Cureus Journal of Engineering

Open Access Original Article

Shell Protection of Styrene-Rich Core Polymer for Exterior Paint Durability

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Received 02/18/2025
Review began 02/19/2025
Review ended 03/04/2025
Published 03/19/2025

DOI:
https://doi.org/10.7759/s44388-025-03368-8

Abstract

The study addresses the inherent photo-oxidative degradation of styrene-rich polymers by altering their morphology. The synthesis of core-shell polymers of styrene and acrylates by emulsion polymerization process has been reported. The core polymers are styrene-based copolymers with a glass transition (Tg) of 60°C, while the shell polymers are polyacrylates with a Tg of 0°C. The core-shell structure of the polymers is confirmed by transmission electron microscopy. The emulsion polymers are characterized by various properties, including particle size, viscosity, % non-volatile material, free monomer content, and differential scanning calorimetry analysis. These emulsion polymers are then evaluated for use in exterior paint. The paint properties examined include tensile strength and elongation at break. Additionally, the yellowing behavior of paint containing styrene-rich latex particle is studied using QUV testing. The results indicate that it is feasible to prepare non-yellowing styrene-rich polymer for use in exterior durable paint.

Categories: Advanced Manufacturing Technologies, Advanced Materials, Polymer Science and Engineering
Keywords: core-shell latex, emulsion polymerization, non-yellowing, exterior durability, styrene-acrylate polymer

Introduction

Styrene acrylates are the choice of materials when looking for water-based coatings in decorative paints due to their high chemical and water resistance and low cost [1-3]. The major disadvantage of styrene-acrylic emulsion polymers is that they undergo photo-oxidative degradation during exposure to ultraviolet (UV) light and thermo-oxidative degradation during storage and exposure to hot environment [4,5]. This degradation causes breaking of polymer chains and reduces the molecular weight and forms the phenyl and hydrogen radicals. Molecular weight reduction and formation of radicals cause rapid yellowing of the coating and gradual embrittlement, which results in poor mechanical properties of the coating and poor esthetics [6].

Nearly all the synthetic polymers undergo degradation during exposure to UV light and turn yellow. The study shows that this yellowing of polystyrene (PS) can be prevented by modification in the morphology of the particle such as incorporation of heat stabilizers, free radical scavengers, light screeners, peroxide decomposers, and photostabilizers [7].

The exterior durability can be enhanced by using fluoromonomers [8]. UV-absorbing silicon fluorinated emulsions were reported for achieving a long-term UV resistance coatings [9].

However, although fluoro and organo-siloxane monomers improve the exterior durability, their handling, limitations on using large quantities for copolymerization in emulsion polymerization, and high price hinder their large-scale utilization.

Nanomaterials such as $FeTiO_3$, CeO_2, TiO_2, and ZnO are used to enhance the weather-resistance of exterior paint [10-13]. However, some of their properties, such as long-term stability and compatibility with paint, are still challenging.

There are several research papers on the success of theory and synthesis process for the core-shell emulsion. However, these studies focused only on core-shell structure. In the present work, an effort has been put into synthesizing styrene-rich latex particles which would overcome the yellowness of paint.

Materials And Methods

Experimental

Materials

How to cite this article
Maiti J, Joshi A, Raghavendra V B, et al. (March 19, 2025) Shell Protection of Styrene-Rich Core Polymer for Exterior Paint Durability. Cureus J Eng 2 : es44388-025-03368-8. DOI https://doi.org/10.7759/s44388-025-03368-8

Styrene, butyl acrylate (BA), methyl methacrylate (MMA), cyclic trimethylpropane formal acrylate (CTFA), Hydroxy butyl acrylate (HBA), methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), vinyl trimethoxy silane (VTMO), tricyclodecane dimethanol diacrylate (TDD), potassium persulfate (PPS), sodium bicarbonate (SBC), and water (DMW) were used as received.

Latex Synthesis

Core-shell latex: The polymerization was done in a glass kettle. The water, surfactants, were poured into the glass kettle and it was heated to 80°C under stirring.

