

Full Length Research Paper

# Synthesis and characterization of methyl methacrylate and 2- methacrylate and their application on pigment printing textile fabrics

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This paper was reported the synthesis and characterization of two samples of styrene – acrylic emulsion copolymers. It was performed in the presence of acrylic- acid, acryl amid, ammonium persulfate as a free radical initiator and sodium dodecyl benzene sulfate as an anionic emulsifier at 80°C. Thereafter, styrene – acrylate copolymers thus synthesized were subjected to characterization by means of IR spectral data, particle size determination. The synthesized emulsion copolymers was formulated by pigmented printing paste in the presence of an acrylic thickener in two different concentration 3 and 5% then printed on cotton and polyester fabrics and then dried at 95°C at 2 min and then fixation at 150°C at 3 min. The characteristics of cured prints such as paste add-on, colour fastness to washing, K/S and dry/wet rubbing were evaluated, together with fabrics stiffness. The highest K/S is obtained and the fastness properties range between good and excellent for samples printed using methyl methacrylate styrene (MMA) based, this is true irrespective of the type of printed fabric. The lowest K/S is obtained in case of using ethyl acrylate styrene (EA) as a commercial binder. The binder of 2-ethylhexylacrylate (2-EHA) gives K/S better than the binder of butyl acrylate styrene (BA) for two the types of printed fabrics.

**Key words:** Styrene-acrylic binders, pigment printing of cotton, polyester textile fabrics.

## INTRODUCTION

Acrylic resins, which have an important commercial application in paint industry, are prepared through the polymerization of acrylic and methacrylic acids or their corresponding esters. The key attribute of acrylic coatings is their resistance to hydrolysis during extended exterior exposure (weathering), high block resistance, hardness, gloss and high alkali and oxidation resistance (El-Molla and Schneider, 2010).

Emulsion polymerization is an important industrial method, because it produces high molecular weight polymers, and because there is no or negligible content of volatile organic compounds (VOC). In a normal emulsion polymerization technique, the oil is emulsified in water with a conventional surfactant using a mechanical

shearing device, to produce droplets of 1 to 10 μm diameter. The polymerization is achieved with the assistance of a water or oil soluble initiator or catalyst. These emulsions are generally opaque, milky, and viscous; but they can also be translucent emulsions with particle sizes ranging from about 8 to 80 nm, when a very high surfactant concentration is employed (Smith and Gastonia, 2001; Arslan, 2001).

Pigment textile printing is not only the oldest but also more than 80% of the printed goods are based on pigment printing to its obvious advantages, such as versatility, ease of near final print at the printing stage itself (Hotton and Ronald, 1990; Najafi, 2009). This pigment printing makes use of mineral turpentine which is involved in making emulsion thickeners. In this system, the oil in the emulsion gets evaporated to the atmosphere at the time of curing of the pigment printed fabric (Schymitzek and Esche, 1997).

It is almost impossible to reclaim this kerosene. In spite

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**Table 1.** Preparation of printing pastes for pigment.

<b>Imperon (pigment) dye</b>	<b>3– 5%</b>
Acraconz F	3
Binder	4
Ammonium sulfate	1
Urea	0.5
Balance to water	100

of the superior thickening properties of oil/water emulsion which also contribute towards a soft hand of the print, good fastness properties, ease of application methods, economy, several other factors have compelled the search for a replacement for oil (Weiss, 1997; Javadian, 2006).

The use of synthetic thickening agents and new developments in printing auxiliaries have also contributed to the increasing importance of pigment printing, all together, environmental aspects such as minimization of formaldehyde emissions and carbon dioxide content must be taken into account. At the same time, novel binder systems allow a much softer handle to be attained (Gornowicz et al., 2001).

