Global Journal of Science Frontier Research: B
Chemistry
Volume 18 Issue 1 Version 1.0 Year 2018
Type: Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

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GJSFR-B Classification: FOR Code: 039999

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I. INTRODUCTION

Regulation of volatile organic compounds (VOC), incorporation of biomaterials, demand for long lasting sustainable high performance water based coating are the recent research trend in the field of organic coating. To enhance the performance of acrylic latex, alkyds are incorporated in the acrylic latex system as alkyd impart flexibility and acrylics have excellent durability and toughness properties [1]. A suitable combination of alkyd and acrylic may perform faster drying through crosslinking of acrylics and alkyd by auto oxidation process. However, it is very difficult to incorporate alkyd into acrylic system by emulsion polymerization to form alkyd – acrylic hybrid polymer [2]. Etham et. al. reported the modification of soya bean oil by sequential amidation and acrylation in the terminal double bonds which was used as co-monomer in acrylic emulsion polymerization [3]. Several efforts have been made via mini emulsion polymerization technique for incorporation of alkyd into acrylic phase [4 - 7]. It was also reported that the alkyd and acrylic polymer can be blended by melt condensation reaction [8]. Nabuurs et.al. reported the total conversion of acrylic monomers in presence of colloidal alkyd droplets [9]. Other than synthesis techniques, the performance of the coating film have also been enhanced by using allylic fatty acid derivative (AFAD) and an acrylic fatty acid derivative (AcFAD) by crosslinking process as both are reactive coalescing agents and co monomers [10]. Morenoa et.al. reported the modification of oleic acid and linoleic acid by methyl methacrylate to form methacrylated oleic acid and methacrylated linoleic acid by grafting [11]. It has also been reported the emulsion polymer of methyl methacrylate modified soya bean oil formed by emulsion polymerization technique [12]. A series of work have been reported on acrylated alkyd emulsion formed by grafting of acrylic polymer from different monomers like methyl methacrylate, butyl acrylate, styrene, acrylic acid onto different alkyds based on linseed/soya been oil followed by mini emulsion polymerization [13-18]. However, emulsion polymerization is an effective technique to synthesise hybrid latex and alkyd may be used as emulsifier after proper modification and acrylic monomers can be polymerized in presence of colloidal alkyd droplets.

In the present study, specially designed water dispersible soya bean oil fatty acid based alkyd resin having low molecular weight, low poly disparity with a balanced hydrophilic and hydrophobic structure was synthesized and used for the synthesis of alkyd-acrylic hybrid emulsion by free radical seeded semi continuous emulsion polymerization technique. To optimize the efficiency of alkyd in emulsion polymerization as well as hybrid emulsion stability, alkyds at different percentage of fatty acid, hydroxyl value and acid value were evaluated. The performance of such alkyd stabilized acrylic emulsion have also been evaluated and compared against conventional surfactant based acrylic emulsion.

II. EXPERIMENTAL

a) Materials

Commercial grade monomers, methyl methacrylate (MMA) (Gujarat State Fertilizers & Chemicals Ltd., India), n - butyl acrylate (BA) (LG Chem. Ltd. Korea) were used as received. Sodium lauryl sulphate (SLS) (Fisher Scientific, India) was used as surfactant. A water soluble initiator, Potassium persulfate (PPS) (Calibre Chemicals Pvt. Limited, India) was used for emulsion polymerization. Organic initiator Tert-butyl hydro peroxide (TBHP) (70% solution) (Spectrochem Pvt Ltd, India) and Sodium meta bisulfite (SMBS) (Fluka, USA) were used as redox pair initiator. Sodium bicarbonate (SBC) (Darshan Chemicals, India) was used as buffer to control pH during reaction. Distilled water was used in all steps of the processes. Liquid ammonia (28% aq. Solution), (Indian Scientific

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Enterprises, India) was used as such for neutralization. Soya bean oil fatty acid (SOFA) (Kargill Ltd., India), Tri methylol propane (TMP) (Perstrop Ltd.,Sweden), Pentaerythritol (PE) (Perstrop Ltd., Soudi Arabia), Phthalic anhydride (Thirumalai Chemicals Ltd. India), Benzoic acid (BZA) (IG Petrochemicals Ltd., India) all these materials used for the synthesis of resin are of commercial grade and used as received without any further purification.

b) Preparation of Alkyd and Alkyd Dispersion

The formulation of different alkyds and their properties are presented in Table 1. For preparation of different alkyds, fatty acid, polyols, poly acid and monobasic acid were charged in a four necked round bottom flask fitted with a mechanical stirrer, a condenser attached with a Dean and Stark apparatus and a thermometer. The reaction was carried out at 160o C to 220o C and continued to achieve the desired final acid value.

