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Synthesis and Characterization of Siloxane Containing Styrene-Acrylic/ Acrylic Latex Systems Through Emulsion Polymerization

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Poly acrylic siloxane coatings are generating a lot of interest due to their high durability and superior performance properties in different applications. The study presented here is on the synthesis and characterization of siloxane containing styrene-acrylic/acrylic latex systems through emulsion polymerization. The polymers have been characterized for their physical, chemical, thermal and surface properties using different characterizing techniques like FTIR, DSC, SEM, DLS and Contact angle measurements. The incorporation of siloxane in the polymers was found to improve properties such as hydrophobicity and film formation. The paints prepared using the hybrid polymers as binders exhibited superior performance properties like weather ability, Dirt pick up resistance and mechanical properties.

Keywords: Poly acrylic siloxane coatings, Hydrophobicity, Weatherability, Paints, DLS.

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Синтез и характеристики силиоксаносодержащих стирол-акрил / акрил латексных систем, полученных посредством эмульсионной полимеризации

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Полиакрилсилоксановые покрытия вызывают большой интерес благодаря их высокой прочности и превосходным эксплуатационным свойствам. В настоящей работе представлены результаты по синтезу и характеристикам силиоксаносодержащих стирол-акрил / акрил латексных систем, полученных эмульсионной полимеризацией. Охарактеризованы физические, химические, термические и поверхностные свойства полимеров с использованием методов ИКС, ДСК, СЭМ и измерений контактного угла. Было обнаружено, что включение силиоксана в полимеры приводит к улучшению таких свойств, как гидрофобность и пленкообразование. Краски, полученные с использованием гибридных полимеров в качестве связующих, обладают превосходными эксплуатационными свойствами, такими как устойчивость к атмосферным воздействиям, стойкость к загрязнению и механическим воздействиям.

Keywords: полиакрилсилоксановые покрытия, гидрофобность, атмосфероустойчивость, краски, метод динамического светорассеяния.

1. Introduction

Waterborne coatings are the mainly for masonry coatings for the variety of properties they offer in terms of aesthetic and environmental appeal [1-4]. Acrylic copolymers provide good water and alkali resistance, elasticity and adhesive properties. Polyacrylate and poly (acrylate-styrene) have been widely used in coatings, paints and adhesives so far by the virtue of excellent film-forming property, cohesiveness and drying ability. By far the most acrylics have replaced the solvent borne coatings in masonry surface due to their performance and environment friendly nature [5]. They are also easily achieved through emulsion polymerization which has a very high polymer conversion rate. Acrylic latexes are broadly classified in to Styrene containing latexes and non styrene containing latexes. Styrene being aromatic gives good hardness, strength, adhesion and hydrophobicity to the latex films

[6]. It is also a relatively inexpensive monomer compared to the other monomers which impart similar properties. However, styrene is also prone to yellowing under UV light leading to the loss of aesthetic appeal of coatings. Pure acrylic systems without styrene have been used for out door coatings that are exposed to heat and light and these give good performance over styrene acrylics [7]. However, when the coating is exposed to outdoor conditions or UV light for a prolonged period it fails to sustain its gloss and weathering properties and hence the surface needs to be recoated. Therefore there exists a scope for improvement in the acrylic latex for out door applications. In contrast to the acrylics, polysiloxane is endowed with excellent thermal stability, low surface energy, weather resistance, high flexibility and good biological compatibility owing to its unique structure [8]. However, it is plagued by high cost and is synthesized through solvent based routes. Therefore, a system that is synthesized through the emulsion polymerization route that has the properties of acrylates and polysiloxanes would be highly preferred as binders for paints. Weatherability is generally defined as the property of a material of being able to resist a wide range of environmental conditions. When coatings are exposed to the outdoors, the components of coatings are oxidized by sunlight, heat, water, oxygen, and air-polluting materials. Therefore, weatherability, especially for coatings, is defined as the property of being resistant to loss of aesthetic and mechanical properties. Hence the coating world is now opting for Acrylic-Siloxane hybrid coating for high performance coatings [9-12]. Novel oil-filled microcapsules were prepared by introducing a phase separation method using ethyl cellulose as a shell-forming containing rapeseed oil. The addition of oil-filled microcapsules resulted in a significant improvement in the modulus, strain-to-break, and toughness of the films. The self-healing mechanism of latex films was examined through the colorimetric measurements of the release of dye-containing following the pre-elongation of the samples. These measurements confirmed that pre-elongation of samples resulted in the release of oil within the latex films, hence plasticizing the surrounding polymeric network and partly restoring the mechanical properties of the pre-elongated films [13]. Series of cationic silicone-acrylic latexes used as surface sizing agents were prepared by using the semi-continuous emulsion polymerization of styrene and butyl acrylate in the presence of acrylamide, (2-(methacryloyloxy) ethyl) trimethyl ammonium chloride and vinyltriisopropoxysilane, It was observed that the cationic silicone-acrylic latexes produced possessed remarkable chemical stability. The surface sizing agent containing this type of cationic silicone-acrylic latex, even in the absence of aluminum salt, was excellent in improving the water resistance and mechanical properties of the corrugated paper [14].

The study is based on an effort to synthesize poly acrylate siloxane hybrids using an acrylate core and an organosiloxane shell as such coatings have been identified in literature to give excellent properties in coatings. The technique used is the emulsion polymerization for the acrylate monomers using free radical polymerization.

The objectives of the current study are:

- To synthesize latex of styrene –acrylic copolymers and pure acrylic copolymers using semi-continuous seeded emulsion polymerization.
- To build a shell of organo-siloxane on the core latex particle through cross-linking mechanism.
- To study the effect of the organo siloxane content on the thermal and surface properties of the original latex.
- To characterize the synthesized acrylic siloxane hybrids through various techniques.

- To study the effect of the siloxane content in paint for weather ability and mechanical properties in exterior paints.

2. Materials and Methods

2.1 Materials

All monomers were of commercial grade and used as such. Siloxane was purchased from Dow Corning. Anionic surfactant, initiator, oxidant, reductant and buffer were of commercial grade and were used as such.

2.2 Experimental method of Styrene-Acrylic latex Synthesis

Polymerization was performed in a one liter, three-neck flask (“Kettle”) equipped with a mechanical stirrer, a temperature control system, an inlet for a monomer emulsion fed by an FMI peristaltic pump, and a reflux condenser. The temperature was measured by thermometer immersed in the reaction mixture and is controlled by thermostat which is immersed in water bath and electronically linked to temperature controller system. The reaction mixture was cooled by passing cold water into water bath. By these means, the temperature was controlled within ± 1 °C. A series of emulsion latexes were prepared by varying the amount of hard and soft monomer through seeded semi continuous emulsion polymerization using persulfate as the initiator and anionic/nonionic combination surfactants. The monomer pre-emulsion were added for 210 minutes at a constant rate by using peristaltic pump and the reaction continued for 60 min. Separately, reducing and oxidizing catalysts were added into kettle after a holding time of 60 min. The latex in the kettle was cooled to 40 °C, and a neutralizer was added with continued stirring to adjust the pH to 9.2-9.5. Finally preservative solution was added under stirring. The latex was filtered through a tarred 200-mesh sieve. Coagulum was assessed by drying the sieve and weighing the material collected. The emulsion latex thus obtained was studied for all the following properties through methods described below.

2.3 Experimental method of styrene acrylic siloxane hybrid latex.

The styrene acrylic emulsion which is core was taken in kettle and organosiloxane were added drop-wise into kettle by using peristaltic pump. The reactions were processed at room temperature until homogenous emulsions were obtained. Finally the emulsion latex was filtered by filter cloth and styrene acrylic siloxane hybrid latex was obtained.

2.4 Synthesis of Styrene Acrylic Emulsion polymers

Styrene acrylic polymers with 40 % solid content were prepared as per the recipes given below in Table 1. The three polymers SAE 1, SAE 2 and SAE were of three different Tg's as in 0 °C, 10 °C, 25 °C respectively. The Tg's were altered by changing the percentage composition of the hard and soft monomers.

2.5 Synthesis of Styrene Acrylic Siloxane Hybrids

Synthesis of Styrene acrylic siloxane hybrids was carried out by post addition of siloxane into styrene-acrylic emulsion at room temperature. The styrene acrylic siloxane hybrids were prepared as per the recipes given below in Table 2.