## EXPERIMENTAL

### Materials

Imperon Brilliant red B (Bayer Co.), methyl methacrylate (MMA), ethyl acrylate (EA), butyl acrylate (BA), methyl acrylate (MA), which were supplied from Roehm Company (Germany), were purified by treating with 10% sodium hydroxide solution followed by washings with deionized water to remove inhibitor. Ammonium Per sulphate (Merck), Ammonia (Merck) and Sodium loryl ether sulphate (Henkel, Germany). Aqueous binders of (MMA) based on either (BA), (EA) and (2- EHA) had been synthesis, Acraconz BN (thickener synthetic) Bayer Co, Germany. Ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ , Merck, Germany. Desizing, scoured, bleached and mercerized wave cotton fabric  $130 \text{ g/m}^2$ , and polyester fabric  $90 \text{ g/m}^2$  supplied by Texlab Co. Urea Merck, Emulsifier V0<sub>2</sub>, Acraconz Bayer Co, Germany.

### Polymerization procedure

Semi- continuous emulsion copolymerization were carried out by using a 500 ml five necked round-bottom flask equipped with a reflux condenser, stainless-steel stirrer device, and two separate feed streams. The first feed stream was a solution of MMA, BA, EA and 2-EHA and anionic surfactant. The other feed was the initiator solution before emulsion polymerization start up, the reaction vessel was first charged with the desired amounts of water, emulsifier and initiator solution. The reaction mixture was stirred at a rate of 60 rpm, and the temperature was maintained at 60°C after 5 min, 10% of total amount of the monomer mixture was added to the flask in a period of 20 min. Then the temperature was kept at 80°C until the end of polymerization. The polymerization was performed with feeding rate of 1.0 ml/min. The reaction was cooled to room temperature and neutralized, if necessary, to a final pH of 8.

### Printing recipe

Preparation of printing pastes for pigment printing was prepared according to the following recipe found in Table 1 (Najafi, 2007).

## RESULTS AND DISCUSSION

### Solubility and FTIR analysis

These copolymers, which have been the synthesized samples from 2- EHA with or without NMA, were not exceptions. They are not soluble even in aprotic polar solvents such as NMP, DMSO and DMF. This insolubility could be due to conversion of the polymer samples to gelation immediately during of drying under air atmosphere or vacuum. For example, the product was isolated by filtration after precipitation with a large amount of methanol and dried under vacuum at 60°C. After 48 h it was observed that it is insoluble in all of the above mentioned solvents. It is worth to mention that the obtained copolymers will turn to gel by adding two drops of ethanol after dissolving in the DMF, DMSO, THF, toluene and benzene, respectively. The characterization of these copolymers is very difficult due to their solubility. For example, NMR study of these copolymers is nearly impossible to perform, but FTIR spectra in the region from  $4000$  to  $500 \text{ cm}^{-1}$  were recorded with a sample prepared by making a film of the latex on the surface of a glass and drying it, then removing the film from the glass. Figure 1 shows the FTIR spectra of (A) 2-EHA and (B) with  $0.25 \text{ mol/L}$  NMA added copolymers, respectively.