An amount equivalent to 5% of the pre-emulsion (PE1) was added to the kettle at 80°C and then initiator was added. The remaining PE1 was added to the kettle over 2 hours. PE2 was added to the kettle over 2 hours. After that, tert-butyl hydroperoxide (TBHP) and sodium formaldehyde sulfoxylate (SFS) were added one by one to the kettle. The reaction was continued for another 45 minutes. Then, it was cooled down to 45°C, and ammonia was used for maintaining the pH of the emulsion.

The above procedure with single PE was followed for non-core-shell styrene acrylate latex and pure acrylate latex. The recipes are given in Table *1*.

Ingredients	Core-shell latex	Non-core-shell latex	Pure acrylic latex
	Grams	Grams	Grams
Monomer for pre-emulsion (PE1)			
Styrene	18	27	-
MMA	-	-	27
BA	5.25	21	21
MAA	0.25	0.75	0.75
EGDMA	0.15	-	-
VTMO	-	0.3	0.3
Monomer for pre-emulsion (PE2)			
BA	12.6	-	-
CTFA	2	-	-
TDD	0.15	-	-
MMA	7.65	-	-
HBA	2	-	-
MAA	0.5	-	-
VTMO	0.15	-	-
Other ingredients			
Dowfax 2A1	1.0	1.0	1.0
Atpol 5731/70N	0.75	0.75	0.75
SBC	0.1	0.1	0.1
PPS	0.2	0.2	0.2
TBHP	0.05	0.05	0.05
SFS	0.05	0.05	0.05
Liquid ammonia	0.75	0.75	0.75
Kathone LX 150	0.2	0.2	0.2
DMW	48.2	47.85	47.85

TABLE 1: Emulsion formulation

MMA, methyl methacrylate; BA, butyl acrylate; MAA, methacrylic acid; EGDMA, ethylene glycol dimethacrylate; VTMO, vinyl trimethoxy silane; CTFA, cyclic trimethylpropane formal acrylate; TDD, tricyclodecane dimethanol diacrylate; HBA, Hydroxy butyl acrylate; SBC, sodium bicarbonate; PPS, potassium persulfate; TBHP, tert-butyl hydroperoxide; SFS, sodium formaldehyde sulfoxylate; DMW, water

The paint recipe is given in Table *2*. Paints were made with core-shell polymer, non-core-shell polymer, and pure acrylate-based polymers.

Material used	Weight %
Binder	35
Opaque polymer	10
Water	21.9
Surfactant (anionic)	0.5
Rutile TiO_2	16
Defoamer	0.1
Marble powder (10 micron)	7
Calcined clay	6
Coalescent	1
Cellulose thickener	0.5
Antifungal	1
In-can preservative	1

TABLE 2: Formulation of the paint

Characterization

Particle Size Measurement

Zetasizer Nano ZS (Malvern) was used to measure the particle size of latex. A total of 50 mg of latex sample was dispersed in 5 mL of DMW solutions.

Differential Scanning Calorimetry (DSC)

DSC D250, TA instruments, was used for DSC analysis. A 10-15 mg sample was put in an aluminum pan and heated in the temperature range of -80 to 150°C at a heating rate of 10°C/min in an N_2 atmosphere.

Transmission Electron Microscopy (TEM)

A microscopy study of the samples was conducted using Tecnai G2 20 S-TWIN High Resolution Transmission Electron Microscopy (HR-TEM) from Field Electron and Ion (FEI) Company in cryo-mode. The pH value of the emulsion was 9 and was stained with 2% phosphotungstic acid (PTA) prior to imaging. A drop of the stained emulsion was freeze-dried and imaged in TEM at 200 kV.

Results

Results and discussion

Preparation of Core-Shell Latex

The polymerization was done in seeded emulsion polymerization with a two-PE system. Styrene, BA, and MAA were polymerized first to form the core, then acrylate monomers were polymerized to generate the shell. The core was crosslinked with EGDMA and shell was crosslinked with VTMO and TDD.

Latex Physical Properties

The properties of core-shell, non-core-shell, and pure acrylate latexes are given in Table 3. The solid content (NVM) of all the emulsion lies in the range of 49-50%. The viscosity is in the range of 70-77 grams. The particle size is in the range of 125-147 nm. The dry film of latexes is transparent, and polymers have excellent freeze-thaw, mechanical, and thermal stability. The weight per liter (WPL) of emulsion is in the range of 1.03-1.07.