Table 1. Recipes of Styrene acrylic emulsion

Phase	Materials	SAE 1	SAE 2	SAE3
Kettle charge	DMW	19.85	24.45	24.45
	Anionic Surfactant	0.15	0.15	0.15
	DMW	17	22	22
	Anionic Surfactant	0.2	0.2	0.2
Pre-Emulsion	Non-ionic Surfactant	0.5	-	-
	Hard monomer	15	15	25.5
	Soft monomer 1	15	10	
	Soft monomer 2	-	-	14.5
	Soft monomer3	15	15	
	Monomeric acid	0.2	0.5	0.3
	Buffer	0.17	0.17	0.17
	DMW	3.4	3.4	3.4
Catalyst 1 addition at 80 °C	Initiator	0.13	0.13	0.13
	DMW	3.4	3.4	3.4
	Reducing agent	0.04	0.04	0.04
Chaser Catalyst addition at 80 °C	DMW	0.6	0.6	0.6
	Oxidizing agent	0.04	0.04	0.04
	DMW	0.6	0.6	0.6
Additives (after cooling at 45 °C)	In-can preservative	0.1	0.1	0.1
	Neutralizer	0.8	0.8	0.8
	DMW	2.92	2.92	2.92
TOTAL		100	100	100

Table 2. Recipes of Styrene Acrylic Siloxane hybrid polymer

Exp. No.	SA Emulsion	SAE (wt %)	Siloxane (wt %)
SAE 1.5	SAE 1	95	5
SAE 1.10	SAE 1	90	10
SAE 1.15	SAE 1	85	15
SAE 2.20	SAE 2	80	20
SAE 2.25	SAE 2	75	25
SAE 2.30	SAE 2	70	30
SAE 3.2.5	SAE 3	97.5	2.5
SAE 3.5	SAE 3	95	5
SAE 3.10	SAE 3	90	10
SAE.3.15	SAE3	85	15

2.6 Synthesis of pure Acrylic Emulsion polymers

Acrylic polymers with 40 % solid content were prepared as per the recipes given below, see Table 3. The polymer SAE 4 was of Tg' 15 °C.

2.7 Preparation of Acrylic Siloxane Hybrids

Synthesis of acrylic siloxane hybrids was carried out by post addition of siloxane into styrene-acrylic emulsion at room temperature. The styrene acrylic siloxane hybrids were prepared as per the recipes given below in Table 4.

2.8 Methods for Emulsion Characterization.

2.8.1 Solid Content or Non Volatile Material (NVM)

The solid content or non volatile materials were measured by gravimetric method. Approximately 1 gm of emulsion were cast onto a Petri dish and dried in room temperature, then were placed into dry oven at 120°C for one hour. The solid content was calculated by the following formula:

$$S\% = \frac{W2 - W0}{W1 - W0} \times 100.$$

Table 3. Recipes of pure Acrylic emulsion

Phase	Materials	SAE 4
Kettle charge	DMW	24.45
	Anionic Surfactant	0.15
	DMW	22
	Anionic Surfactant	0.2
	Non-ionic Surfactant	0.5
Pre-Emulsion	Hard monomer	15
	Soft monomer 1	10
	Soft monomer 2	15
	Soft monomer3	0.2
	Monomeric acid	0.17
Cataylst 1 addition at 80 °C	Buffer	3.4
	DMW	0.13
	Initiator	3.4
Chaser Catalyst addition at 80 °C	DMW	0.04
	Reducing agent	0.6
	DMW	0.04
	Oxidizing agent	0.6
	DMW	0.1
Additives (after cooling at 45 °C)	In-can preservative	0.8
	Neutralizer	2.92
TOTAL	DMW	100

Table 4. Recipes of Styrene Acrylic Siloxane hybrid polymer

Exp. No.	SA Emulsion	SAE (wt %)	Siloxane (wt %)
SAE 4.5	SAE 4	95	5
SAE 4.10	SAE 4	90	10
SAE 4.15	SAE 4	85	15
SAE 4.20	SAE 4	80	20
SAE 4.25	SAE 4	75	25
SAE 4.30	SAE 4	70	30

Where W_0 is the weight of clean Petri dish, and W_1 and W_2 are the total weight of Petri dish and casted emulsion before and after drying to constant weight, respectively.

2.8.2 Viscosity

Viscosity is the resistance of a fluid to flow. This resistance acts against the motion of any solid object through the fluid and also against motion of the fluid itself past stationary obstacles. In terms of shear stress and shear rate, it is the ratio of the shear stress required to move the solution at a fixed strain rate to that strain rate.

$$\text{Viscosity} = \frac{\text{Shear stress}}{\text{shear rate}}$$

It may be measured in poises or centipoises, or Pascal-second or Krebs unit or gram. The viscosity of paint was measured by Krebs unit viscometer model KU-2. The displayed reading can be held by depressing the hold switch at any time. With the viscometer in the hold configuration, the display may be switched to compare the Krebs (KU) or centipoise (cP) reading with the associated gram (gm) reading. If the spindle is stalled, no damage will result, as a torque-limiting circuit protects the spindle drive.

2.8.3 Electrolytic Stability

It is defined as “The volume of electrolyte solution in mL required to turn 100 gram of emulsion into a solid hard mass”. 100 gram of emulsions were taken in a 250 mL beaker. A glass rod was introduced to be used as agitator. 5 % freshly prepared Aluminum Sulphate solution was taken in a burette and added drop wise to the latex under stirring until it turned completely into a solid hard mass. The volume of Aluminum sulfate solution required was recorded and is given as the electrolytic stability of the latex.

2.8.4 Freeze-Thaw stability

The stability of latex to freezing is partly a function of the polymer, optionally plasticized, and partly of the medium. The latex samples in a container are kept at -5 °C for 16 hrs followed by a thaw process at room temperature for 8 hrs. If the latex passes 5 cycles, then it is said to be Freeze-Thaw stable.

2.8.5 Particle size Analyzer

Particle size of the synthesized emulsions was measured on Zeta Potential Analyzer Zetatrac Model NPA152 (Microtrac Inc) a unit of Nikkiso (USA, PA).

2.8.5.1 The Basics of Dynamic Light Scattering

Dynamic light scattering (DLS) can be used to determine the size distribution profile of small particles in suspension or polymers in solution. The scattering of photons by moving particles is quasi-elastic. DLS is a nondestructive technique which does not require a blank solvent calibration. DLS is based on the analysis of constructive and destructive interference arising from the scattered light from particles. The interference varies by time due to the Brownian motion of particles. The larger particles diffuse more slowly while smaller particles diffuse faster, which influences the scattered intensity by time. When the sample is exposed to the laser beam, the scattered light is measured as a function of time intervals called delay times. Latexes were diluted to 0.1 vol. % in water. Intensity-average particle size and particle size distribution were analyzed in dynamic light scattering at 25°C, each sample was run for 180 seconds and analyzed by using non-negative least squares (NNLS) algorithm. The display shows the average width of the latex particle and the polydispersity of the latex.

2.8.6 Minimum film forming temperature (MFFT)

A very important characteristic of a binder is the temperature at which it forms a clear and homogeneous film. This temperature is called the minimum film forming temperature (MFFT). It can be determined experimentally with a special apparatus. It consists of a support that provides a temperature gradient along its length. The emulsion polymer is drawn down on it. After equilibration the transition from a cracked to a clear film determines the MFFT. The MFFT of an emulsion polymer is usually a few centigrade lower than its glass transition temperature (T_g). One reason is a small amount of water being dissolved in the latex particle acting as a plasticizer. Most coatings are applied under ambient conditions (either on a job site or in a factory) at typical temperatures between 5°C and 40°C. For obvious reasons the MFFT of paints and coatings should be lower than the temperature at the application side. The low end of the temperature range is defined by architectural coatings used exterior that should still form a neat paint film under unfavorable conditions. The MFFT of paints can be temporarily lowered by the use of a coalescing agent. It works by partitioning into the emulsion polymer particles, disrupting the packing of the polymer chains and thus lowering the MFFT. After film formation the coalescent evaporates.

2.8.7 Contact Angle

The contact angle is the angle, conventionally measured through the liquid, at which a liquid/vapor interface meets a solid surface. The equilibrium contact angle is specific for any given system and is determined by the molecular interactions across the liquid/vapor, solid/vapor, and solid/liquid interfaces. Contact Angle of emulsion films using the sessile drop method were measured on a glass plate by the 3S surface tensiometer. The drop was placed on the plate with the film and the angle measured using live video capture after 10 seconds.

2.8.8 Glass transition temperature of polymers through differential scanning calorimetry

The glass transition is exhibited by amorphous polymers or the amorphous regions of partially crystalline polymers when a viscous or rubbery state is transformed into a hard, brittle, glass-like state. The glass transition of polymers is observed by DSC as a stepped increase in the heat capacity of the sample during heating due to an enhancement of molecular motion in the polymer. DSC analyses were carried out on 48 h dried films using a TA Instruments Q10 under nitrogen atmosphere at a ramp of 10 °C with the temperature range of -50 °C to 100 °C. It was measured through two cycles.

