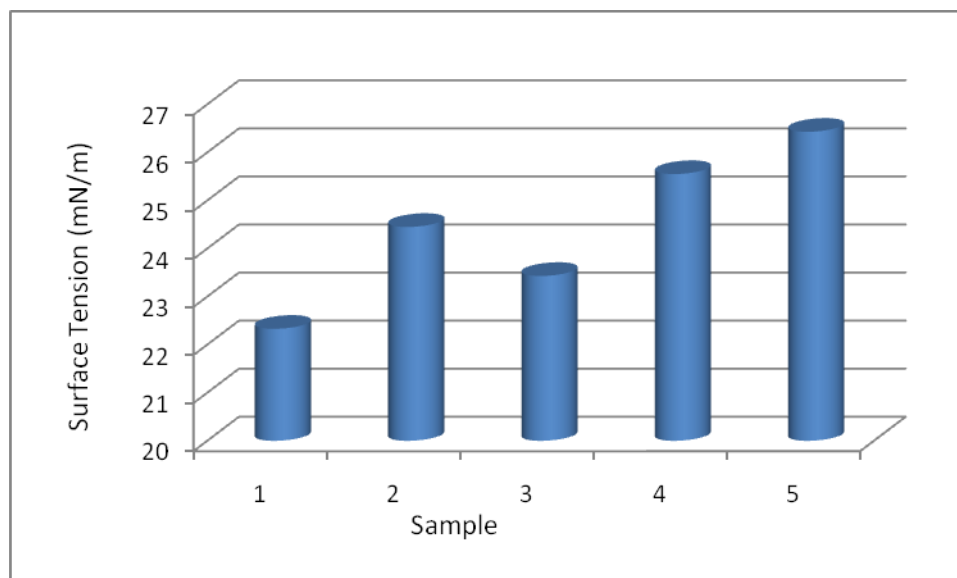


Fig. 4. Surface Tension (nM/m) of Prepared Binder Sample

Lower the surface tensions better the product quality. As all most all the surface tensions are within 27% so the binder quality is good

3.5. Dilution Stability Test

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. No change found in the emulsion.

Table 1. Emulsion Stability Test Result

Test Type	Sample-1	Sample-2	Sample-3	Sample-4	Sample-5
Acid Stability	Stable	Stable	Stable	Stable	Stable
Alkali Stability	Stable	Stable	Stable	Stable	Stable
Dilution Stability	Stable	Stable	Stable	Stable	Stable

3.6. 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. No change found, Emulsion is resistant to both acid and alkali.

Table 2. Emulsion Stability Test Result

Sample	P ^H					Emulsion Stability	Dimensional Stability
	P ^H -6	P ^H -7	P ^H -8	P ^H -9	P ^H -10		
Sample-1	Good	Excellent	Good	average	bad	Stable	Stable
Sample-2	Good	Excellent	Good	average	bad	Stable	Stable
Sample-3	Good	Excellent	Good	average	bad	Stable	Stable
Sample-4	Good	Excellent	Good	average	bad	Stable	Stable
Sample-5	Good	Excellent	Good	average	bad	Stable	Stable

A polyacrylate binder for pigment printing according to claim 1, the T_g should be between 10-25°C. If T_g greater than 25°C; then polymer becomes hard, as a result hand feel is not good. Also if the T_g goes less than 10°C the polymer become soft but hand fell is sticky. We have taken the hard monomers 55%; soft monomers 42%; Functional/cross-linking Monomers 3% and by applying Flory-Fox equation we have obtained the resultant T_g about 21°C.

A polyacrylate binder for pigment printing according to claim 1, the silicone is methyl trichlorosilane and methyl phenyl dichlorosilane are taken 12% of the total monomers will increase the mechanical properties, thermal oxidation, water resistance, excellent in weathering resistance, pretty good stain resistance, good air permeability. It also increase the cross linking between polymer chain.

A polyacrylate binder for pigment printing according to claim 1, de-ionized water will control the conductivity of the latex. A polyacrylate binder for pigment printing according to claim 1, ammonia water (5-7% of total deionized water) will adjust the pH 7-8.

3.7. Resultant Properties

- These binders offer the greatest durability, color stability, and dry/wet performance.
- Strong thickening ability, good water cohesive property.
- Good Evenness of the fabric.
- Good printing effect with precise printing edge.
- Toxic free like APEO and Formaldehyde
- Heat and oil resistance.
- Excellent pigment stabilization with color constancy.
- Acrylic binders have the widest range of fabric hand properties.

4. Calculation

Pigment Printing in Feel and Color Fastness of the Balance, Environmental Issues Have Not Been Applied Satisfactorily Resolved, And The Solution to These Problems Is the Core of Synthetic Environmentally Friendly Printing Binder, And Will Conduct Research in The Following Aspects. Reduce Product Cost. Accelerate The Development of Lower Temperatures Less Time Crosslinking of New Products, Especially from Non-Formaldehyde Crosslinking Agent and Catalyst for The Development of High Performance. Researches are performed into New Methods and New Polymeric Fixation Methods such as Emulsion Polymerization, Radiation Fixing and So On.

In this article hard monomers, soft monomers and function monomers were used to get the film having pretty good elasticity, very soft hand fell, 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 will ensure the good conversion rate of monomers & low solid content into the copolymer.

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