No.	Properties	Core-shell styrene acrylate latex	Non-core-shell styrene acrylate latex	Pure acrylate latex
1	Appearance	Bluish white free flowing liquid	Bluish white free flowing liquid	Bluish white free flowing liquid
2	Dry film properties			
	i) Clarity	Clear	Clear	Clear
	ii) Tack	Tack free	Tack free	Tack free
	iii) Bits	No bits	No bits	No bits
3	% NVM @120°C /1 h	49	49.03	50.4
5	WPL	1.05	1.03	1.07
11	Viscosity on Stormer (gm)	84	70	72
12	Free monomer content (%)	(BA= 0.007)	(BA= 0.1559)	(BA= 0.01081)
13	Particle size (nm)	125	139.2	147
14	Accelerated stability on oven (55°C/15 days)	Pass	Pass	Pass
15	Minimum film forming temperature (°C)	17.7	26.4	23.1
16	Tg (°C)	60 & 0	27.7	25
17	Electrolytic stability	Pass	Pass	Pass
18	Freeze-thaw stability	Pass	Pass	Pass

TABLE 3: Synthesized binders and their physico-chemical properties

NVM, non-volatile material; BA, butyl acrylate; WPL, weight per liter

Minimum film Forming Temperature (MFFT)

Minimum film formation temperature (MFFT) for different copolymer latexes is close to their relative Tgs [14]. MFFT of core-shell latex is 17.7°C, whereas non-core shell and acrylate latexes show 26.4°C and 23.1°C, respectively. The results revealed that core-shell latex having high Tg of core and low Tg of shell, showed lower MFFT compared to non-core-shell and pure acrylate systems. Theoretical studies of latex film formation disclose that the outer surface of latex particles has an influence on the film formation process [15]. Therefore, by controlling shell Tg of latex particles, it is possible to optimize the MFFT of polymer.

The Morphology Analysis by Transmission Electron Microscopy

The internal morphology of the emulsion was imaged using HR-TEM as displayed in Figure *1*. The PTA-stained acrylic part appears dark in the images while PS part is brighter, forming sea-island like morphology [16]. However, the PTA-stained standard sample shows no phase separation, indicating both acrylic and styrene phases are mixed homogeneously.