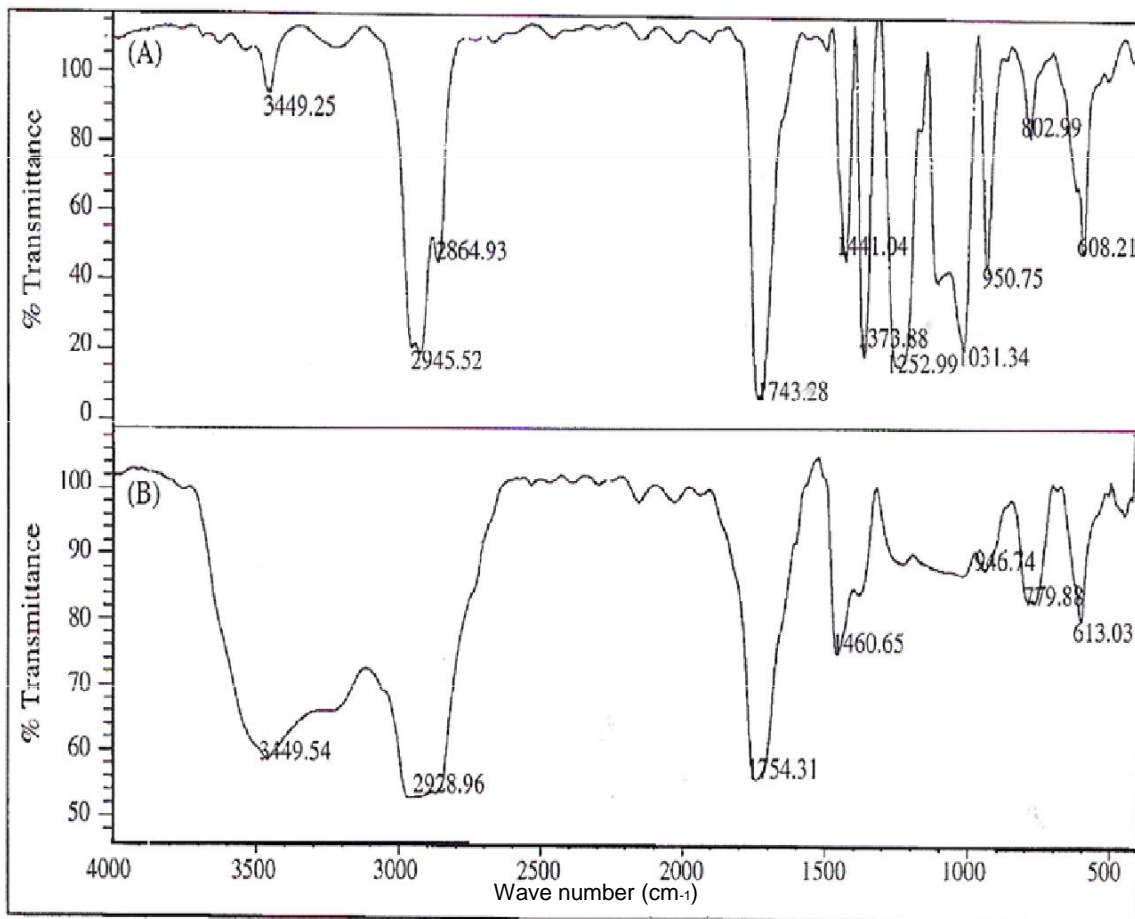
### Effect of initiator concentration

Figure 2 shows the percentage of conversion against time at three initiator levels. As it is shown, polymerization rate increases with increasing initiator concentration. This behavior can be explained as follows. First, the higher the initiator concentration, the higher the number of adsorbed fixed radicals on the particle surface and therefore the lower the retardation of polymerization due to the seed particles.

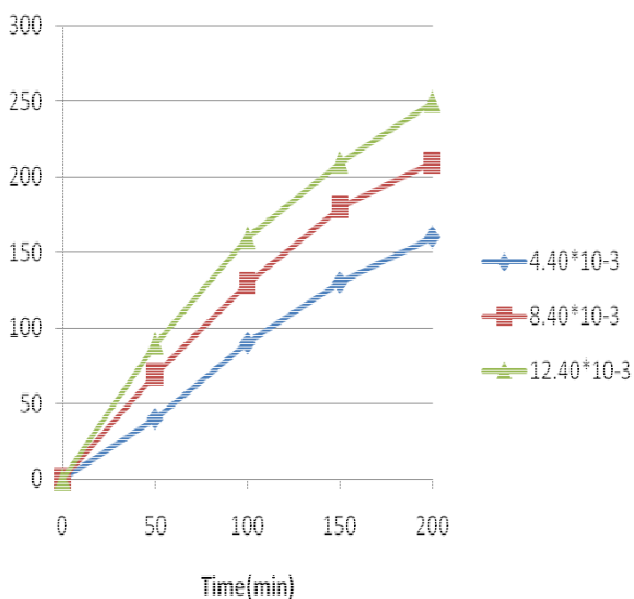
Secondly, with increasing initiator concentrations the proportion of usual emulsion polymerization increases in the aqueous phase, and, at very high initiator concentrations, the proportion of surface layer polymerization will be negligible. This difference also may be attributed to the homogeneous nucleation of particles that is typical in vinyl acetate emulsion polymerization. Analyzing the above results, it is difficult to decide what the main effect is.