2.8.9 X-ray fluorescence (XRF)

It is the emission of characteristic “secondary” (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis

2.8.9.1 Theory

When materials are exposed to short-wavelength X-rays or to gamma rays, ionization of their component atoms may take place. Ionization consists of the ejection of one or more electrons from the atom, and may occur if the atom is exposed to radiation with an energy greater than its ionization potential. X-rays and gamma rays can be energetic enough to expel tightly held electrons from the inner orbitals of the atom. The removal of an electron in this way renders the electronic structure of the atom unstable, and electrons in higher orbitals “fall” into the lower orbital to fill the hole left behind. In falling, energy is released in the form of a photon, the energy of which is equal to the energy difference of the two orbitals involved. Thus, the material emits radiation, which has energy characteristic of the atoms present. The term fluorescence is applied to phenomena in which the absorption of radiation of a specific energy results in the re-emission of radiation of a different energy

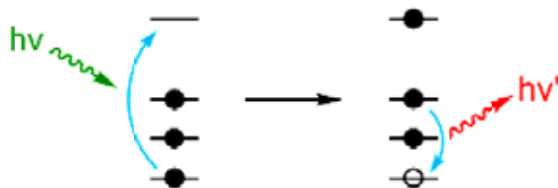


Fig. 1. Physics of X-ray fluorescence

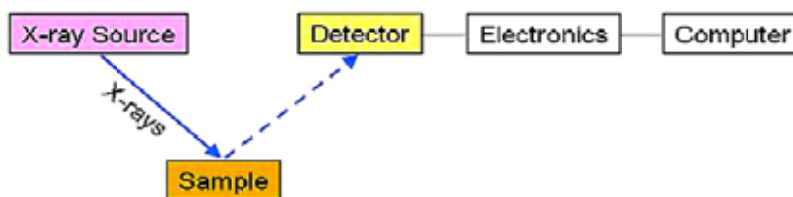


Fig. 2. Schematic arrangement of EDX spectrometer

All XRF characterization was performed in BRUKER AXS INC. S₂ RANGER XRF instrument. The 11.000 grams of emulsions were taken in specimen holder and is tested by using XRF instrument.

2.9 Preparation of Mill base and Final paint

2.9.1 Experimental method for making mill base and final sample

The Exterior mill base was prepared according to the formulation given below in three steps. A large amount of mill base can be prepared according to the requirement. It was prepared in stainless steel container and dispersion of mill base was performed by high speed disperser.

2.9.1.1 Step I-Jelly Preparation

In this step the materials given in Table 3 were added in that order in a stainless steel container. The high speed disperser was used to insure fine dispersion of the below materials. This step was carried out approximately for 30 minutes until a thick jelly was formed. The high speed disperser was operated at second gear in following step, see Table 5.

2.9.1.2 Step II-Pigment Dispersion

In this step the materials given below in Table 6, were added in that order. The high speed disperser was initially operated at second gear in this step. This was done for 10 minutes. On complete addition of the pigment and the water into the stainless steel container the high speed disperser was operated at high speed in the third gear. This was done for 30 minutes to ensure complete and efficient dispersion of the pigment. At constant intervals a flexible scraper blade was used to prevent sticking of mill base to the edges of the container. On complete dispersion of pigments the high speed disperser was stopped and the container along with agitator was removed. The container was covered with a polyethylene bag to prevent water from escaping. The entire system was cooled in a water bath to room temperature.

2.9.1.3 Step III Let down Phase- Addition of Emulsion to make final Paint

After cooling the above mill base was performed the container was once again taken to the high speed disperser. This time high speed disperser was operated at second gear. This was carried out for approximately 15 minutes. The following components given in Table 5, were added to the stainless container in order to get the final complete paint sample.

Table 5. Recipes of jelly preparation

Materials used	Weight %
Water	15.59
Biocides	0.2
Rheology modifier	0.4
Water	0.2
Neutralizer	0.1

Table 6. Recipes of pigment dispersion

Material used	Weight %
Preservative	0.1
Tetra potassium pyrophosphate	0.2
Defoamer	0.1
In can preservative	2
Wetting Agent	0.5
Surfactant	0.2
Defoamer	0.1
Masking Agent	0.5
Antifungal algal	0.8
TiO ₂	21
Marble powder	7
Calcined clay	6
Water	1
Surfactant	0.2
Coalescent	1
Antifungal	0.2

Table 7. Recipes of Let down phase

Materials used	Weight %
Mill- base	60
Emulsion (45%)	40
Defoamer	0.1
Total parts	100.1

2.10 Paint Characterization

2.10.1 Mechanical properties of paints

2.10.1.1 Standard Test Method for Tensile Properties of Organic Coatings

This test method covers the determination of the elongation, tensile strength, and stiffness (modulus of elasticity) of organic coatings when tested as free films. The values stated in inch-pound units are to be regarded as the standard. The values given in parentheses are for information only.

2.10.2 Terminology

2.10.2.1 Elongation

The increase in specimen length from the point of initial load application to the point of film ruptures in a tension test.

2.10.2.2 Gauge length

It is the initial length of the test specimen between the jaws of the tensile tester.

2.10.2.3 Stiffness (modulus of elasticity)

The load per unit area required to elongate the film 1 % from the first point in the stress-strain curve where the slope becomes constant.

2.10.2.4 Stress-strain curve

The curve resulting from a plot of tensile load against the distance of jaw separation (elongation of specimen) is called a stress strain curve.

2.10.2.5 Tensile strength (nominal)

The load per original unit area at which a specimen fails or yields in a tension (pull) test

2.10.3 Apparatus

Equipment for applying films of uniform thickness as described in Practices D 823.

- Micrometer Film Thickness Gage as described in Test Method D 1005.
- Tensile Tester of the constant rate of jaw separation type, equipped with load cells having capacities of 0.2 to 4.4 lb (100 to 2000 g), and equipped with an indicating device such as an electronic constant speed chart recorder, a digital device that displays numerical values, or a printer that records the numerical values.

2.10.4 Test Specimens

Prepare three films by one of the procedures described in Test Method D 4708.

2.10.5 Procedure for making film

The paint films were drawn on release paper by using 625 micron multiple film applicator. The paint film was tested after 7 days curing. The size of film was 1.5 cm x 6 cms and distance between two jaws of universal testing machine was kept at 2.5 inch apart. The speed of testing was. The reading was noted down digitally at the time of film breaking.

2.10.6 Calculations

For each specimen compute the following:

- The elongation E, in percent from the following equation:

$$E = \frac{DL}{L} \times 100$$

Where DL = increase in specimen length to break, and
L = initial specimen length (gage length).

- The tensile strength, TS, in pounds per square inch, from the equation

$$TS = \frac{Pr}{TW}$$

Where Pr = tensile pull to rupture, lb (kg)
T = thickness of test specimen, in. (mm), and
W = width of test specimen, in. (mm).

2.10.7 Opacity/Contrast ratio

The effect of Portafill H-5 as a TiO₂-extender was measured in terms of contrast ratios of the dry paints. The measurements were carried out according to DIN 53778, part 3. To determine the contrast ratio, the paints were generally applied with spiral applicator at the wet thickness of 150 µm on a black & white contrast lanetta paper. After drying for 24 hours, the value of whiteness Y is measured above the white (Y_w) and the black background (Y_B) using the spectrophotometer analyser 2. The contrast ratio (CR) is then calculated as follows:

$$CR = \frac{Y_B}{Y_w} \times 100$$

2.10.8 Yellowness indices

Yellowness indices is defined by ASTM (American society for testing and materials) as the “attribute by which an object color is judged to depart from colorless or a preferred white toward yellow. Negative value denotes blueness”. The ASTM yellowness indices are intended to be used for near white samples that have dominant (or complementary) wavelength between 570 and 580 nm. For samples that do not meet these criteria these indices value may be meaningless. Yellowness indices report a zero value for measurements that match the preferred white value indicate the sample measured deviates from the preferred white towards yellow negative value indicate the sample measured deviates from the preferred white toward blue.

2.10.9 Whiteness indices

Whiteness indices are defined by ASTM (American society for testing and materials) as the “attribute by which an object color is judged to approach the preferred white”. Variety of Whiteness indices are available regardless of which one you choose, it is important to understand how the numerical value relates the visual assessment. It is also important to communicate which one of you chooses other affected particles. If other particles have specified which one to use, be sure to use the one specified.

2.10.8 Dirt pick-up resistance (DPUR)

The paint film was drawn on laneta paper by using 125 micron applicator. The Film was analyzed after 7 days curing by putting carbon black on paint film. It was shacked for 20 strokes and paint film was analyzed with the naked eye.

3. Results and Discussions

Results of Styrene Acrylic Siloxane hybrid polymer latex

All the acrylic siloxane polymers of 0 °C, 10 °C, and 25 °C were characterized for their physical properties and results are given below in Table 8,9 and 10 respectively.

3.2 FTIR spectra of Styrene Acrylic Siloxane hybrid latex

The Fig. 3 (a), (b), (c) shows FTIR spectra of organosiloxane, styrene acrylic core, styrene acrylic siloxane hybrid polymer respectively. The –Si-C- linkage at 801cm⁻¹ was observed in organosiloxane and in styrene acrylic siloxane hybrid polymer which was absent in styrene acrylic core emulsion.

