



The Effect of Diacetone Acrylamide and Adipic Acid Dihydrazide As A Crosslinker System on Styrene/Acrylate Emulsion

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Abstract

Styrene/acrylate emulsion polymers are the most popular polymers applied to paint. They have low volatile organic compounds (VOC) so they are eco-friendly. Recently, the preparation of crosslinked emulsion has become the most effective method to improve its properties. Herein, the crosslinked styrene/acrylate emulsion was prepared by using various ratios of diacetone acrylamide (DAAM) and adipic acid dihydrazide (ADH) as a crosslinker system, where DAAM: ADH (g: g) was 5:1.25, 5:2.5, and 2.5:1.25 to get samples C1, C2, and C3, respectively. The prepared emulsion was investigated by transmission electron microscopy (TEM), storage stability, viscosity, solid content, particle size distribution, and zeta potential. In addition, the films obtained from the as-prepared emulsion were characterized by Fourier transform infrared (FT-IR) and thermogravimetric analysis (TGA), also, their wet scrub resistance and gloss properties were determined. The data showed that the prepared emulsion has solid content in the range of 49 % and a density in the range of 1.01 g/cm³. The samples C1, C2, and C3 show particle sizes 148, 147, and 166 nm, respectively, and zeta potentials -49.7, -50.1, and -52.9 mV, respectively, while the blank (BL) shows particle size of 201 nm and zeta potential of -43.3 mV. Furthermore, sample C2 shows the best washability (18000 cycles) compared to sample BL (3300 cycles). In addition, the thermal stability, and gloss of the crosslinked latex were improved by the addition of crosslinkers in comparison with the BL.

Keywords: Styrene acrylic emulsion; Crosslinker; Diacetone acrylamide; Adipic acid dihydrazide..

1. Introduction

It has been reported that polymer emulsion paints based on styrene and acrylate monomers have several unique characteristics such as heat resistance, weather resistance, corrosion resistance, stain resistance, resistance to chemicals, gloss and color retention resistance, good film-forming, and being eco-friendly, so they can be used in important commercial application such as the paint industry [1-3]. Water sensitivity is one important disadvantage of latex coatings, and it is frequently associated with water whitening, adhesion loss, and poor durability. When latex particles dry to create a continuous transparent film, liquid water evaporates, but ionically charged components such as surfactants, initiators, and buffers stay trapped in the film's interstitial spaces and

function as a driving force for water migration [4, 5]. This migration promotes increased water absorption and coated film whitening. Even so, hydrophilic components are often required in regular commercial goods; hence, attempts to increase the water resistance of latex coatings by polymer structural modifications are widely encouraged. Crosslinking has been the most often employed method of mitigating these difficulties [4, 6].

In the last few decades, there has been a growing trend toward the development of the ambient crosslinking system, which has become the most effective method to improve the linear structure of ordinary emulsions. The selection of crosslinking systems and crosslinking monomers is very important for the coating, in which a high degree of crosslinking and good compactness of

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the coating prevent water absorption while enhancing adhesion, storage stability, and other properties [7]. Several ambient crosslinking reaction systems for latex coatings based on the functional groups and cure agents used in styrene acrylic emulsion have been published in recent years such as siloxane [8-12] and epoxy groups [13]. Furthermore, N-methylolacrylamide (NMA) was once the most frequently used as a crosslinking agent. However, adding NMA to emulsion causes the problem of formaldehyde being released under baking [14-17]. Also, N (isobutoxymethyl)-acrylamide (IBMA) [18], acetoacetate groups [19-21], and keto-dihydrazide/diamine [22] were used.

Recently, self-crosslinking via the reaction between carbonyl and hydrazide functionalities from copolymerized diacetone acrylamide (DAAM) and adipic acid dihydrazide (ADH) has attracted a tremendous amount of research activity **Fig. 1** depicts the typical keto-dihydrazide/diamine reagent is diacetone acrylamide (DAAM)/adipic acid dihydrazide (ADH) [23]. This is known as the keto-dihydrazide reaction [24]. In the process of emulsion polymerization, ketone carbonyl group is grafted to the emulsion backbone molecule, and then hydrazide or diamine is added through keto-dihydrazide reaction to obtain the self-crosslinking emulsion. The integration of self-crosslinking chemistry in styrene/acrylic emulsions is widely recognized for improving the mechanical characteristics, chemical resistance, and water resistance of the coating.