Table 1: Composition of Different Alkyd Resins and their Properties

Resin Code	Resin Composition					Formulation constant		Physical Properties of Resin			
	SOFA	TMP	PE	PA	BZA	Oil length, %	Hydroxyl value, mg KOH/gm	Acid value, mg KOH/gm	Mw	PDI	Viscosity, cp
Alk 01	42.5	22.2	5.5	24.3	5.5	53	78	30	3793	1.59	54983
Alk 02	35	25	5	29	6	45	78	28	5012	2.09	2390000
Alk 03	51	21	5	19	4	62	78	26	2812	1.53	11550
Alk 04	42.5	22.2	5.5	24.3	5.5	53	78	21	6915	2.83	350000
Alk 05	42.5	22.2	5.5	24.3	5.5	53	78	41	2840	1.64	110370
Alk 06	42.24	20.55	5.55	26.66	5	53	57	31	3160	1.75	103430
Alk 07	42.22	22.22	6.66	23.35	5.55	53	103	30	3000	1.65	94000

For preparation of alkyd dispersion, 50 gm. of alkyd, 47.9 gm. of D.M. water and 2.5 gm of ammonia (28 percent in aqueous solution) were taken in a container and mixed under high speed dispersion at rpm of 900-1000 for 1hr.

c) Use of Alkyd Dispersion in the Preparation of Acrylic Emulsion

The water dispersible alkyd was used as a stabilizer for the preparation of acrylic emulsion (O/W). Three different types of latex (Type I, II and III) were designed to identify the effectiveness of alkyd as emulsion stabilizer. Type I: Surfactant used in nucleation process and pre-emulsion stabilization. Type II: Initiation started with surfactant nucleated process while alkyd dispersion was used in the pre-emulsion. Type III: Alkyd dispersion was used in nucleation process as well as pre-emulsion stabilization. The formulation recipe for all different types of emulsion is presented in Table 2. The emulsion polymerization was carried out in a three necked 2 litre capacity reactor equipped with stirrer, reflux condenser, feeding inlet and thermometer. Initially, the reactor was charged and equivalent quantity of monomers i.e. methyl methacrylate and n-butyl acrylate. After initial charging, the reactor was heated up to 800 C followed by addition of initiator to start the initiation. After initiation, 5% pre-emulsion, 6% initiator PPS (5% wt. solution) and 6% SBC (6% wt. solution) solution w.r.t. monomer were charged into the reactor under continuous stirring. After initiation and continuous feeding of pre emulsion was done for 4 hrs. Alkyd was used in the reaction medium during synthesis of Type II and III emulsion. The completion of reaction was monitored after measurement of solid content of the reaction mixture. Finally, TBHP and SMBS (8% wt. solution) were added in the reactor to deactivate any unreacted monomer present in the reactor.

Table 2: Formulation Recipe of Different Latex and their Properties

Latex/Emulsion type	Pre emulsion composition		Reactor charge		Emulsion Properties	
	Ionic surfactant	Alkyd dispersion (Alkyd Type)	Ionic surfactant	Alkyd dispersion (Alkyd Type)	Solid, %	Tg, ^{0}C
AL/Type I	1.13	0	0.34	0	48.9	12
ASAL01/Type II	0	2.3(Alk03)	0.34	0	44.8	10.77
ASAL02/Type II	0	2.3(Alk06)	0.34	0	44.9	11.8
ASAL03/Type II	0	2.3(Alk05)	0.34	0	44.8	10.92
ASAL04/Type II	0	2.3(Alk02)	0.34	0	44.9	11.57
ASAL05/Type III	0	2.3(Alk01)	0	2.3(Alk01)	44.9	10.42
ASAL06/Type II	0	2.3(Alk01)	0.34	0	44.9	10.54

d) *Film Preparation*

The newly synthesised acrylic emulsion samples were coated on mild steel and glass panels using box coater of 50 microns. The coated panels were cured at ambient temperature (300C) for 48 hrs, for complete maturation of the films before testing.