Table 8. Properties of styrene Acrylic siloxane hybrid polymer latex (Tg 0°C)

Property	SAE 1	SAE 1.5	SAE 1.10	SAE 1.15
Appearance	Transparent film with slight tack	Transparent film with slight tack	Transparent film with slight tack	Transparent film with slight tack
Viscosity (in gm)	81	81	80	81
pH	10.4	10.32	10.35	10.26
Electrolytic stability	36	38.5	34.5	38
MFFT (°C)	>-5 °C	>-5 °C	>-5 °C	>-5 °C
Freeze-Thaw stability	passed 5 cycles	passed 5 cycles	passed 5 cycles	passed 5 cycles
Actual Tg (°C)	-8.9	-10.4	-8.1	-4.5

Table 9. Properties of styrene Acrylic siloxane hybrid polymer latex (Tg 10°C)

Property	SAE 2	SAE 2.20	SAE 2.25	SAE 2.30
Appearance	Transparent	Transparent	Transparent	Transparent
Viscosity (in gm)	80	80	90	96
pH	10.34	10.16	10.23	10.27
Electrolytic stability	33	37	35	36
MFFT (°C)	15.08 °C	17.26 °C	17.08 °C	16.28 °C
Freeze-Thaw stability	Passed 5 cycles	Passed 5 cycles	Passed 5 cycles	Passed 5 cycles
Actual Tg (°C)	17.8°C	25.4°C	25.9°C	26.8°C

Table 10. Properties of styrene Acrylic siloxane hybrid polymer latex (Tg 25°C)

Property	SAE 3	SAE 3.2.5	SAE 3.5	SAE 3.10	SAE 3.15
Appearance	Transparent, fully cracky film	Transparent, fully cracky film	Transparent, fully cracky film	Transparent, fully cracky film	Transparent, fully cracky film
% NVM	41.18	41.57	42.12	47.66	48.92
Viscosity (gm)	51	56	56	60	60
pH	10.14	10.17	10.07	10.14	10.13
Electrolytic stability	21	21	20.5	19	18.9
MFFT (°C)	<30 °C	<30 °C	<30 °C	<30 °C	<30 °C
Freeze-Thaw stability	Passed 5 cycles	Passed 5 cycles	Passed 5 cycles	Passed 5 cycles	Passed 5 cycles
Actual Tg (°C)	44.8°C	44.2°C	44.9°C	45.4°C	45.7°C

Additional peak at 1133 cm^{-1} was observed in Fig. 3 (a) and Fig. 3 (c) which was absent in styrene acrylic core emulsion Fig. 3 (b). Hence, an FTIR spectrum proves the presence of siloxane in hybrid system.

3.3 X-Ray Fluorescence (XRF) of Styrene Acrylic Siloxane hybrid latex

X Ray Fluorescence analysis of the hybrid polymers showed that the silicon content in the hybrids to be steadily increasing as expected. The results of the various hybrid samples are given below in Fig. 4 (a) and (b).

3.4 Dynamic Light scattering of Styrene Acrylic Siloxane hybrid latex

DLS analyses of the hybrid polymers are shown in Fig. 5 (a), (b) and (c) it was observed that there is a steady increase in polymer latex sizes with increasing siloxane content in the system. Interestingly, the poly dispersity of the system remains unaffected thereby confirming that the organo siloxane is getting crosslinked to the emulsion latex particle. Hence this affirms the view that these hybrids are core shell particles.

3.5 DSC of Styrene Acrylic Siloxane hybrid latex

DSC thermograms of the styrene acrylic core emulsion and styrene acrylic siloxane hybrid core shell polymer hybrid polymers are shown in Fig. 6 (a) and Fig. 6 (b) respectively. DSC analyses of styrene acrylic siloxane hybrid polymer show that the Tg of the polymer showing two transitions

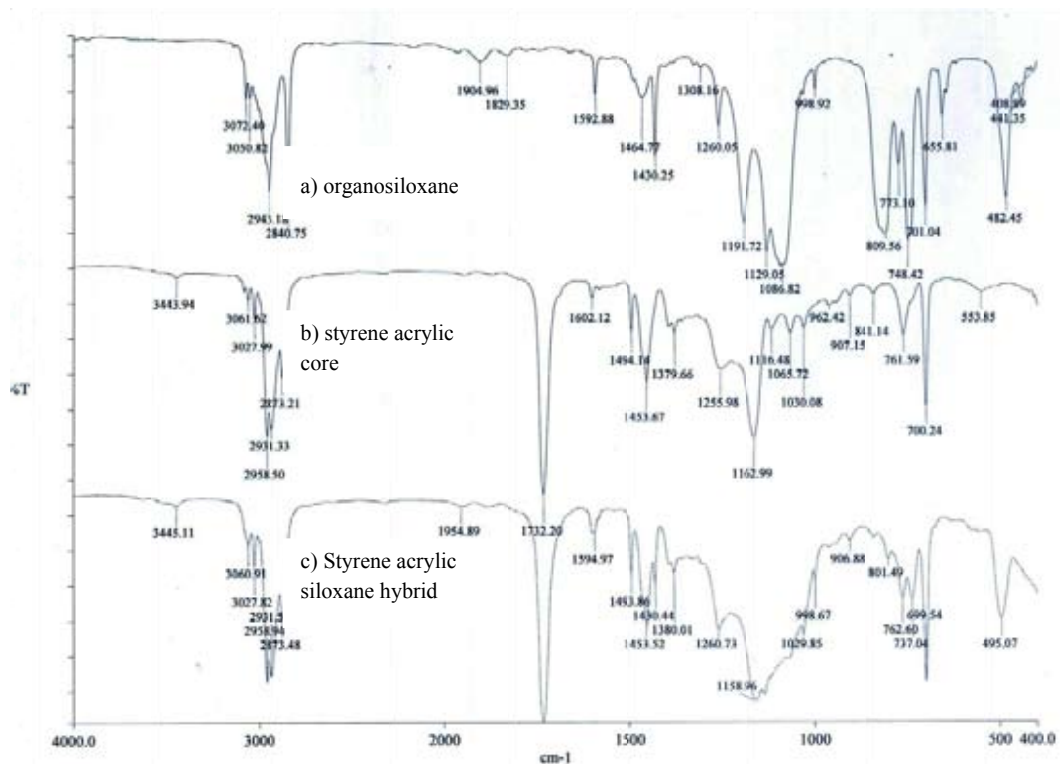


Fig. 3. FTIR spectra of (a) organosiloxane, (b) styrene acrylic core, (c) styrene acrylic siloxane hybrid polymer

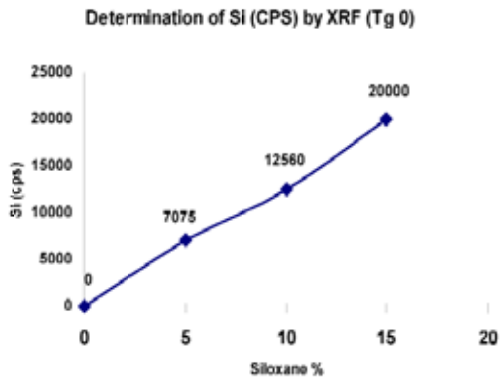


Fig. 4 (a): XRF of SAE (Tg 0 °C)

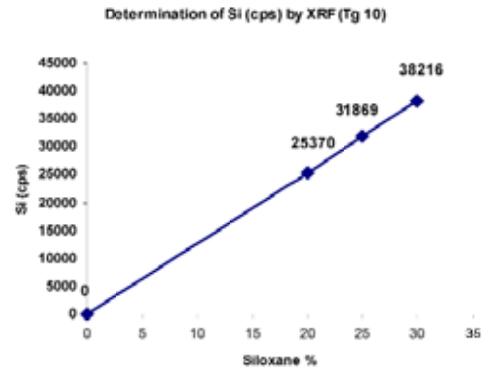


Fig. 4 (b): XRF of SAE (Tg 10 °C)