The ongoing investigation centers on diacetone acrylamide (DAAM) and adipic acid dihydrazide (ADH) as two promising and environmentally friendly inter-particle crosslinking agents for one-component self-crosslinking aqueous coatings at ambient temperature. The stability of the latex and the performance of the coatings, with a particular focus on water sensitivity, were assessed and juxtaposed with those achieved using the conventional ADH crosslinking agent.

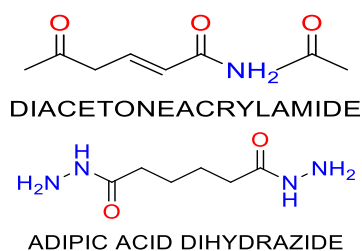


Fig. 1: Structure of Diacetone acrylamide and Adipic acid dihydrazide.

2. Material and Experimental Techniques

2.1 Materials

The crosslinkers diacetone acrylamide (DAAM) and adipic acid dihydrazide (ADH) were obtained from S.D Fine-Chem, India, and used as received. Styrene

(St), butyl acrylate (n-BA), acrylic acid (AA), and acrylamide (AAM) were purchased from Sigma-Aldrich and used after distillation in darkness under reduced pressure to remove the inhibitors, and stored at 5 °C. Sodium lauryl ether sulfate as an anionic surfactant, nonylphenol ethoxylate (NP30) as a nonionic surfactant, sodium acetate (NaHCO₃, SA), and potassium persulfate (K₂S₂O₈, KPS) were supplied from S.D Fine-Chem, India. Ammonia solution (25%) was of analytical grade and used as received without further purification. Deionized water was used in the synthesis of the latexes.

2.2 Procedure

The pre-emulsion was prepared from deionized water (272 g), anionic emulsifier (20 g), BA (252 g), St (219 g), AAM (6 g), and AA (12 g), which were added in a beaker equipped with continuous homogenization for 30 min at ambient temperature.

The copolymerization of St and BA was carried out by semi-continuous emulsion polymerization through a controlled water bath with a 1 L stainless steel reactor equipped with a reflux condenser, stirrer, and 2 feed streams. The first feed stream was for pre-emulsion and the other one was for the initiator solution. The preparation of seed emulsion was done with 100 ml of distilled water and 1 g sodium acetate introduced into a glass reactor, followed by NP30 (5 g), then 29 ml of distilled water and 1.3 g of KPS as the initiator. The mixture was stirred at 80±5 °C. Subsequently, 10% of the attained pre-emulsion was fed over 30 minutes after performing the seed emulsion. After the addition was completed, the reaction mixture was stirred and heated for another 10 min. The typical recipe for the crosslinked latex prepared is listed in **Table 1**.

The remaining pre-emulsion was introduced over 240 minutes while an initiator solution (0.7 g KPS in 50 g deionized water) was loaded over 250 minutes to afford the emulsion latex. After the various ingredients had been completely added, the emulsion was maintained at 80 °C for 90 minutes and then the temperature was raised to 90 °C for 15 minutes to ensure that all monomers had reacted. Finally, the obtained latex was cooled to 45 °C and then the pH was adjusted to 9 using ammonia to get sample BL. The previous method was repeated in the presence of the crosslinker system, where DAAM: ADH (g: g) was 5:1.25, 5:2.5, and 2.5:1.25 to get samples C1, C2, and C3, respectively.

2.3 Characterization

2.3.1 Solid content test equation

The samples were dried in an oven at 105 °C to a constant weight. The solid content (S.C.) was determined from the following equation:

$$SC = \left(\frac{S_f}{S_i} \right) * 100\%$$

Where S_i and S_f are the initial and final weights of the sample.

2.3.2 Coagulum content equation

The filterable solids were dried and weighed, then the coagulum content was calculated according to the following equation:

$$\text{Coagulum content (\%)} = \left(\frac{M_f}{M_t} \right) * 100\%$$

Where M_f and M_t are the weights of dried filterable solids and the total amount of emulsion, respectively.

2.3.3 Viscosity test

The viscosity of the latex was determined by using a Brookfield viscometer; model DV-E (Middleboro, MA, USA). For the measurement, 500 mL of sample latex was poured into a 600 ml beaker. The analysis condition was fixed by using spindle "S5" at 20 rpm at around 25 to 26 °C. Thereading was taken only after it showed a constant value.

