

MMA/BA COPOLYMER WITH HIGH SOLID CONTENTS EMULSION FOR WATERBORNE COATINGS

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ABSTRACT:

The high solid content acrylic emulsion with a low viscosity is achieved by copolymerization of methylmethacrylate (MMA) and butylacrylate (BA) through emulsion polymerization method. By adopting the semi continuous copolymerization method of methylmethacrylate and butylacrylate, it was found that the 63% solid content resin can be prepared through this polymerization in presence of water soluble initiator (Potassium Persulphate, KPS) and Sodium Lauryl Sulfate (SLS) is used as a emulsifier . The effect of the initiator concentration, monomer to solvent ratio on solid content was studied. The copolymer was characterized by Fourier Transform Infrared (FTIR) spectroscopy. The thermal stability of synthesized resins was studied by Thermo Gravimetric Analyzer (TGA). The high solid content acrylic emulsion mostly used as a binder in water borne paint formulations because its having less volatile organic compound (VOC) which provides environmental protection and exhibits an excellent film formation ability and appearance.

KEYWORDS: high solid content, acrylic emulsion, emulsion polymerization, copolymerization.

1. INTRODUCTION:

Increased environmental awareness and some legal provisions are forcing the coatings industry to reduce the emission of solvents (VOC / volatile organic compounds). There are various concepts in the coatings industry for the development of environmental friendly coating systems such as water-based coatings, high solid coatings, powder coatings, UV-curing systems etc. These different environmental friendly systems may be combined to provide excellent results. So now a day the waterborne paints with high solid contents have been an important field for research throughout the world. The Environmental Protection Agency (EPA) has driven the coating industry to produce high performance polymers with low or no solvents for industrial applications.[9]

However, all types of traditional paints are being converted into waterborne paints, and all new waterborne paints require new aqueous resins. This requirement can be fulfilled by the application of pure acrylic resins which has been synthesized by emulsion polymerization method. Acrylic resins, which have an important commercial application in paint industry. The acrylic resin is prepared through the polymerization of acrylic and methacrylic acids or their corresponding esters. The acrylic resins are more suitable in a variety of paint and coatings among the binders. The main properties of acrylic coatings is their resistance to weathering, high block resistance, hardness, gloss and high resistance to alkali and oxidation.

One of the most important processes to manufacture acrylic resin is emulsion polymerization. In emulsion polymerisation the heat transfer is very efficient and the viscosity build-up of the latex is quite low and the lowest particle size achieved as compared to other techniques. In short duration, emulsion polymerisation yield high conversion (almost 100%). So the emulsion polymerization is widely used for paint and adhesives. In this technique the polymerisation proceeds at the micelle, where the surface to volume ratio is very high, the rate of polymerisation is also quite high. It is important to optimize polymerization process with regard to emulsifiers; initiator and water soluble monomers for obtain the well structured latex. The factors such as particle size, glass transition temperature (T_g), surface charge density of latex particles and type of monomers change the properties of polymers. So the regulation of these factors is the prime concern in whole system. The emulsion system generally utilizes water soluble initiator such as persulphates.

It was aimed to investigate the usage of pure waterborne poly (acrylate) resins, in which methyl methacrylate (MMA) was used as the main monomer, as binder in paint industry. The film formation structure and properties of resins, which were synthesized systematically, were investigated in order to determine the properties of monomers in acrylic resin structure

which characterize properties of binders. The emulsion polymerization was carried out for 3 h with 200 rpm shaking rate at a temperature of $70 \pm 1^\circ\text{C}$. The selected polymers have low Tg values (between 21 and 37.5°C) showing that synthesized polymers have moderate flexibility. [7]

It was found that, for the semi continuous copolymerization of methylmethacrylate and butylacrylate coagulum-free 45.20% solid content latexes can be obtained through micro emulsion polymerization using Dowfax 2A-1 surfactant. The degradation starts around 220°C and 30% degradation is observed at 420°C . [5]

In the present work the effect of synthesis parameter i.e. initiator concentration, monomer to solvent ratio on solid content and properties of latex has been thoroughly investigated. The initiator plays a dominant role in the free radical polymerisation of high solid acrylic based resins. High solid content acrylic latex with low viscosity exhibits excellent property for binder which also takes care of environmental safety by formulating solvent free coatings.