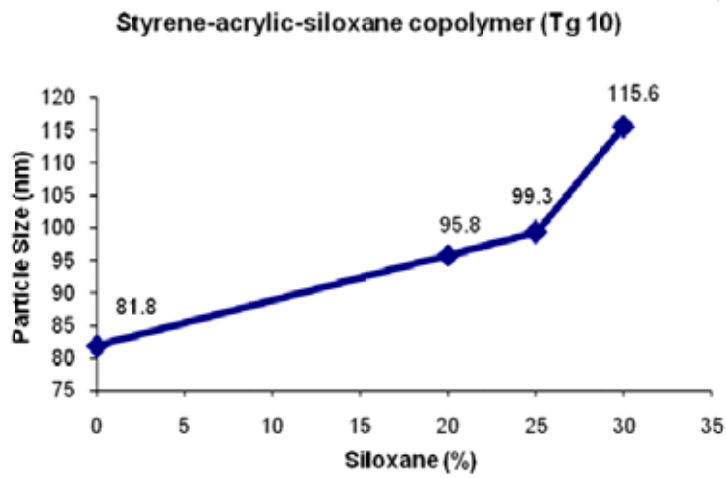


Fig. 5 (a): Particle size of Styrene Acrylic Siloxane hybrid

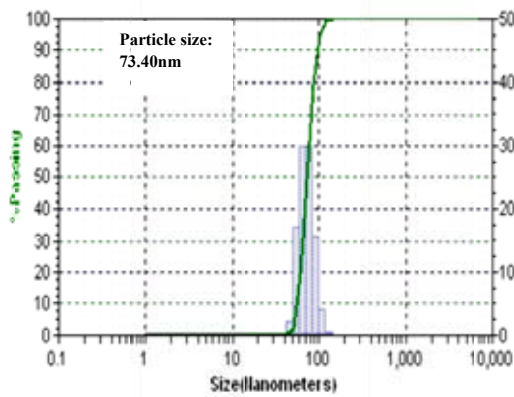


Fig. 5 (b): Particle size of SAE 2 with 0 % siloxane

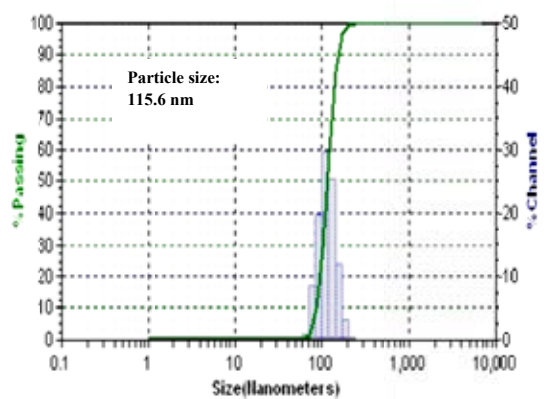


Fig. 5 (c): Particle size of SAE 2. With 30 % siloxane

indicative of heterogeneity in the hybrid. The pure core particle does not show double transition. This reaffirms the view that these are core shell particles.

3.6 Contact Angle Measurements of Styrene Acrylic Siloxane hybrid latex

The contact angle is a measure of the surface wettability of the film with respect to water. Wettability is inversely proportional to the contact angle of the surface to water. Low wettability is a highly desired phenomenon in coatings. It is observed that the contact angle increased in acrylic siloxane hybrids with respect to only styrene acrylic systems.

It was observed from figure that contact angle of emulsion films increased steadily by increasing amount of siloxane. The contact angles were improved because of hydrophobic

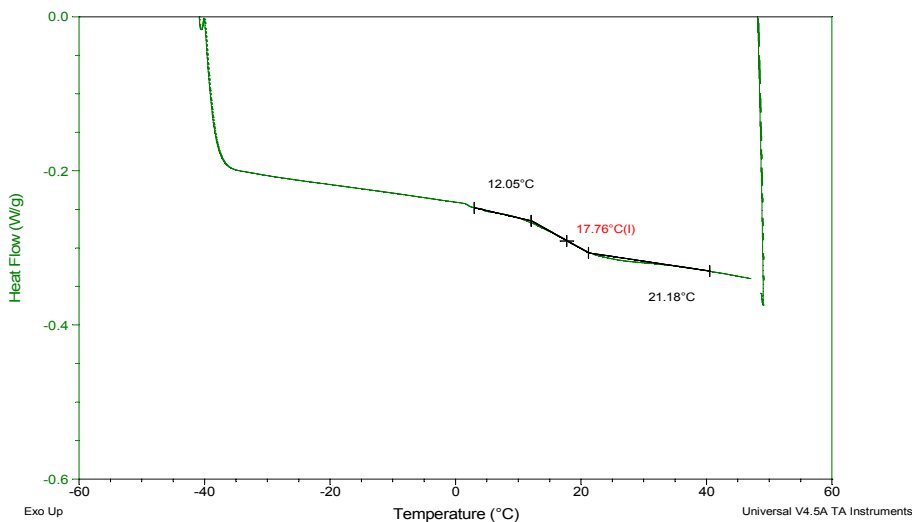


Fig. 6 (a): DSC Thermogram of styrene acrylic core emulsion

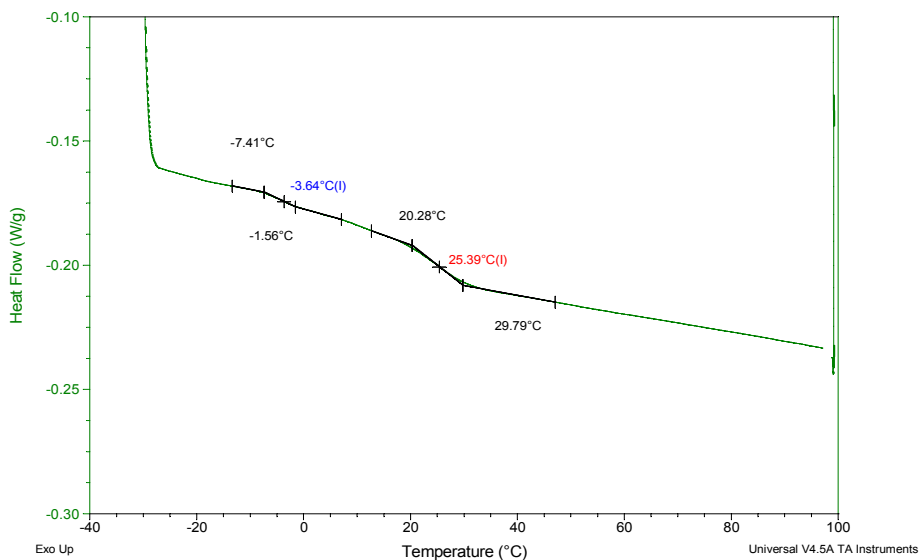


Fig. 6 (b): DSC Thermogram of styrene acrylic siloxane hybrid polymer

Table 11. Contact angle of Styrene Acrylic Siloxane emulsion (Tg 0 °C)

Experiment No.	Siloxane(%)	Contact angle
SAE 1	0	55.7
SAE 1.5	5	73.5
SAE 1.10	10	78.7
SAE 1.15	15	81.2

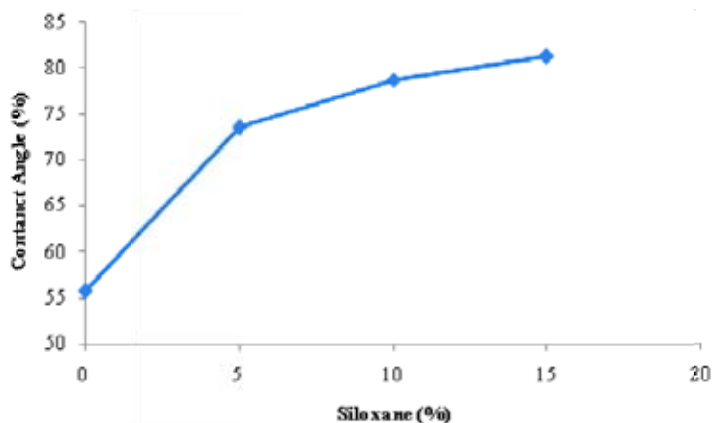


Fig. 7. Contact angle of Contact angle of Styrene Acrylic Siloxane emulsion

nature of siloxane which repels water and hence is a promising moiety for water proofing characteristics.

3.7 Scanning electron microscopy with EDXS of Styrene Acrylic Siloxane hybrid polymer.

The hybrid films were characterized using Scanning Electron Microscopy coupled with Elemental Analysis. The Fig. 8 and Fig. 9 shows the SEM image of Styrene Acrylic Siloxane hybrid polymer and elemental compositions respectively. The Fig. shows the presence of silicon distributed uniformly across the film structure. There is no disparity in the concentration of silicon through out the sample.

According to Table 12, the weight % of silicon is 5.59. The SEM image shows the presence of silicon into hybrid polymer.

3.8 Performance Properties of Styrene Acrylic Siloxane paints

Paints were prepared as given earlier and they showed the following optical properties on testing which is shown in Table 13.

According to Table 13, all the paints had a very high contrast ratio and were visibly similar. There is no much difference in contrast ratio of all paints before exposure to accelerated weathering test.