2.3.4 Storage stability testing

The final self-crosslinking latex binders were stored at 50 °C for 60 days. Their storage stability was evaluated from the point of view of changes in the apparent viscosity. The apparent viscosity of latexes was determined at 25 °C by the use of Brookfield DV-E (Middleboro, MA, USA)

2.3.5 The pH determination

The pH testing for as-prepared samples was performed at 25 ± 1 °C using the digital pH meter HI2202 (UBA (Hanna Instrument Baltics) Limena, Italy).

2.3.6 Transmission electron microscopy (TEM)

The morphology of the prepared samples was examined using Transmission Electron Microscope (TEM; JEOL-2100, Japan) operated at 80 kV with magnification of 600000 and a resolution of 0.2 nm.

2.3.7 Fourier transform infrared (FT-IR)

The copolymer composition of dried samples was recorded by FTIR spectra in the range of 400– 4000 cm^{-1} on 8400S FT-IR Spectrophotometer (Shimadzu, Jaban).

2.3.8 Zeta potential and size distribution

A particle size analyzer (Nano-ZS, Malvern Instruments Ltd., UK) was used to determine the average particle size distribution and zeta potential of as-prepared samples. The sample was diluted first using distilled water and then sonicated for 10-20 minutes just before the assessment by the particle size analyzer.

2.3.9 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed with a Shimadzu TGA-50 thermogravimetric analyzer (Columbia, EUA) under nitrogen gas at 10 °C/min heating rate in the range between room temperature and 700 °C.

2.3.10 Differential scanning calorimetric analysis (DSC)

The thermal properties of each copolymer sample were measured using a differential scanning

calorimetric analysis (DSC). DSC was recorded on TA Instruments DSC Q20 V24, 11 Build 124. All samples were heated with a scan rate of 10 °C/min over a temperature range of 30 to 700 °C under a nitrogen atmosphere.

2.4 Preparation and characterization of coatings

Water-based coating formulations were prepared through a two-step process. Initially, water, pigment, filler, and an antifoaming agent were combined and homogenized using high-speed mixing. Subsequently, the polymer latex was gently introduced into the resulting suspension from the first step, with mixing performed at a lower speed to ensure uniform dispersion. The detailed compositions of matte and gloss coatings are presented in **Table 2**.

The Elcometer 3540 four-sided film applicator (Elcometer Inc., USA) was used to apply the self-crosslinking latexes to glass and metallic panels. Wet coating films had a thickness of 200 μm . There was no coalescing agent applied. At room temperature (23 °C), the coatings were air dried. Gloss, wet scrub resistance, adhesion, impact resistance, and water absorption were all assessed for the coating films.

2.4.1 Wet scrub resistance (washability) test

Apply the paint samples to be tested on Leneta Scrub test of suitable dimensions (200 μm) using the SIMEX film applicator. Let it dry for one week before doing the washability test. Put the painted panel into the wet abrasion scrub tester REF 903 (Sheen Instruments Ltd, England) and apply the test according to ASTM D 2486.

2.4.2 Gloss test

The gloss of the coatings was measured with a Statistical Mini Gloss meter model Elcometer 406L (Twosome Trading Corp. *Taipei* Taiwan) according to ASTM D 1455 using a gloss-measuring geometry at 60 °C.

3. Results and discussion

The reaction between DAAM and ADH is facilitated by the removal of water and the concurrent decrease in pH, induced by the evaporation of ammonia or amines during the film-forming process. The ambient crosslinking latexes undergo rapid crosslinking at room temperature and do not necessitate the addition of extra crosslinkers before use. Consequently, this keto-hydrazide reaction offers a notable advantage of fast and ambient-temperature crosslinking in functionalized PSA/BA [25]. The overall mechanism of this reaction is illustrated in **Fig. 2**.

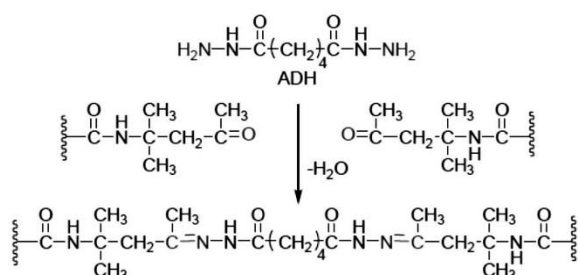
The semi-continuous technique was used to produce styrene acrylic polymers. With a conversion of greater than 95%, contained a negligible amount of coagulum (0-0.5 wt.%), which indicated good colloidal stability during the polymerization, yielding stable, semitransparent, and blue latex. **Table 3** summarizes the results of the polymer physical analysis. **Table 3** shows that the polymer latex was synthesized with a high solid content and a pH value of 7-8, which is suitable for paint manufacture.