III. Test Methods, Calculations And Polymer Characterization

a) *Scratch Hardness Test as per BS 3900 Part E2*

Scratch resistance of a paint film is a measure of resistance to penetration by scratching with a needle. In this test, a scratching needle of 1mm diameter with hemispherical hardened steel tip, along with different specified load is applied over the needle and scratched the cured coating surface of the test paint. The loading on the needle is increased until the needle penetrates through the coating to the substrate. The minimum weight, which penetrates the coating, is recorded as the scratch resistance.

b) *Flexibility as per ASTM D522*

The test is carried out by bending the coated metal panel over round cylindrical mandrels of varying diameters, the film being bend on the outside. After bending, the coating is examined for cracking, flaking etc. The smaller the diameter of mandrel at which cracks appear in the film, the better is the flexibility of the coating material.

c) *Adhesion as per ASTM D 3359-95a*

The cross cut adhesion test was performed on the samples coated on mild steel panels and cut into squares of 1x1 mm, adhesive tape was applied to the cross cut area firmly rubbed with a fingertip and removed after 2 min. the number of squares intact gives a measure of adhesion of the sample.

Adhesion (%) = Number of squares intact in the tape applied area / Total number of squares in the tape applied area x 100

d) *Percentage Conversion*

Percentage Conversion (% NVM) was measured by gravimetric analysis after completion of reaction. 1 g of latex sample was weighed in a steel lid (Wi), dried it for 1 h at 120 °C and again weighted (Wd). The final non-volatile matter (% NVM) was estimated by the following equation.

$$\% \text{ NVM} = \text{WdWi}\ x\ 100$$

e) *Emulsion Stability*

Shelf life stability was measured by placing 30 ml of the emulsion in a capped glass vial and kept at ambient temperature (30^0C). The time needed for separation in the form of two layers to appear was monitored.

f) *SEM Study*

Specimen for SEM micrographs were prepared by sputter-coated with gold and micrograph images were taken under low vacuum mode, 10 kV voltages within a JEOL JSM 8360 SEM device.

g) *DSC Analysis*

The glass transition temperature (Tg) of different latex film sample was measured by differential scanning calorimetry (DSC), Perkin Elmer DSC 4000 model. The latex film sample in the range of 3 – 5 mg was held within a dedicated sample pan. The sample was scanned between - 60 ^{o}C to 120 ^{o}C at heating rate of 10 ^{o}C/min and cooling rate of 10 ^{o}C/min for two cycles under nitrogen atmosphere and the heat flux versus temperature data was recorded.

h) *GPC Study*

The relative values of weight average (Mw) and number average (Mn) molecular weights of all the alkyd resins were measured by Gel permeation chromatography (Waters). Tetrahydrofuran was used as eluting solvent. The instrument contains three poly styragel column (1000A^0, 500A^0, 100A^0). Flow rate was

0.3 ml/min. calibration was made using polystyrene standards.

i) Viscosity

Viscosity of different alkyd resins were measured at 25 ^{0}C using modular compact Rheometer (MCR 102) over the range of shear rate 0 – 60 s^{-1}. Viscosity was reported at 20.5 s^{-1} and 2.5 s^{-1} in the case of high viscous alkyd like Alk-02 and Alk-03.

j) Contact Angle

The emulsions were applied by brush on glass panels and cured for 7 days at room temperature (30°C). The static contact angle was measured by dropping water droplet on the surface of the dry coated film.

k) Water Resistance

The emulsion was applied on glass panel at a thickness of 200 micron and dried for 7 days at 30^{0}C. After proper drying, the coated panels were immersed in water and the film defects were monitored at different time intervals.

l) Alkali Resistance

The emulsion was applied on glass panel at a thickness of 200 micron and dried for 7 days at 30^{0}C. After proper drying, the coated panels were immersed in 0.1(N) aqueous NaOH solution and the film defects were monitored at different time intervals.

m) Solvent swelling

The coating applied on glass panels at a film thickness of 200 micron and dried for 7 days at 30^{0}C. After drying aromatic solvent like xylene was dropped on the surface of the film and swelling was monitored.

IV. RESULTS AND DISCUSSION

a) Effect of Emulsion Stability on the alkyd oil length, acid value and hydroxyl value

The stability of hybrid emulsion is a very important characteristic for storage of emulsion. The synthesised hybrid emulsions were kept in airtight bottle and stored at room temperature for a period of 12 months. The variation of emulsion stability with oil length of the alkyd is presented in Fig. 1.