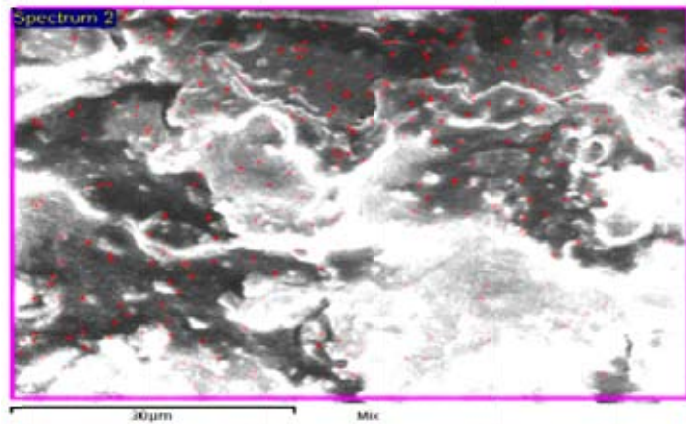


Fig. 8. SEM image of Styrene Acrylic Siloxane hybrid polymer

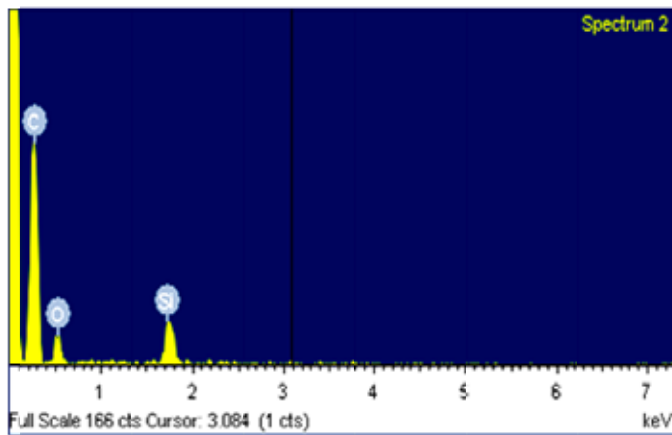


Fig. 9. SEM image of hybrid polymer showing elemental analysis

Table 12. Elemental compositions of Styrene Acrylic Siloxane hybrid polymer

Element	Weight %	Atomic %
C	73.99	80.68
O	20.41	16.71
Si	5.59	2.61

3.8.1 Weatherability

The paints panels were exposed to the UV A radiation for 600 hrs. UV radiation is of high energy and caused deterioration of paint films. The data shown in the Table 14 gives the color change (dE *)

It may be observed clearly from the Fig. that the hybrid polymers perform better in weatherability, while the styrene acrylic systems show deterioration of coating. The coating with 15 wt % was showing

Table 13. Contrast ratio, whiteness index and yellowness index of styrene acrylic siloxane hybrid

Exp. No.	Contrast ratio	Whiteness index	Yellowness index
SAE 1	99.93	75.329	7.903
SAE 2	99.916	74.81	8.348
SAE 1.5	100.546	74.936	7.903
SAE 1.10	97.558	74.116	9.44
SAE 1.15	97.435	74.229	7.045
SAE 2.20	97.977	74.544	9.071
SAE 2.25	98.045	73.974	9.354
SAE 2.30	98.476	74.175	9.39

Table 14. Color difference of Styrene Acrylic Siloxane paint after 624 hours exposure at Q-UV A

Exp. No.	Siloxane (%)	Color difference (dE*)
SAE 1	0	5.596
SAE 1.5	5	3.072
SAE 1.10	10	2.319
SAE 1.15	15	2.24
SAE 2.20	20	1.207
SAE 2.25	25	1.856
SAE 2.30	30	2.615

very good color retention properties. This is because of strong bond energy of $-\text{Si}-\text{O}-$ (445 KJ/Mol) of siloxane which is very stable against the UV light. The UV light doesn't break $-\text{Si}-\text{O}-$ bond easily as compared to $-\text{C}-\text{C}-$ bond. Hence, the coating with 15 % siloxane was showing very good color retention properties.

3.8.2 Mechanical Properties of Paints Properties

The mechanical properties are shown in Table 15. According to Table 3.8 siloxane were improving color retention property of coating.

It was observed from Fig. 11 that siloxane were improving the elongation properties of coating. This may be due to the fact that the hard core is being covered by the soft shell of the siloxane. The coating having 10 wt % siloxane was showing very high elongation. As per the studies at different T_g 's the ratio of siloxane content in the range of 10-20 % yields best results in improving mechanical properties. According to Table 15 the tensile strength and % elongation of coatings were optimized by adjusting the combination of hard and soft monomer composition during latex synthesis.

Fig. 12 shows the % elongation of styrene acrylic siloxane coating (T_g 10 °C). Fig. 12 and Table 16 shows that styrene acrylic siloxane with 20 weight % of siloxane had good tensile strength as well as good elongation.

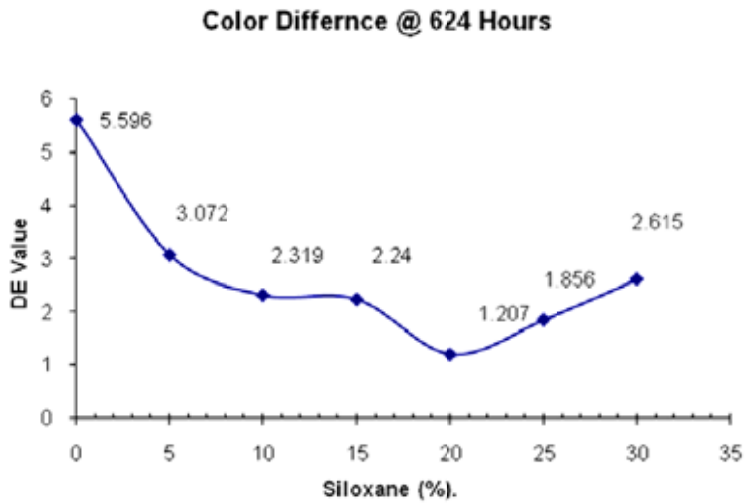


Fig. 10: (a). Color difference of Styrene Acrylic Siloxane paint after 624 hours of exposure at Q-UV A



Fig. 10 (b): SAE 1 with 0 % of siloxane



Fig. 10 (c): SAE 2.20 with 20 % of siloxane

Table 15. Mechanical Properties of Styrene Acrylic Siloxane coating (Tg 00c)

Experiment No.	Siloxane (wt%)	% Elongation	Tensile strength (MPa)
SAE 1	0	820	0.433
SAE 1.5	5	925	0.467
SAE 1.10	10	1110	0.438
SAE 1.15	15	950	0.412

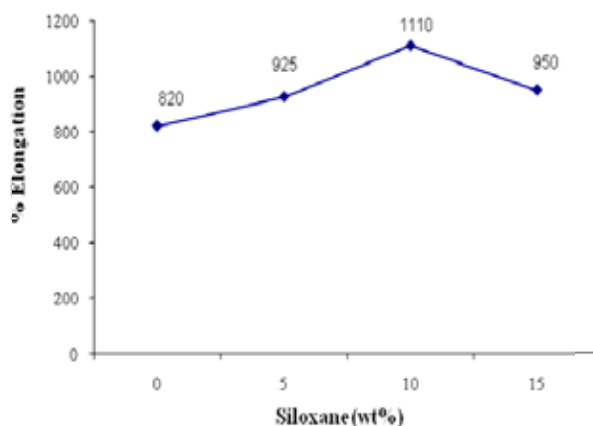


Fig. 11. %Elongation of styrene acrylic siloxane coating (Tg 0 °C)

Table 16. Mechanical Properties of Styrene Acrylic Siloxane coating (Tg 0 °C).

Experiment No.	Siloxane (wt%)	% Elongation	Tensile strength (MPa)
SAE 2	0	116	2.563
SAE 2.20	20	150	2.445
SAE 2.25	25	112.7	2.3
SAE 2.30	30	61.5	2.201

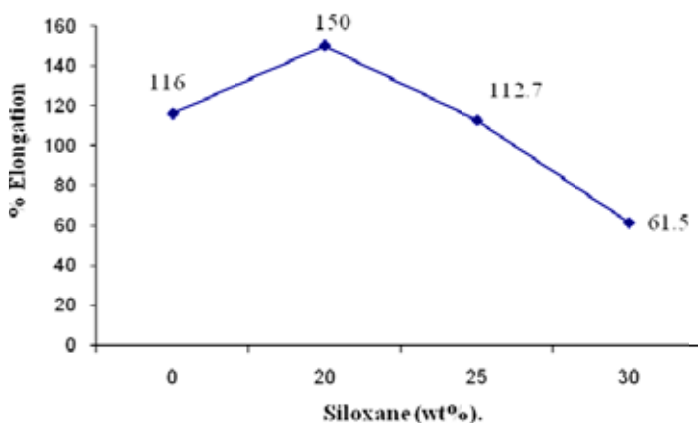


Fig. 12. % Elongation of styrene acrylic siloxane coating (Tg 0 °C)

3.8.3 Dirt-pick up resistance (DPUR)

It was observed from Fig. 13 that DPUR were improving by increasing siloxane content into hybrid polymer. This is because of siloxane is a low surface energy material, it won't allow dust particles to stick on the surface and hence they contribute majorly in dust repellency characteristics

3.9 Results of acrylic siloxane hybrid polymer latex

All the emulsion polymers were characterized for their physical properties and results are given below in Table 17.

3.10 X-Ray Fluorescence (XRF) of acrylic siloxane hybrid polymer latex

X Ray Fluorescence analysis of the hybrid polymers showed that the silicon content in the hybrids to be steadily increasing as expected. The results of the various hybrid samples are demonstrated in Fig. 14.

3.11 Dynamic Light scattering of acrylic siloxane hybrids latex

DLS analyses of the acrylic siloxane hybrid polymers are shown in Fig. 15 (a), (b) and (c). it shows that there is a steady increase in polymer latex sizes with increasing siloxane content in the system. Interestingly, the poly dispersity of the system remains unaffected thereby confirming that the organo siloxane is getting crosslinked to the emulsion latex particle. Hence this affirms the view that these hybrids are core shell particles.