Table 1. The typical recipe for the latex emulsion preparation.

Ingredients	Flask charge (g)	Crosslinked pre-emulsion (g)	Blank
Distilled water	68.5	272	272
Anionic surfactant	-	20	20
Nonionic surfactant	5	-	-
SA	1	-	-
St	-	219	219
BA	-	252	252
AAm	-	6	6
AA	-	12	12
DAAM	-	2.5-5	-
ADH	-	1.25-2.5	-
KPS	-	2	2

Table 2. The typical recipe for the latex emulsion preparation.

Ingredients	Paint wt. %
Latex	20-40
Propylene glycol	2
Hydroxy ethyl cellulose	0.6
Ammonia	0.2
Defoamer	0.1
TiO ₂	46.3-35

**Fig. 2:** Crosslinking reaction of DAAM latex particles with the crosslinking agent ADH.**Table 3:** Physical analysis results of the prepared polymer latex.

	Solid Content (%)	pH	Coagulation (%)	Density @ 25 °C
Blank	49.1	7.8	0.2 %	1.0206
C1	49.1	8.8	1.0 %	1.0170
C2	50	8.7	0.5 %	1.0165
C3	49.3	7.9	Nil	1.0183

The chemical structure of the prepared latex films (BL, C1, C2, and C3) was investigated using FT-IR spectroscopy, as shown in **Fig. 3**. It can be seen that the spectra display a typical pattern of acrylic polymers with a characteristically strong absorption band of the C=O bond at 1727cm⁻¹ assigned to the carboxylic acid ester group. A broad band of OH

stretching observed at 3250 cm⁻¹ is due to the free carboxylic group (from AA) and hydrogen bonded water. The absorption bands at 2961 cm⁻¹ and 2873 cm⁻¹ can be attributed to asymmetric (C-H) and symmetric (C-H) vibrations of CH₃ group, respectively. The weak absorption band of (C-H) and a shoulder of (C-H), which appeared at 2934 cm⁻¹ and 2853 cm⁻¹, respectively, were related to vibrations of the CH₂ group [26, 27]. The characteristic absorption band at 1537 cm⁻¹ appearing in all the spectra was assigned to bending vibration of N-H bonds and proves that DAAM was copolymerized with acrylic monomers [28]. All the crosslinked latexes further manifested a weak absorption band at 1652 cm⁻¹ corresponding in all probability to N=C vibration, which indicates that the keto-hydrazide self-crosslinking reaction proceeded in latex polymers unlike the uncrosslinked latex, which shows the absence of this peak [4]. The spectrum data signifies the following bands: the aromatic C-H stretching frequencies at 3060-3027 cm⁻¹, and 1063-1028 cm⁻¹, C=C ring stretching at 1601-1451 cm⁻¹ [10].

The examination of the zeta potential curve derived from styrene acrylate copolymer emulsions yields critical insights into their surface charge properties, which are fundamental for grasping their stability and behavior within colloidal systems. Zeta potential analysis specifically investigates the electrical potential at the interface of the particles, illuminating

aspects related to dispersion stability and potential interactions between particles.

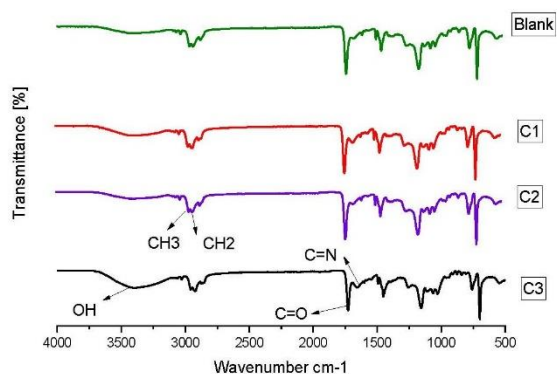


Fig. 3: FTIR spectra of the prepared latex

This analytical approach proves indispensable for understanding the overall stability and efficacy of styrene acrylate copolymer emulsions across a broad spectrum of applications including coatings, adhesives, and paints. Through the interpretation of the zeta potential curve, significant details concerning stability, sensitivity to pH variations, and the impact of additives can be extracted, providing essential direction for the design and enhancement of formulations [29].