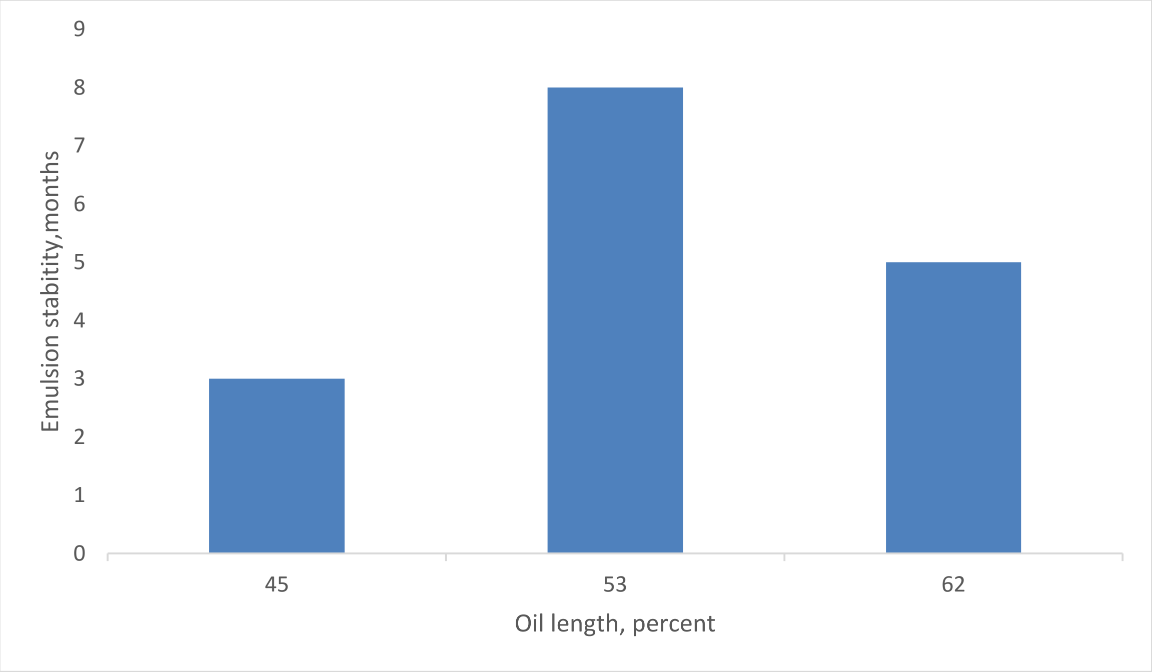

Fig. 1: Effect of emulsion stability on oil length of alkyd resin

The dispersion of alkyd after neutralization of the acid functional groups, depends on the molecular weight of the alkyd. The dispersion stability of emulsion using 45 percent oil length alkyd is not good due to high molecular weight compared to 53 and 62 percent oil length alkyd. However, with increase in oil length of the alkyd, the hydrophobic nature of alkyd mainly control the emulsion stability [19]. As a result, although the molecular weight of 62 percent oil length alkyd is low, but the hybrid emulsion stability with this alkyd inferior due to the presence of higher percentage of oil in the alkyd. The effect of hybrid emulsion stability on acid value and hydroxyl value of alkyd resin are presented in Fig. 2 and 3 respectively.