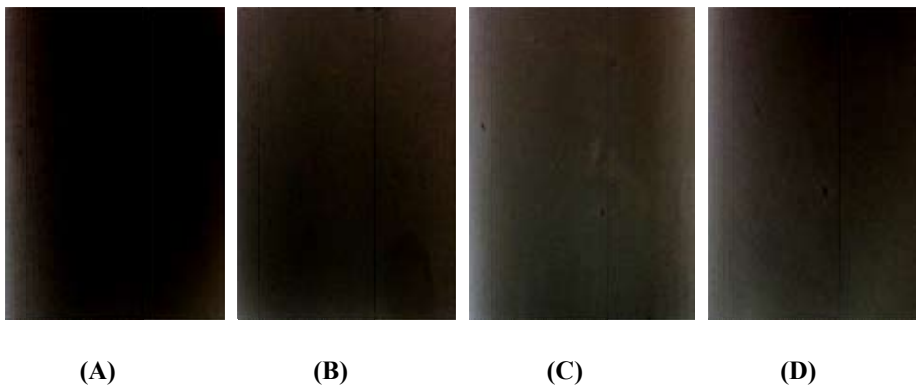


Fig. 13. Dirt pick up resistance of styrene acrylic siloxane (Tg 10⁰c) coating in Carbon black test

Table 17. Properties of Acrylic siloxane hybrid latex (Tg 15⁰C)

Exp No.	SAE 4	SAE 4.15	SAE 4.20	SAE 4.25	SAE 4.30
Appearance	Transparent	Transparent	Transparent	Transparent	Transparent
Viscosity (in gm)	61	73	73	73	76
Ph	10.35	10.23	10.23	10.14	10.13
Electrolytic stability	30	24	25	26	21
MFFT (°C)	<30	<30	<30	<30	<30
Freeze-Thaw stability	Passed 5 cycles	Passed 5 cycles	Passed 5 cycles	Passed 5 cycles	Passed 5 cycles
Actual Tg (°C)	30.1 °C	33 °C	31.8 °C	33.7 °C	32.4 °C

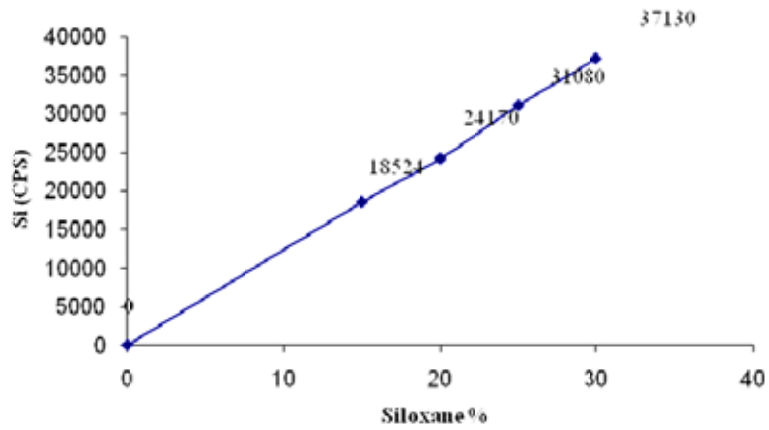


Fig. 14. XRF of pure Acrylic Siloxane hybrid polymer (Tg 15 °C)

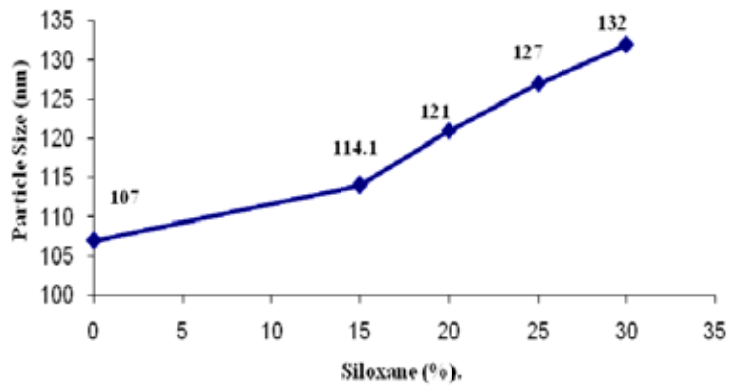


Fig. 15(a). particle size of acrylic-siloxane hybrid polymers

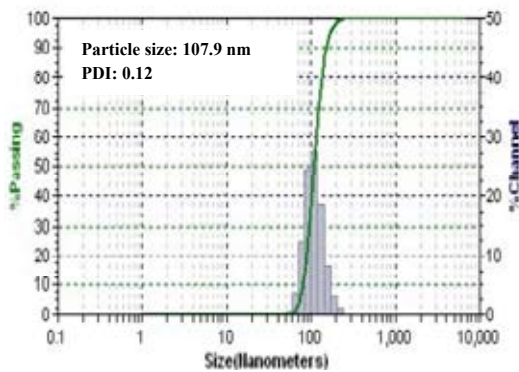


Fig. 15(b). Particle size of SAE 4 with 0 % siloxane

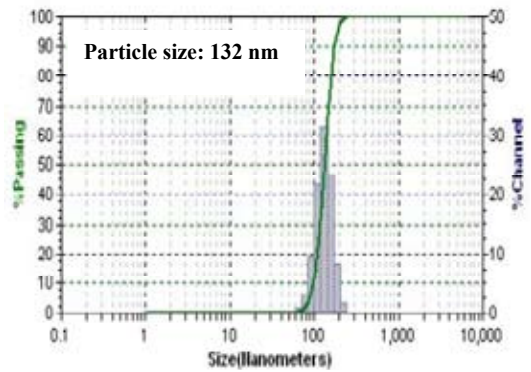


Fig. 15(c). Particle size of SAE 4.30 with 30 % siloxane

3.12 DSC of acrylic siloxane hybrid polymer latex

DSC analyses of the hybrid polymers show that the T_g of the polymer shows two transitions indicative of heterogeneity in the hybrid, see Table 18. The pure core particle does not show double transition. This reaffirms the view that these are core shell particles.

3.13 Contact Angle Measurements

of acrylic siloxane hybrid polymer latex

The contact angle is a measure of the surface wettability of the film with respect to water. Wettability is inversely proportional to the contact angle of the surface to water. Low wettability is a highly desired phenomenon in coatings, see Table 19. It is observed that the contact angle increased in acrylic siloxane hybrids with respect to only styrene acrylic systems.

It was observed from Fig. 16, that contact angle of emulsion films were increase steadily by increasing amount of siloxane. The contact angles were improved because of hydrophobic nature of siloxane which repels water and hence promising moiety for water proofing characteristics.

3.14 Scanning Electron Microscopy with EDXS

of acrylic siloxane hybrid polymer latex

The hybrid films were characterized using Scanning Electron Microscopy coupled with Elemental Analysis (Fig. 17(a), 17(b)). This shows the presence of silicon distributed uniformly across the film structure. There is no disparity in the concentration of silicon through out the sample.

Table 18. Results DSC analysis

Experiment No	Weight % of Siloxane	Major T _g (°C)	Minor T _g (°C)
SAE 4	0	30.1	--
SAE 4.15	15	33	2.8
SAE 4.20	20	31.8	4.3
SAE 4.25	25	33.7	7.1
SAE 4.30	30	32.4	11.1

Table 19. Contact angle of Acrylic Siloxane emulsion (T_g 15 °C)

Experiment No.	Siloxane (%)	Contact angle
SAE 4	0	43.17
SAE 4.15	15	68.7
SAE 4.20	20	71.5
SAE 4.25	25	75.6
SAE 4.30	30	78.1

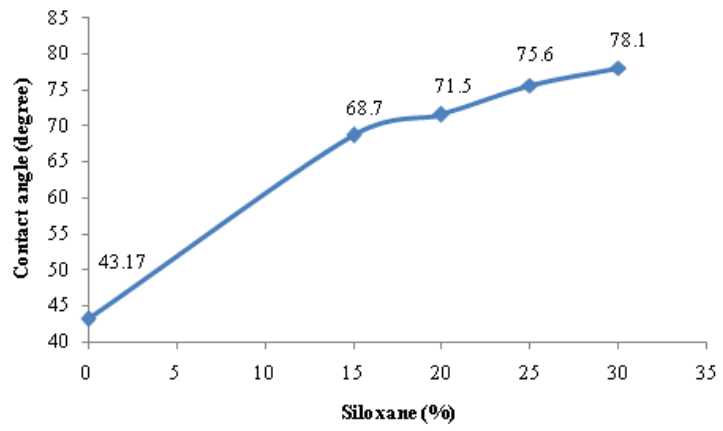


Fig. 16. Contact angle of Acrylic Siloxane emulsion (Tg 15 °C)