2. EXPERIMENTAL WORK:

2.1 MATERIALS:

Methyl methacrylate (MMA) (LobaChemie, Mumbai, India) and butyl acrylate (BA) (Otto Chemie, Mumbai, India) were purified by treating with 10% Sodium hydroxide (NaOH) (LobaChemie, Mumbai, India) solution followed by washing with De-ionized water (Aquapath, Mumbai, India) to remove inhibitor. Potassium persulfate (KPS) (LobaChemie, Mumbai, India) of extra pure grade were used without further purification, Sodium lauryl sulfate (SLS) (LobaChemie, Mumbai, India) surfactant was used as received.

2.2 METHODOLOGY:

The polymerization reaction is a chemical aspect. In this system, polymerization system, catalyst system and the solvent system includes. This refers to the physical aspects of polymerization reactions which decide whether the monomer is polymerized in its condensed or gaseous state. It is polymerized as such or along with other inert components such as solvents and non-solvents, a factor such as the nature of the monomer and the type of polymerization mechanism chooses.

The experimental apparatus consisted of a two liter cylindrical four neck flask made of glass. Standard Four neck flask provided with a high speed stirrer. It is equipped with motor and with external jackets for heating and cooling. Proper arrangements are provided for the control of reaction temperature and the speed of the stirrer.

Emulsion polymerization was carried out in four neck flask with a mechanical stirring at 200 rpm to 300 rpm, under constant nitrogen supply. Temperature of reactor system was kept constant at $55^\circ\text{C} \pm 5^\circ\text{C}$. Pre-weighed surfactant, sodium lauryl sulfate (SLS) and water were charged in the reactor and the addition of Methylmethacrylate(MMA) and Butylacrylate(BA) monomer by certain time interval was followed. N_2 gas supply is mandatory to ensure absence of oxygen into reactor. Agitation was start at rate of 200 rpm and simultaneous purged the N_2 gas into reaction mixture. After one hour of agitation the aqueous Pottasium persulphate (KPS) solution was then added from the top and the polymerization was initiated. During the polymerization, adequate of the reaction mixture were withdrawn from the reactor at different time interval to check viscosity.

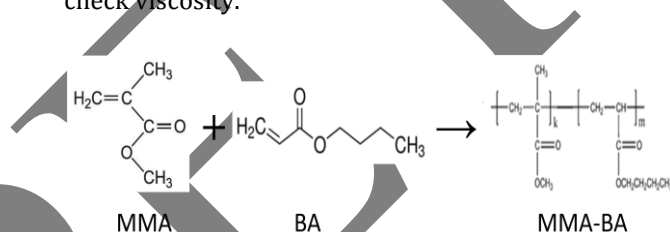


Fig. 1: Reaction of synthesis of MMA-BA

Anionic surfactant which is sodium lauryl sulfate(SLS) is used for micelle formation its CMC (Critical micelle concentration) is 2.6 g/l. Methyl methacrylate is a monomer and Butyl acrylate is a co-monomer, the ratio of monomer to co-monomer is 1:1 which is kept constant throughout the recipes.

Recipes used in the semi continuous polymerization of Methyl methacrylate (MMA) and butyl acrylate (BA) are given in Table 1.

Table 1: Sample recipes with solid contents

Sample ID	Polymer	Mo no mer r(w/w)	Mon omer :Solv ent	Solvent(w/w)	Surfacta nt(w/w)	Initiator (w/w)	Solid Cont ent (%)
Sample-A	Poly(MMA /BA) 1:1.5	36.20	1:1.6	60.3	3.37	0.13	54
Sample-B	Poly(MMA /BA) 1:1.5	37.5	1:1.5	57.56	4.56	0.38	73
Sample-C	Poly(MMA /BA) 1:1.5	40	1:1.4	56	3.66	0.44	60
Sample-D	Poly(MMA /BA) 1:1	39	1:1.54	60.25	0.3	0.45	63
Sample-E	Poly(MMA /BA) 1:1	35	1:1.60	58.72	5.81	0.47	75
Sample-F	Poly(MMA /BA) 1:1	35	1:1.67	58.67	5.76	0.57	77.68
Sample-G	Poly(MMA /BA) 1:1	46.77	1:1	46.77	5.87	0.58	66.57

2.3 FILM PREPARATION-

The synthesized acrylic emulsion samples were coated on cement blocks and glass panels, using a coater. The coated panels were cured at room temperature for

12-24 hours and kept at ambient condition for 24-48 hours to ensure complete maturation of films before testing.