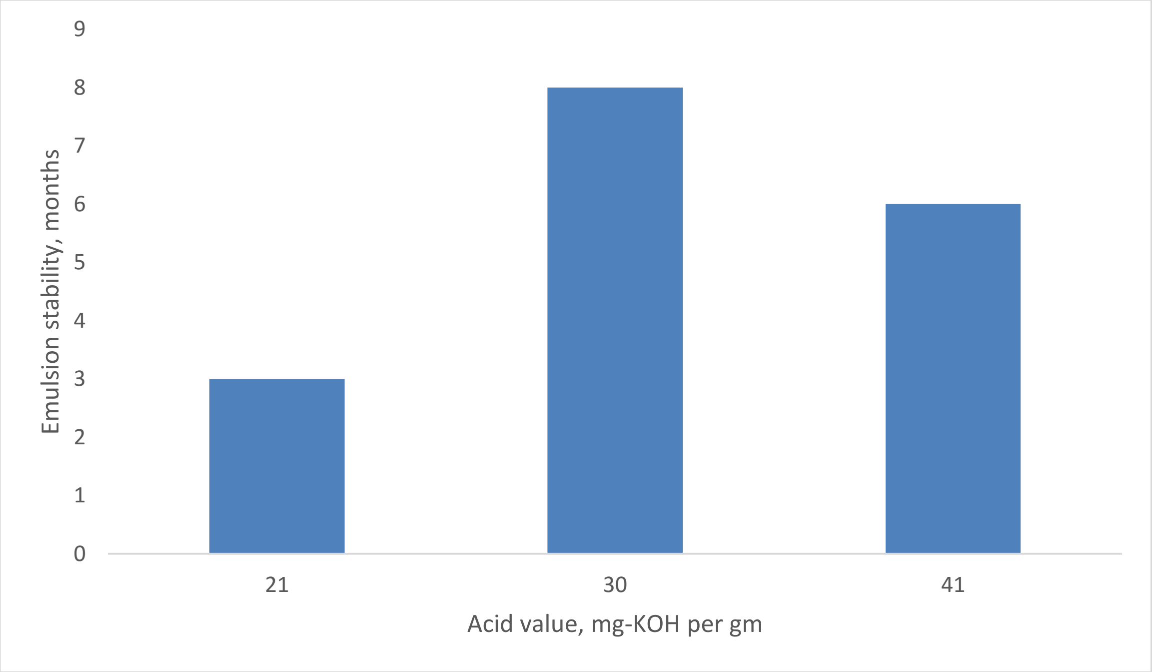

Fig. 2: Effect of emulsion stability on Acid value of alkyd resin

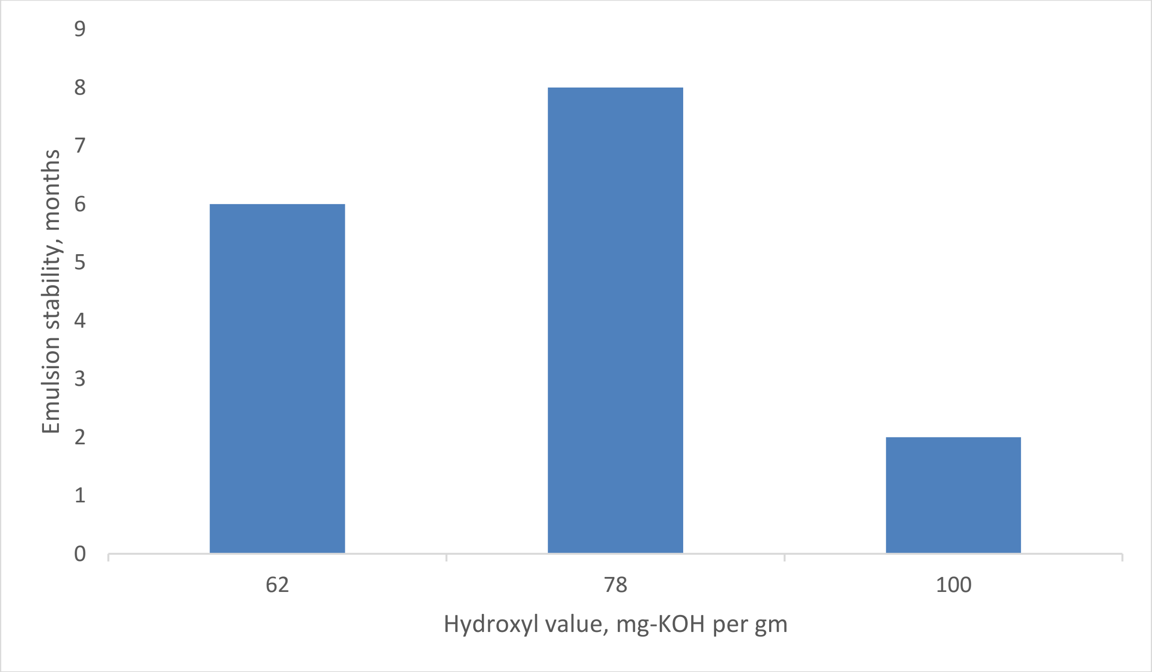

Fig. 3: Effect of emulsion stability on Hydroxyl value of alkyd resin

The increase of acid and hydroxyl value of any alkyd resin, increases the polarity of the resin. The acid functional groups of alkyd resin control water solubility after neutralization with any base. During nucleation and stabilization of growing particles in emulsion polymerization, the specially designed alkyd molecules (i.e. a balanced hydrophilic and hydrophobic structure and optimum molecular weight) were dynamically arranged on the particle surface and helps for the growth of particles without affecting the conversion of monomer [20]. The polarity of alkyd chain controls the dynamic orientation of alkyd chain. However, the surfactant nucleated latexes in combination with alkyd showed comparatively better emulsion stability in terms of phase separation as compared to the alkyd nucleated surfactant free latex due to a balanced polar structure. The hybrid emulsion containing alkyd resin having 53 percent oil length, 30 mg-KOH per gm acid value and 78 mg-KOH per gm is an optimum combination to achieve maximum stability.