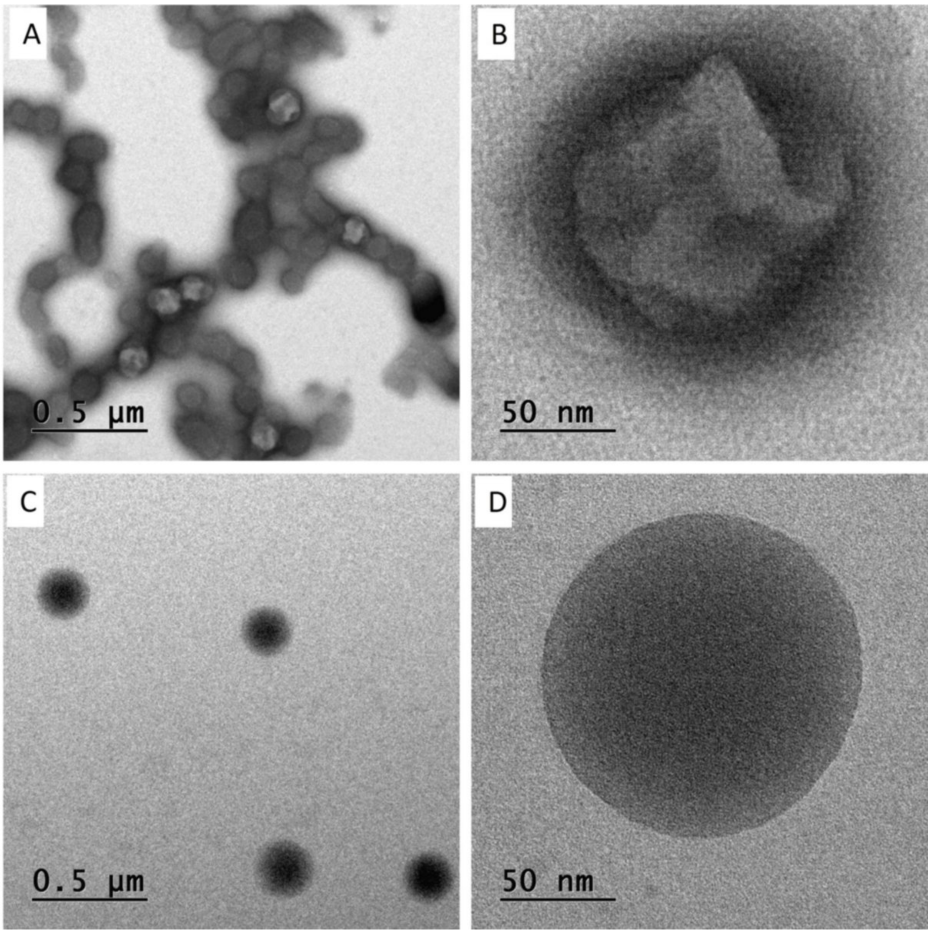

FIGURE 1: TEM images of emulsion: (A) low magnification and (B) high magnification of core-shell styrene acrylic emulsion; and (C) low magnification and (D) high magnification non-core-shell styrene acrylic emulsion

TEM, Transmission Electron Microscopy

Differential Scanning Calorimetry (DSC) Study

Figure *2* shows the DSC thermogram of core, core-shell, and non-core-shell latex samples. For core sample as shown in thermogram A, the glass transition was found at 65°C with ΔCp value of 0.32 J/g °C. In case of core-shell sample, thermogram B shows two distinct glass transitions at 0°C and 60°C, respectively, indicating the presence of two different, mostly immiscible phases in the sample. Here, the Tg of the core is slightly shifted to lower temperature, possibly due to the initial diffusion of shell phase toward the core at the core-shell phase boundary. Single transition was observed at 27.7°C in the case of non-core-shell latex sample (thermogram C).

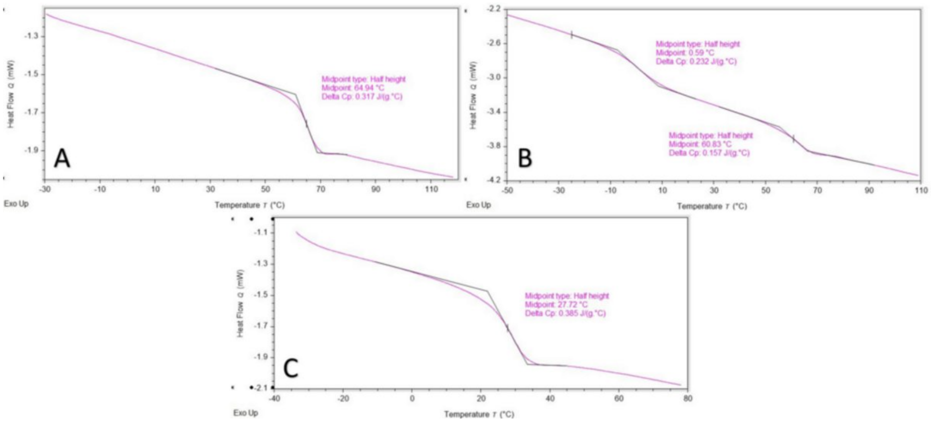

FIGURE 2: DSC thermogram of (A) core, (B) core-shell sample, and (C) non-core-shell sample

As melting enthalpy is used for quantitative analysis of crystalline phase, change in Cp at glass transition can be used for amorphous materials. ΔCp value of the pure core sample was 0.32 J/g °C, while the value of ΔCp at second Tg in core-shell sample is around 0.16 J/g °C. This shows that the weight fraction of core phase in core-shell sample is reduced by 50%. In other words, the weight fraction of the core to the shell in this core-shell sample might be around 1:1. This estimation of weight fraction is in line with the solid content calculated based of monomer addition.