### Screen printed cotton and polyester fabrics

The effect of increasing the fixation temperature on the



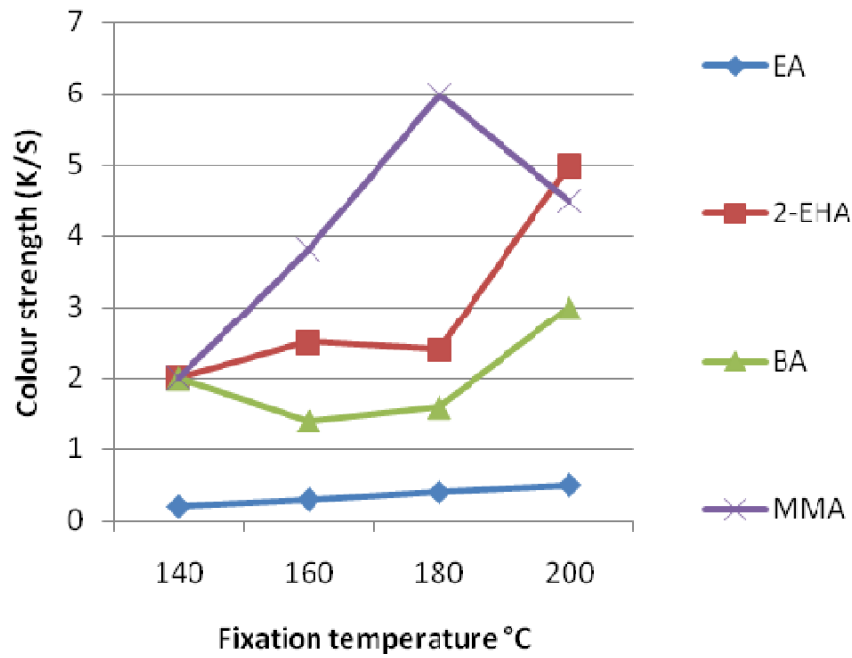
**Figure 1.** FTIR spectra of (A) 2-EHA copolymer and (B) with 0.25 molar NMA.  $[M]_0 = 5.30 \text{ mol L}^{-1}$ , 60 rpm,  $[I]_0 = 8.40 \times 10^{-3} \text{ mol L}^{-1}$ ,  $T=80^\circ\text{C}$ .



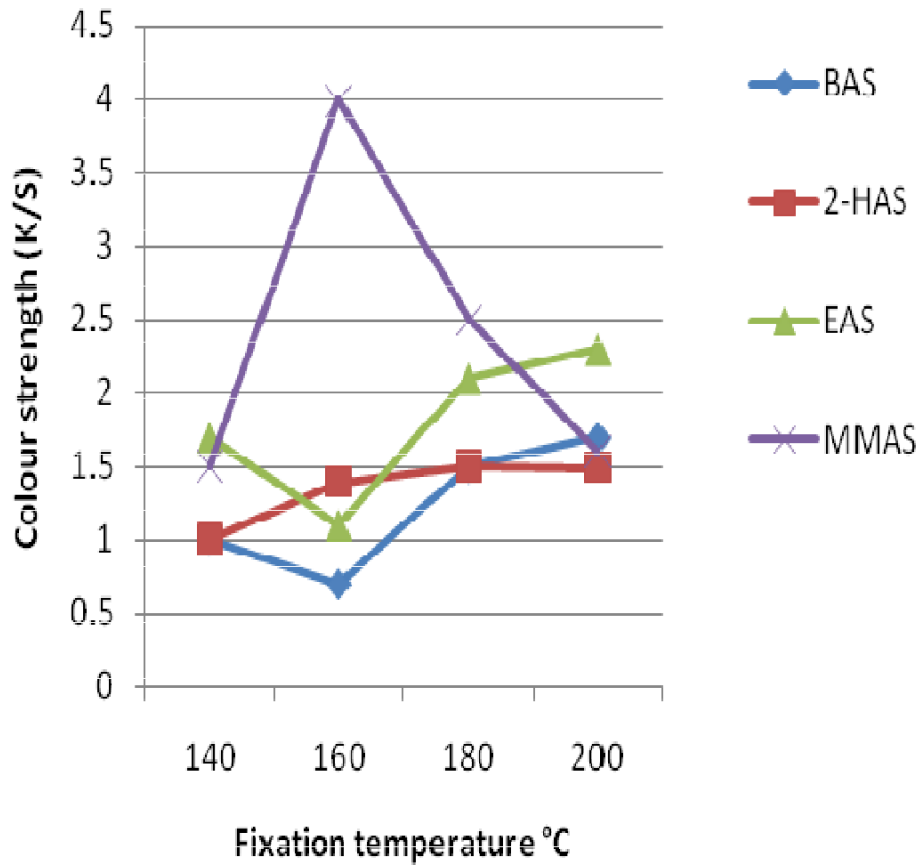
**Figure 2.** The effect of initial initiator concentration on monomer conversion time at  $[(\text{NH}_4)_2\text{S}_2\text{O}_8] \times 10^{-3}$ , 60 rpm  $T= 80^\circ\text{C}$ .