b) Effect of alkyd resin on emulsion Polymerization

The dispersion of alkyd helps for stabilization of monomer pre emulsions and finally, converted into acrylic polymer through free radical emulsion polymerization technique. It has been found that the initiation of alkyd stabilized monomer pre emulsion for free radical emulsion polymerization was quite slow compared to conventional ionic surfactant stabilized system. The higher concentration of unsaturated fatty acids retards the rate of polymerization. Grafting can occur on the acrylic chain by free radical chain transfer mechanism [21, 22].This indicates the participation of alkyd in the reaction kinetics after capturing some radicals. This slow induction does not affect the overall conversion in the polymer chain. From gravimetric analysis, it was found that nearly 100 percent conversion achieved without any unwanted coagulum formation using 1.15 and 2.3 percent of alkyd (Type II & Type III) in the emulsion polymerization. Similar observation was also reported earlier by mini emulsion polymerization [17].

c) Comparative study on the coating properties of pure acrylic and alkyd acrylic hybrid emulsion

The coating properties of pure acrylic and alkyd acrylic hybrid emulsion (ASAL06/Type II) is presented in Table 3.

Table 3: Comparative evaluation of pure acrylic and alkyd acrylic hybrid emulsion

	Pure Acrylic	**Alkyd Acrylic Hybrid**
Emulsion Properties		
Appearance	Milky white emulsion	Off white emulsion
Non - volatile content, Percent	45.21	44.9
p^H	7.8	8.2
Viscosity in Ford Cup B4@ 30^0C, Second	44	42
Dry Film Properties		
Drying time, minutes	60	70
Scratch hardness, gm	1100	1000
Adhesion (cross hatch), %	95	100
Flexibility, ¼ inch	Slight inferior	Good
Water resistance, hrs	52	48
Alkali resistance, hrs	40	32
Glass Transition Temperature (Tg, ^{0}C)	12	10.5
Contact angle, Degree	88.5	100
Swelling resistance , Rating 1 poor and 10 best	5	7

The drying time of hybrid acrylic film is almost comparable with pure acrylic although alkyd have been incorporated in hybrid emulsion. This is due to grafting of acrylic monomers onto the unsaturated part of fatty acid. It has been observed that the hybrid emulsion film have very good adhesion and flexibility compared to hardness due to the presence of flexible alkyd component. This indicates excellent compatibility between alkyd and acrylate phases in hybrid emulsion [19]. It has been found that the swelling resistance and contact angle increases in the alkyd stabilised acrylic resin. This indicates the existence of post oxidative crosslinking in the alkyd stabilized latex system which reduces the surface swelling tendency [19]. However, it has also been found that the resistance to solvent swelling was better for high oil length alkyd which was also an indication of effective grafting. It has been found that the alkyd emulsion stability of the combination like ASAL01 with Alk-03, ASAL02 with Alk-06 and ASAL03 with Alk-05 were good and the contact angle were more than 80 for all cases. However, it has been found that the reduction of hydroxyl value decreases swelling and hydrophobicity of latex film. This is due to lower molecular integration or association in the hybrid emulsion. The contact angle of surfactant containing alkyd stabilized latex was higher than surfactant free latex ASAL05. This is an indication of surface modification of latex by alkyd molecules. It has also been found that a combination of higher dose of alkyd with zero surfactant does not enhance the contact angle. The effect of surface swelling on different hybrid latex and method of preparation is presented in Fig. 4. This was due to the generation of poor nucleation but effective acrylic grafting onto alkyd chain. The poor nucleation and effective alkyd grafting produced improper crosslinking. Out of these three, Alk-06 was comparatively more hydrophobic. Hence, this hydrophobicity enhancement depended on the availability of hydrophobic soybean fatty acid, molecular integration into acrylic phases and stability after latex synthesis.