2.4 CHARACTERIZATION-

2.4.1 Fourier Transform Infrared-

As per ASTM E168, ASTM E1252 the infrared spectra of the samples were obtained by a FTIR 1-S Affinity from 400 - 4000 cm⁻¹ range. Michelson interferometer (30° incident angle) Equipped with dynamic alignment system sealed interferometer with auto dryer with Diamond as a ATR crystal and DLATGS detector equipped with temperature control mechanism.

2.4.2 Thermogravimetric Analyzer-

The decomposition profile of acrylic emulsions were thermogravimetrically analyzed using TG analyzer. The test was carried out on TGA-50 (Shimadzu, India) under nitrogen atmosphere. The rate of heating was 10°C/min and the sample were heated upto 600°C.

2.4.3 Total solid content-

As per ASTM D2834, the total solid content in acrylic emulsion is calculated at 750C temperature for 60 minute.

2.4.4 Viscosity determination-

The viscosity of the samples was determined by B ford cup according to ASTM D1200. The Ford viscosity cup is a simple device that permits the timed flow of a known volume of liquid passing through an orifice located at the bottom.

2.4.5 Pencil Hardness-

As per ASTM D3363, the hardness of the film was measured by rating the hardness of lead pencils.

2.4.6 Adhesion test-

The adhesion test was performed as per ASTM D3359. The samples were coated on glass panels cement blocks and cut into squares of 1×1mm. Adhesive tape was applied to the cross-cut area, firmly rubbed with a fingertip, and removed after 2 minutes. The number of squares intact gives a measure of adhesion of the sample.

2.4.7 Chemical Resistance-

Chemical resistance was checked as per ASTM D1647-89. The glass panels were dipped into 2% sulphuric acid and 2% sodium hydroxide solutions and the change in the appearance was monitored after 24 hours.

3. RESULTS AND DISCUSSION:

3.1 TOTAL SOLID CONTENT-

The solid content is calculated as per ASTM D2834 at 75°C temperature for 60 minute.

$$\text{Solid Content} = \frac{W3 - W1}{W2 - W1} \times 100$$

Where,

W1 is the weight of petridish; W2 is weight of petri dish along with sample before heating and W3 is weight of petri dish and sample after heating.

In the series of reactions, to optimize the initiator concentration, initiator concentration was varied between 0.1 to 0.6 with the monomer to co monomer concentration. Very little difference was observed in solid content with variation in initiator concentration around 54-77%. At lower and higher concentrations of initiator, coagulum formation was observed. To improve the percentage of solid in the latex, monomer to co monomer concentration was varied from 1:0.3 to 1:1.5 At higher concentrations of monomers to co monomer ratio coagulum formation was observed because of reduced stability of the latex. With increase in ionic concentration of the continuous phase, solid percent was improved from 54 to 77.8. At 77.8% solid content the initiator concentration was 0.57, whereas at 54% it was 0.13.

3.2 EFFECT OF INITIATOR CONCENTRATION ON HIGH SOLID CONTENT:

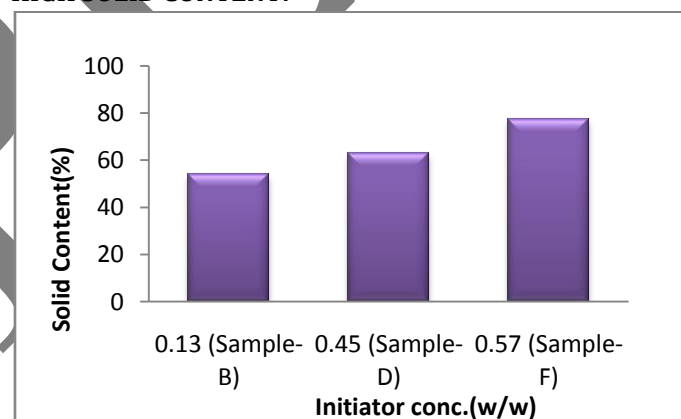


Fig. 2: Initiator conc. v/s Solid content

Above Graph shows that when initiator concentration increases with constant reaction temperature then high initiator concentration leads to excess generation of free radical which increases rate of initiation of polymerization hence solid content will increase.