The analysis of Zeta potential in these lattices reveals a clear trend: as the concentration of crosslinker increases, so does the stability of the latex, particularly when compared to the baseline Zeta potential of the BL. Notably, all measured values consistently surpass ± 40 mV, indicating robust stability across all prepared latexes, as summarized in **Fig. 4**. This trend suggests that the incorporation of crosslinker strengthens the electrostatic repulsion between particles, thereby reducing the likelihood of particle aggregation and enhancing overall colloidal stability [30]. Despite variations in crosslinker concentration, the Zeta potential values consistently remain comfortably above the stability threshold.

In conclusion, the results indicate a positive correlation between increasing crosslinker concentration and latex stability. Moreover, the consistently high Zeta potential values across all prepared latexes affirm their suitability for a wide range of applications, underscoring their resilience and stability.

Particle size distribution was assessed to ascertain whether agglomerates disintegrated during synthesis. The styrene acrylate polymer blank, synthesized sans crosslinker, exhibited a particle size ranging around 201. Data presented in **Fig.5** revealed that C1, C2, and C3 exhibited sizes of 148, 147, and 166, respectively, with a difference in the amount of DAAM. Comparison with the BL, which displayed a size distribution of 201, indicated a noticeable reduction in size distribution for C1 and C2, attributed to a decrease in DAAM content from 0.5% to 0.25%. This decrease in size distribution was also observed in C3; however,

its size distribution remained higher than C1 and C2 due to the lower DAAM content. Hence, it can be inferred that an increase in DAAM concentration results in a reduction in emulsion particle size.

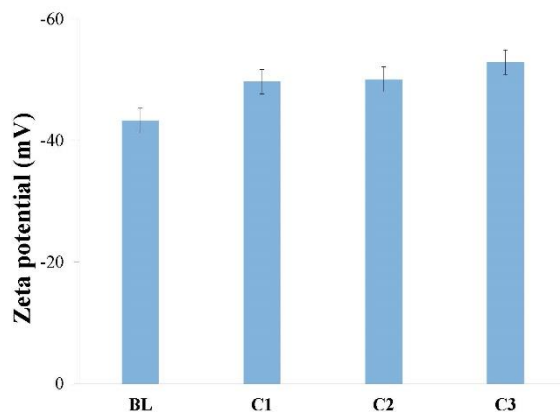


Fig. 4: Zeta Potential for prepared latexes

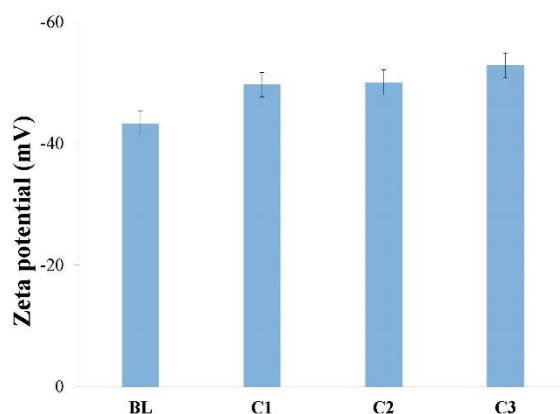


Fig. 5: Particle size distribution for prepared latexes

The morphology of both BL and crosslinked latex particles was analyzed. Conventional transmission electron microscopy (TEM) offers detailed information in real space, particularly in localized areas, allowing for the examination of morphology and defect structures. Moreover, it is essential for determining the nature of the latexes. The morphology and structure of the latex particles synthesized under various polymerization conditions were investigated using TEM, as depicted in **Fig. 6**.

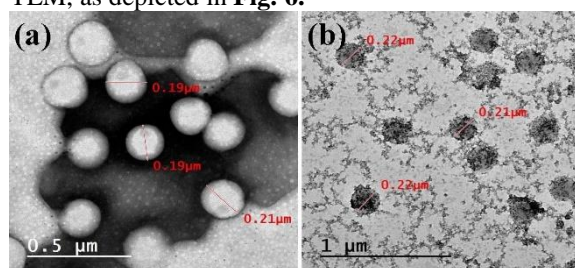


Fig.6: TEM images of the blank (a) and C2 (b).