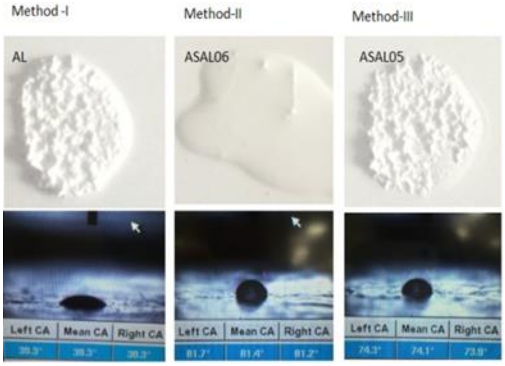

Fig. 4: Effect different preparation methods on the swelling of different emulsion film

d) *FTIR Analysis*

The FTIR spectra of pure acrylic and alkyd acrylic hybrid resin are shown in Fig. 5a and 5b respectively. The presence of sharp peak at 1723 cm-1 indicate the ester group of acrylate and alkyd resin. In Fig. 5 b, the bands at around 1129 cm-1 and 1273 cm-1 are assigned to stretching and bending frequency of C-O-C, CH bond respectively. The broad band at 3453 cm-1 in Fig. 5b is due to the presence of free O-H group of alkyd resin. The absorption bands in the region of 2925 cm-1 to 2850 cm-1 is due to C-H stretching of –CH3 and –CH2 groups respectively [23, 24]. In Fig 5b, the CH out of plane bending frequencies at 729 cm-1 suggest the presence of aromatic residues in the resin and the stretching frequencies at 1580 cm-1 and 1607 cm-1 is due to residual C=C in alkyd resin. However, the absence of absorption bands in this region (Fig.5a) indicate that all monomers are converted into acrylic polymer.

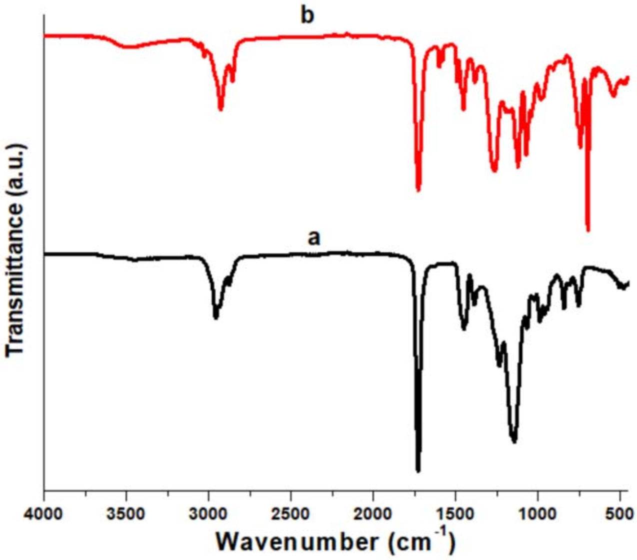

Fig. 5: FTIR spectra of pure acrylic resin 5(a) and alkyd acrylic hybrid resin 5(b)

e) *SEM Study*

The scanning electron micrograph of surfactant stabilized acrylic latex and alkyd stabilized acrylic latex are presented in Fig. 6