3.3 FTIR ANALYSIS:

Infrared spectra of the samples were obtained by a FTIR 1-S Affinity from 400 - 4000 cm⁻¹ range. Michelson interferometer (30° incident angle) Equipped with dynamic alignment system sealed interferometer with auto dryer with Diamond as an ATR crystal and DLATGS detector equipped with temperature control mechanism.

Fourier Transform Infrared (FTIR) Spectroscopy is only supporting tool for identification of structures. -CH₃ & -CH₂ aliphatic group is between 2990-2850 cm⁻¹ because MMA-BA copolymer has long aliphatic chain of

Butyl Acrylate, CH₃ aliphatic compound is between 1465-1440 cm⁻¹ because MMA-BA copolymer has CH₃ group, C=O aldehydes is between 1740-1720 cm⁻¹ and C-O-C ether is between 1240-1070 cm⁻¹ because both MMA and BA has C=O and C-O-C group, the presence of MMA and BA monomer can be predict by intensity of C-H peak for alkenes. In the Fig.3 both the spectrum C-H peak is weak with very short intensity hence the concentration of monomer is negligible.

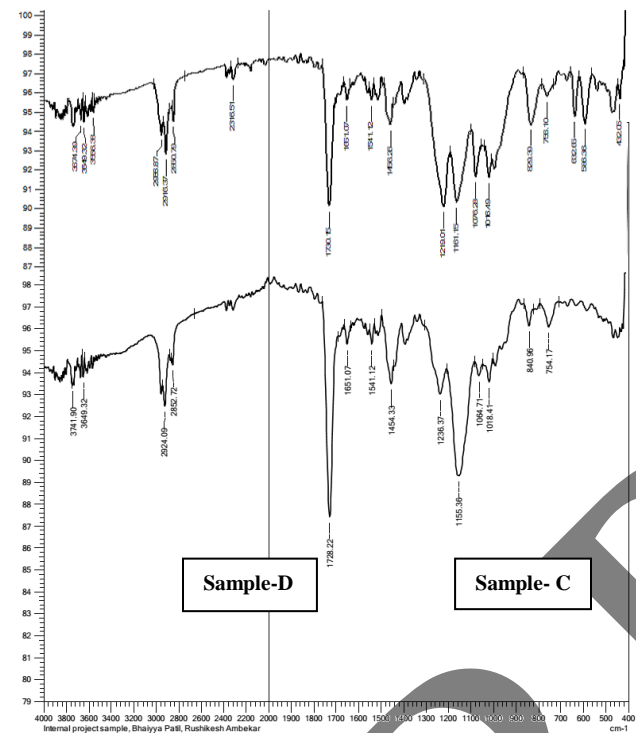


Fig. 3: FTIR spectrum of Sample-C and Sample-D with monomer to solvent ratio 1:1.4 and 1:1.54 respectively.

3.4 THERMO GRAVIMETRIC ANALYSIS (TGA) :

TGA curves determine that degradation process which goes along with the weight reduction, started just after the thermal decomposition. Thermo Gravimetric Analyzer (TGA) was carried out on TGA-50 (Shimadzu, India) under nitrogen atmosphere. The rate of heating was 10°C/min and the samples were heated up to 600°C. Fig.4 and Fig.5 shows the TGA thermograms of acrylic latex. The TGA thermogram investigated by peak of sample-A (Fig.4) at 478.54°C for the derivative of the weight loss for acrylic latex up to 95.19%. While in the case of sample C (Fig.5), peaks at 423.1°C, for the derivative of the weight loss 90.92%.

The presented peaks are close to that observed for TGA analysis. When monomer concentration was increase in the polymerisation system then thermal stability will also increases. The Fig.4 & 5 distinguish when monomer to solvent ratio is 1:1.65 then weight loss start from 142°C and when monomer to solvent ratio is 1:1.4 then weight loss start from 249.8°C because the concentration of solvent is less therefore thermal

stability is more. The final residual weight percents at high temperatures (600°C) are listed.