The thermal degradation temperatures of as-prepared polymers, as extracted from TGA and DSC analyses, are presented in **Table 4** and **Figs. 7 and 8**. The polymer exhibits thermal stability up to 300 °C. The

data was represented as TGA curves (weight loss % versus temperature in °C). It was seen from **Fig. 7** that, both crosslinked and uncrosslinked polymers showed different thermal degradation behaviors. From 355 °C onwards, the uncrosslinked polymer starts to degrade at 355 °C to lose 95.1 % at the end at 437 °C, where the crosslinked latexes show an increase in temperature from 355 to 367, 370, and 382 °C and a decrease in weight loss from 95.1 % to 93.8, 91.8, and 90.7% for samples C1, C2, and C3, respectively. The crosslinked latex (C1, C2, and C3) showed higher thermal stability than BL, which can be attributed to lesser crosslink density [31]. The Differential Scanning Calorimetry (DSC) analysis, as depicted in **Fig. 8**, illustrates a consistent pattern. It reveals that the temperature at which the process initiates, starting at 417°C with the BL sample, gradually rises as the concentration of crosslinker increases, reaching 420 °C with sample C3. This data indicates a direct relationship between the amount of crosslinker and the onset temperature of the process detected by DSC and TGA. Specifically, higher concentrations of crosslinker correspond to higher initiation temperatures. The observed increase in thermal stability indicates the occurrence of the carbonyl-diamine crosslinking reaction. This reaction results in the formation of C=N groups, which require higher temperatures to break down [24].

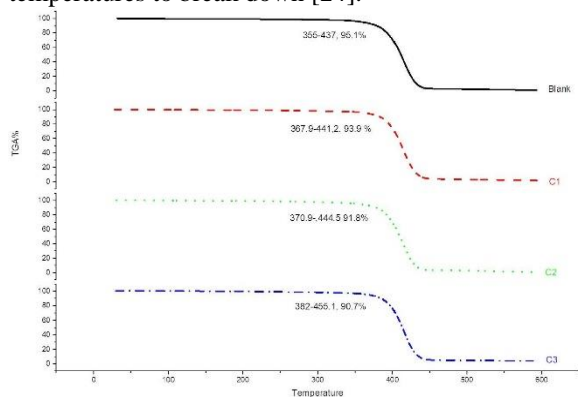


Fig. 7: TGA thermogram of Blank, C1, C2 and C3

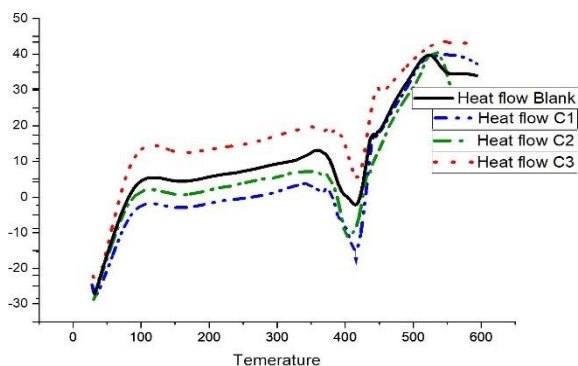


Fig. 8: DSC thermogram of Blank, C1, C2, and C3.

Table 4: TGA and DSC for Blank and crosslinked latexes C1, C2 and C3

Sample	Temperature range (C°)	Weight loss (%)	Heat Flow (C°)
Blank	355 - 437	95.1	417
C1	367- 441	93.9	412
C2	370 - 444	91.8	402
C3	382 - 455	90.7	420

The stability of latexes was assessed based on changes in latex viscosity before and after 60 days of storage at 50 °C [32]. **Fig. 9** summarizes the measures' results. Despite the facts discovered, no significant changes in any of the evaluated characteristics were seen after storage, demonstrating the innovative one-component self-crosslinking compositions based on DAAM inter-particle crosslinkers and ADH's high stability.