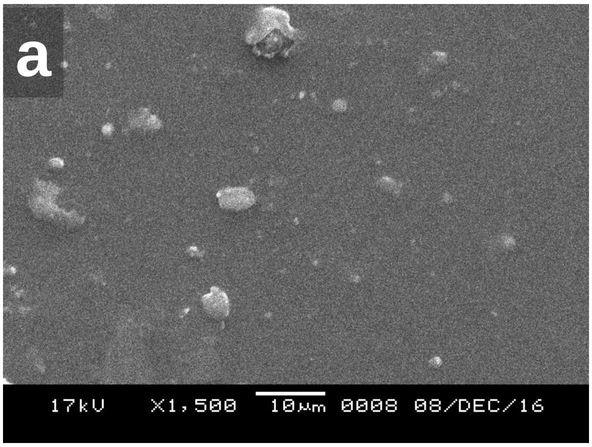

Fig. 6a: SEM of acrylic latex

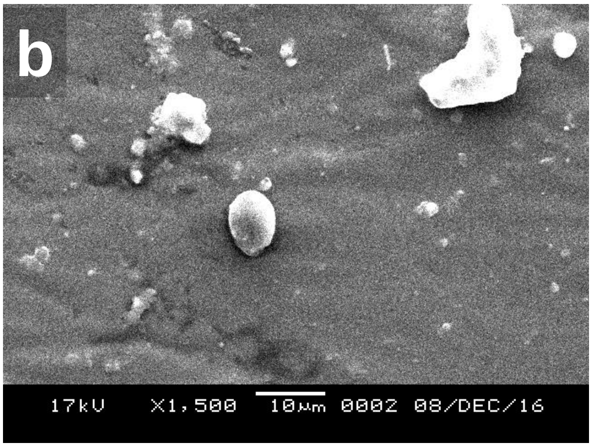

Fig.6b: SEM of alkyd stabilized acrylic latex

The surface morphology of alkyd stabilized acrylic latex (Fig. 6b) was more non uniform than that of surfactant stabilized acrylic latex (Fig. 6a). Pitting and surface roughness were observed in the alkyd stabilized acrylic latex film. On stabilization of acrylic by alkyd chain, the surface of the acrylic film was masked with the alkyd chain and due to uneven masking the roughness of the film were formed. Similar type of observation has also been reported after grafting of acrylic monomer [25, 26]. So the increase of surface roughness in the alkyd stabilized acrylic latex was an indication of surface grafting. During drying process, the oxidative polymerization of alkyd creates shrinkage on alkyd stabilized acrylic film surface and surface roughness is formed.

f) DSC Analysis

The DSC thermogram of different alkyd stabilized acrylic and without alkyd stabilized acrylic film is presented in Fig. 7. In DSC thermogram, the single heat flow indicates that there was no multiple domains of polymer structure was generated in the alkyd stabilized acrylic system. The onset of heat flow were takes place little earlier as compared to pure acrylic emulsion (AL) [Fig. 7 a]. It was reported that alkyd after grafting onto acrylic structure changed the domains of alkyd in such a way that there was no separate phase of alkyd in the acrylic structure [14]. It is also observed that after incorporation of alkyd into acrylic matrix, the glass transition temperature (Tg) of all alkyd stabilized acrylic hybrid emulsion is not affected [Fig. 7 b, c and d]. Because the unsaturation present in fatty acid part was partly participated in the grafting of acrylic onto alkyd structure. After grafting the pendent unsaturation was used for post crosslinking which enhanced the solvent resistance property.

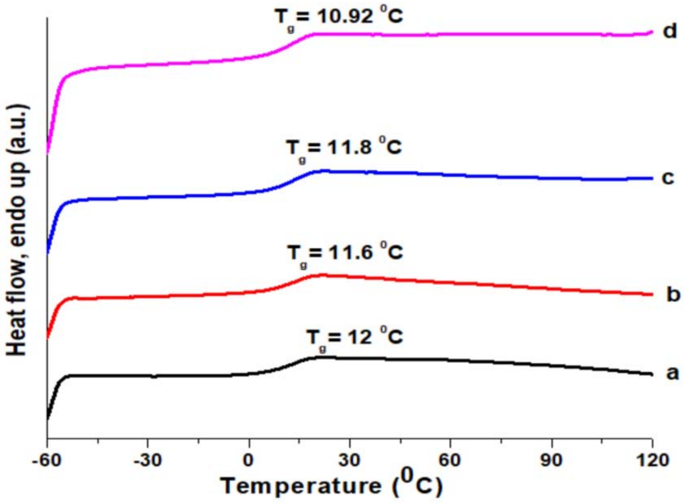

Fig. 7: DSC Thermogram of Pure acrylic (a), 45% oil length alkyd modified acrylic (b), 53% oil length alkyd modified acrylic (c), 62% oil length alkyd modified acrylic (d)

V. Conclusion

The present study shows that stable acrylic o/w emulsion is formed with alkyd dispersion by semi-continuous emulsion polymerization. The optimum conversion of acrylic monomer into acrylic polymer indicates that there is no retardation of monomer transportation from droplets to the locus of the polymerization. The increase in adhesion and flexibility, surface swelling resistance and stability of alkyd stabilized acrylic emulsion indicates that there is an interaction between acrylic resin and alkyd structure. The medium oil length alkyd with acid value and hydroxyl value in the range of 30 and 78 mg KOH per gm respectively and low molecular weight is effective for the stability of alkyd stabilised acrylic emulsion. The higher water repellence and solvent swelling resistance of the latex film are due to greater interpenetration and entanglement of the two phases. This is a novel technique for preparation of stable pre-emulsion without using any surfactant only by using soya fatty acid based water dispersible alkyd.

Acknowledgement

The Authors are thankful to the management of Berger Paints India Ltd. for providing necessary resources in conducting this study and given opportunity to present in the form of paper. We are also thankful to the colleagues, Dr. P. S. Maiti, Mr. T. Koley, Mr. S. Ray and Mr. S. K. Chakrabarti for their support at different stages of this investigation.

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