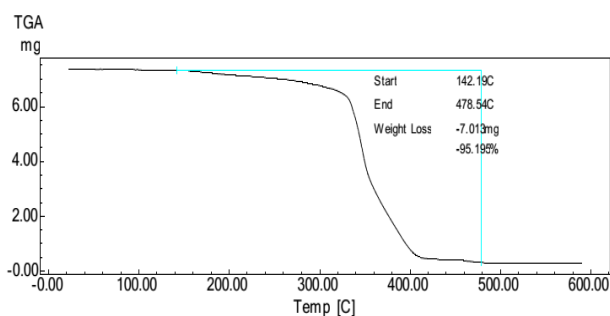


Fig.4: TGA curve for sample A

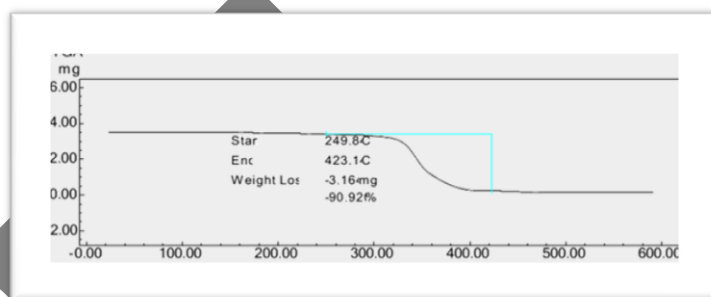


Fig.5: TGA curve for sample C

3.5 DETERMINATION OF VISCOSITY-

The viscosity was determined by B ford cup. The cup was filled up to the mark with a given fluid. The nozzle was closed and kept it on the vertical stand. The nozzle was open and time was noted in seconds. It determines by the formula

$$\eta = 48.5 / B$$

Where, η is viscosity in poise and B is flow time for test liquid. Flowing table shows the viscosity for different compositions.

Table 2: Viscosity of different samples

Sample ID	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G
Viscosity (poise)	1.89	2.16	1.78	1.24	2.27	2.51	2.34

From Table 1 & 2 Sample B,E & F has observed the solid content is more than 70% i.e. got the high solid content but from table 2 these samples has observed the viscosity is more than 2 poise. Sample A, C & D shows the low viscosity value. Amongst this samples D has the lowest viscosity with 63% solid content. So this sample will be more appropriate binder for surface coating due to its optimum solid content with low viscosity.

3.6 PENCIL HARDNESS:

Table 3 shows that sample shows the pencil hardness. There is gradual increase in the hardness with increase in acrylate content in the emulsions. This may be attributed to the crosslinking of polar group of acrylics, which forms the dense network as a rigid

polymer networks. Where there is a higher percentage of acrylate, hardness is more.

3.7 ADHESION TEST:

It can be seen from Table 3 that all the samples of resin have passed the adhesion test indicating excellent compatibility to the substrate.

3.8 CHEMICAL RESISTANCE:

Films were tested for chemical resistance by soaking the coated specimens in 2% w/w sulphuric acid and 2% w/w sodium hydroxide at room temperature. From the data displayed in Table 3 it can be revealed that, all the coatings synthesized by emulsion process exhibited excellent resistance to acid and alkali.

Table 3: Film properties of HS content resin

Sr.No	Properties	Samples		
		D	E	F
1	Pencil Hardness	H	2H	2H
2	Adhesion	88 %	85%	80%
3	Chemical Resistance	Excellent	Excellent	Excellent
4	UV Resistance	Good	Good	Good
5	Transparency	100%	100%	100%
6	Appearance	Almost colorless, transparent	Almost colorless, transparent	Almost colorless, transparent

4. CONCLUSION:

Acrylic monomer of methylmethacrylate (MMA) controls the hardness of the resin where as butyl acrylate (BA) provides the flexibility to the emulsion. Optimization of emulsion polymerization process with regard to initiator concentration and Monomer: Solvent ratio is done with different combinations. The all samples are tested successfully and it is found to have satisfactory appearance and physical properties to be used as binder in the paint industry. Synthesized binder exhibits high solid content, low viscosity, high transparency and excellent film forming ability.

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