Discussion

Evaluation of mechanical properties of paint films

The paint films were casted on silicone release papers for studying their mechanical properties. The ASTM D4708 test method was followed for evaluating the mechanical properties of paints. Having high tensile strength in paint is generally beneficial as it enhances durability. However, it is essential to balance tensile strength with flexibility to avoid brittleness. Having high elongation properties in paint is generally advantageous, as it enhances flexibility, resistance to cracking, and overall durability. However, it is crucial to ensure a balance between elongation and tensile strength to avoid potential failure in high-stress application. The paint with core-shell latex showed high tensile strength with low elongation (Table *4*), whereas non-core-shell and acrylic latex-based paint exhibited high elongation with moderate tensile strength. There is drastic decrease in elongation for core-shell latex paint because of high Tg of core polymer with substantial crosslinking of polymer particle.

Properties	Core-shell styrene acrylate latex paint	Non-core-shell styrene acrylate latex paint	Pure acrylate latex paint
% Elongation	2.06	526.3	136.3
Tensile strength (MPa)	1.68	1.07	1.47

TABLE 4: Mechanical properties of core-shell, non-core-shell, and pure acrylate latex paint

Evaluation of yellowing properties of paint film after accelerated indoor weather (QUV) exposer

The paints containing core-shell styrene-acrylate, styrene-acrylate copolymer (non-core-shell) and pure acrylate binders were coated on panels. The paints were exposed to QUV-A (340 nm) for accelerated weather stability for 1200 h. The ASTM G53 test method was followed for QUV exposure. The initial reflectance readings were taken and found to be comparable for all the samples. Styrene-acrylate copolymer-based paints degraded after 1200 hours of UV exposure while core-shell latex showed comparable yellowness with pure acrylate system (Table *5*). Core-shell styrene-acrylate binder reduced the yellowing considerably. The acrylate shell with crosslinked styrene core resists degradation and therefore protects the paint from UV exposure. This is because the acrylate shell can encompass core efficiently and shield the styrene polymer.

Time (hour)	Latex system	Yellowness index	Deviation from initial value
			(Final hours–zero hour)
0	Core-shell	0.728	0
0	Non-core-shell	0.615	0
0	Pure acrylate	0.591	0
650	Core-shell	2.418	1.69
650	Non-core-shell	2.522	1.907
650	Pure acrylate	2.111	1.52
1200	Core-shell	2.994	2.266
1200	Non-core-shell	4.451	3.836
1200	Pure acrylate	2.479	1.888

TABLE 5: QUV result

Conclusions

The styrene core and acrylate shell polymer were successfully synthesized. The distinct core-shell structure of the synthesized polymers was confirmed through DSC and TEM analysis. This core-shell emulsion polymer offers the possibility of incorporating higher styrene content into existing paint formulations without compromising the final paint properties, particularly the yellowness appearance. The core-shell morphology helps maintain paint performance despite the increased styrene content. The versatility of this core-shell emulsion system can also be leveraged to design more cost-effective paint formulations in the face of monomer price fluctuations, such as high prices of MMA. The ability to use higher styrene content as a more economical monomer provides a way to mitigate the impact of volatile monomer prices.

Additional Information

Author Contributions

All authors have reviewed the final version to be published and agreed to be accountable for all aspects of the work.

Concept and design: Jatindranath Maiti, Subarna Shyamroy

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Disclosures

Human subjects: All authors have confirmed that this study did not involve human participants or tissue. **Animal subjects:** All authors have confirmed that this study did not involve animal subjects or tissue. **Conflicts of interest:** In compliance with the ICMJE uniform disclosure form, all authors declare the following: **Payment/services info:** All authors have declared that no financial support was received from any organization for the submitted work. **Financial relationships:** All authors have declared that they have no financial relationships at present or within the previous three years with any organizations that might have an interest in the submitted work. **Other relationships:** All authors have declared that there are no other relationships or activities that could appear to have influenced the submitted work.

Acknowledgements

Authors thank Modern Instruments Lab, Asian Paints for their support in characterization. Authors thank Dr. Gururajan Padmanaban, Dr. Amit Joshi for reviewing the manuscript. Thanks are due to Mr. Rajeev Goel and Asian Paints Management for their continuous support.

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