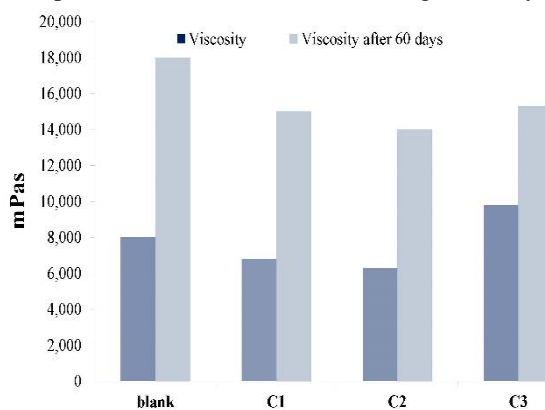


Fig. 9: Characteristics of standard and self-crosslinking latexes differing in the crosslinker type before and after storing at 50 °C for 60 days.

Table 5 presents the impact of inter-particle self-crosslinking using DAAM and ADH as crosslinking agents on the properties of the resulting coatings. Coating films with a wet thickness of 200 µm were applied onto glass panels by drawing down the self-crosslinking latexes using a blade applicator. No coalescing solvents were employed in this process. Subsequently, the films were cured at room temperature (23 °C) [32].

The gloss of the coatings was quantified at a 60° angle using a digital gloss meter. A slight increase in gloss was observed with an increasing degree of crosslinking of the film in the range of 44-48, as shown in **Table 5**. The optimal outcome was achieved when the ratio of DAAM to ADH content was 2:1%. Emulsion paint applied on a dark background demonstrated the disappearance of the black fraction after coating. **Fig. 10** (A-D) illustrates notable differences among samples containing varying concentrations of DAAM and ADH indicating distinct outcomes. It's important to note that the washing and

abrasion resistance tests were conducted by applying films on a plastic surface measuring 10 cm in width and 30 cm in length using a 200 μm applicator [33]. These films were then placed on the testing apparatus for 48 hours, with a velocity of 37 ± 1 rpm, until no abrasion was visible on the films. The measurement of the washing apparatus is determined by the number of brush rounds on the paint film. Typically, paints with a homopolymer binder exhibit a washing and abrasion resistance of around 1000 cycles, while those with copolymers demonstrate a higher resistance ranging from 5000 to 7000 cycles [33]. However, **Table 5** illustrates the stabilities of these paints reaching up to 13000 rounds attributed to the presence of DAAM and ADH crosslinker. Furthermore, **Fig.10** demonstrates that as the concentration of DAAM to ADH increases, the washing and abrasion resistance also increase accordingly.

Table 5: Comparison of final properties of coating films based on standard and self-crosslinking Latexes differing in the amount of crosslinker.

	Gloss at 60° (G.U.)	Wet Scrub
Blank	44	3300 cycles
C1	48	13500 cycles
C2	48	18000 cycles
C3	45	10000 cycles

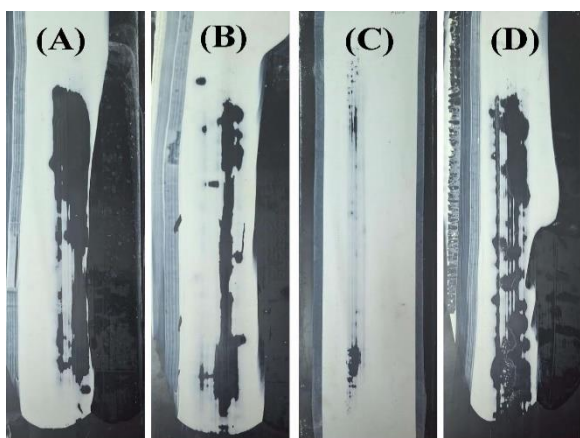


Fig. 10: (A-D) illustrates notable differences in wet scrub between prepared latexes (A) Blank, (B) C1, (C) C2, (D) C3.

4. Conclusion

A crosslinked system of diacetone acrylamide (DAAM) and adipic acid dihydrazide (ADH) was used in various ratios to create crosslinked polyacrylate emulsions via semi-continuous seeded emulsion polymerization. FTIR measurement demonstrated the occurrence of a chemical reaction between the crosslinker and acrylate monomers. In addition, the crosslinked polyacrylates showed high thermal stability and good washability compared to uncrosslinked ones. Furthermore, the best ratio of DAAM to ADH (g: g) was 5:2.5. Therefore, emulsion paints made from styrene-acrylate polymers that have

been crosslinked may find use in interior ornamental paints. Therefore, attention must be directed to developing new crosslinkers that can be used in the preparation of polyacrylate emulsions that are applied to paints.

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