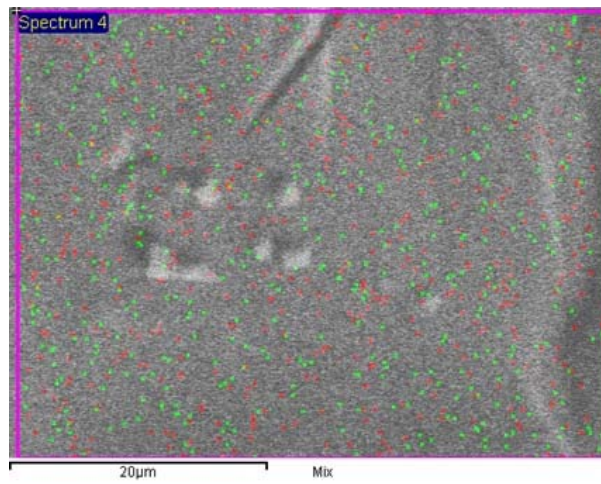


Fig. 17(a). SEM image of acrylic siloxane hybrid polymer latex

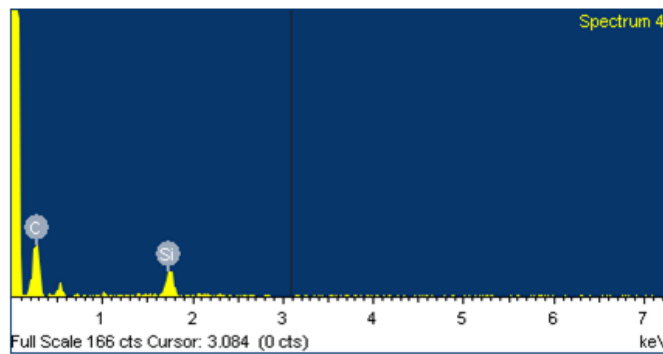


Fig. 17(b). Elemental Analysis of acrylic siloxane hybrid polymer

3.15 Performance Properties of Paints

3.15.1 Weatherability

The paints panels were exposed to the UV A radiation for 600 hrs. UV radiation is of high energy and caused deterioration of paint films. The data shown in the Table 20 gives the colour change (dE *)

It may be observed clearly from the Fig. 18(a) & (b) that the hybrid polymers perform better in weather ability while the styrene acrylic systems show deterioration of coating. The coating with 15

Table 20. Color difference of Acrylic Siloxane paint after 624 hours exposure at Q-UV A

Exp. No.	Siloxane (wt %)	Color difference (DE*)
SAE 4	0	4.519
SAE 4.15	15	2.013
SAE 4.20	20	2.713
SAE 4.25	25	2.788
SAE 4.30	30	2.857

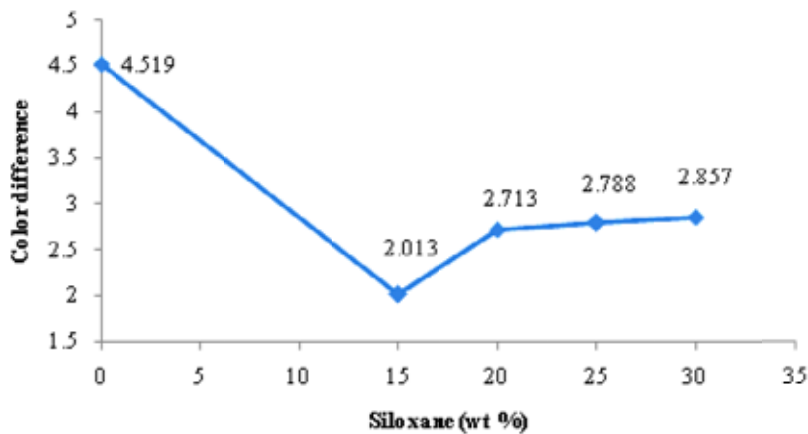


Fig. 18. Color difference of Acrylic Siloxane paint after 624 hours of exposure at Q-UV A

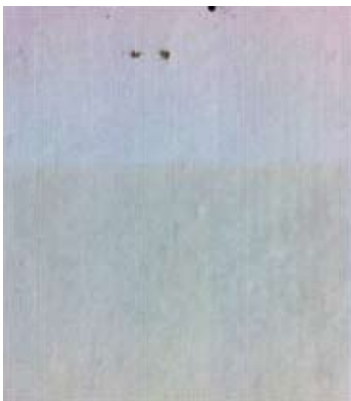


Fig. 18(a). SAE 4 with 0 % of siloxane



Fig. 18(b). SAE 4.15 with 15 % of siloxane

wt % was showing very good color retention properties. This is because of strong bond energy of $-\text{Si}-\text{O}-$ (445 KJ/Mol) of siloxane which is very stable against the UV light. Hence, the coating with 15 % siloxane was showing very good color retention properties.

3.15.2 Mechanical Properties of Paints Properties

It was observed from Fig. 19, that siloxane were improving the elongation properties as well as tensile strength of coating. The coating having 15-20 wt % siloxane was showing high elongation as well as very good tensile strength. This is because of siloxane are cross-linking with acrylic.

3.15.3 Dirt-pick up resistance (DPUR)

It was observed from Fig. 20, that DPUR were improving by increasing siloxane content into hybrid polymer. This is because of siloxane is a low surface energy material, it won't allow dust particles to stick on the surface and hence they contribute majorly in dust repellency characteristics. The coating containing 15-20 wt % siloxanes were showing good DPUR as well as good mechanical properties.

4. Conclusions

In this study we synthesized styrene-acrylic resins and pure acrylic resins by free radical copolymerization to making core and this resin is processed with post addition of an organo-siloxane to making shell on top of core and also we synthesized pure acrylic-siloxane resins by free radical

Table 21. Mechanical properties of Styrene Acrylic Siloxane coating

Experiment No.	Siloxane (wt%)	% Elongation	Tensile strength (MPa)
SAE 4	0	137.45	2.04
SAE 4.15	15	154.6	2.23
SAE 4.20	20	154.1	2.23
SAE 4.25	25	127.7	2.47
SAE 4.30	30	124.6	2.38

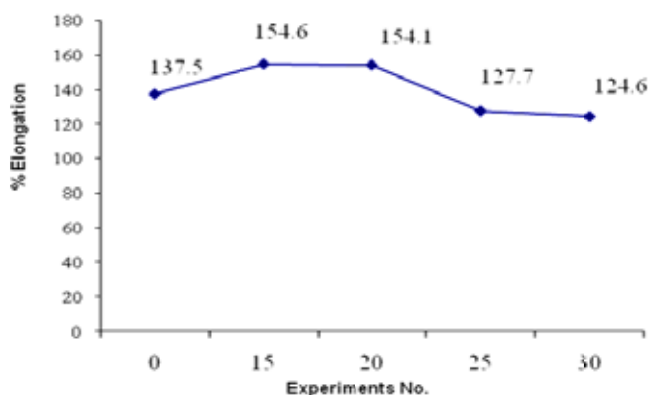


Fig. 19. Elongation of acrylic siloxane hybrid polymer

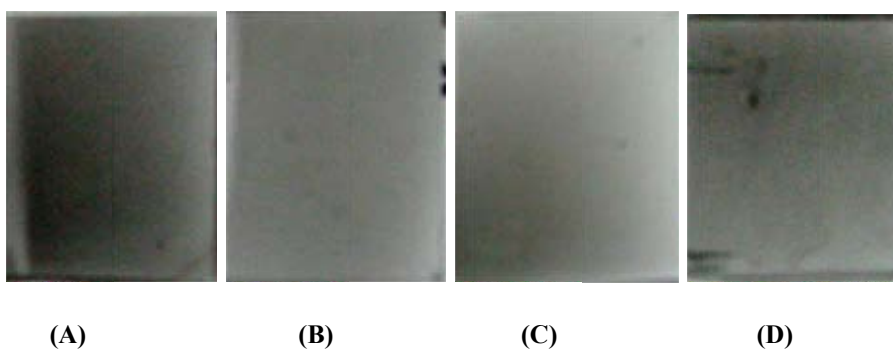


Fig. 20. Dirt pick up resistance of acrylic siloxane (Tg 15 °C) coating in carbon black test

copolymerization. White coatings were formulated according to the formulation chart for general-purpose architectural coatings, and these resins were blended with the mill-base in a 4:6 ratio. We studied the effect of siloxane content on the mechanical properties and weather ability of coatings in order to develop superweatherable coatings. Weather ability was tested using the outdoor exposure and accelerated weather ability tests.

The conclusions from the present study are:

- Latexes of styrene–acrylic copolymers and pure acrylic copolymers using semi-continuous seeded emulsion polymerization were synthesized smoothly using a combination of anionic and nonionic surfactants.
- A shell of organo-siloxane on the core latex particle was synthesized through cross-linking mechanism.
- The acrylate siloxane hybrid polymers were characterized for their thermal, and surface properties
- The DSC showed that there was a double transition in hybrid polymers which was non-existent in the core particles.
- The particle analyses of the hybrid polymers clearly showed that there is an increase in the size of the core particles indicative of a core shell nature.
- The contact angle measurements were indicative of an increasing hydrophobic nature of the hybrid polymers.
- The paints made using the hybrid polymers as binders were found to display superior weather ability
- The mechanical properties of the paints such as elongation and tensile strength were found to improve with the siloxane content in hybrid polymeric binders.

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