color strength of screen printed on either cotton or polyester upon using EAS as a commercial binder and BAS containing Imperon brilliant red B of different concentrations 3 and 5% and the time of fixation of 2 min. It is clear from the Figures 3 to 5 that the color strength of the printed fabrics (using either 3 or 5% dye) is nearly comparable. This may be attributed to the increase in the temperature.

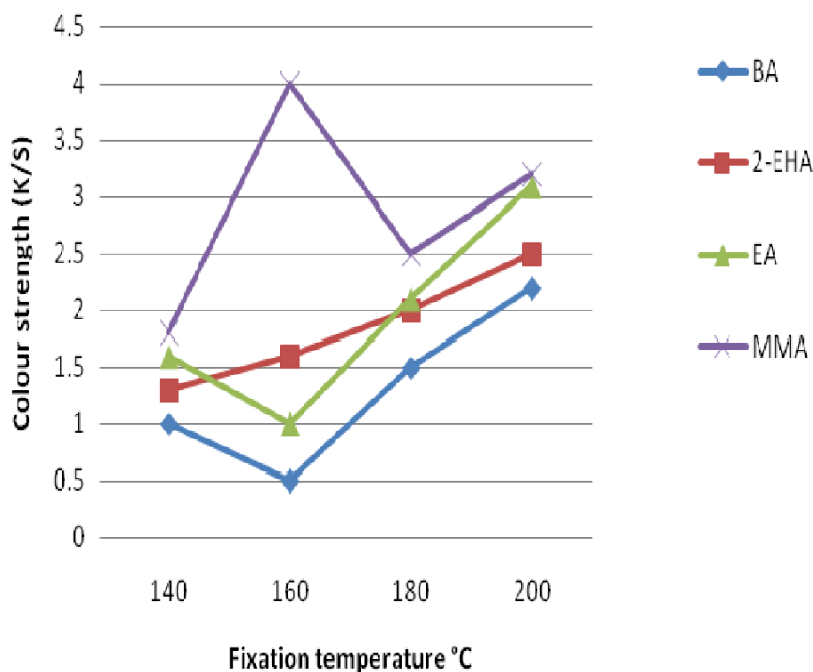
Dye concentration needed to increase in the binder concentration to make fixation to this dye through the polymerization process to this binder. It is also clear from Figures 3 to 5 that the highest color strength values were obtained in case of using styrene acrylate based as a binder in the printing paste as compared to the results obtained upon using the commercial binder of EA, which gives the lowest value of color strength in case of screen printed cotton fabrics, while in case of using 2-EHA, the K/S values were better than the values obtained in case of using BA. The K/S values of screen printed cotton and polyester fabrics fixed at temperature  $160^\circ\text{C}$  were 0.31, 1.9, 1.77, 6.83 and 0.85, 1.01, 0.65, 4.73 by using E, styrene based on 2-EHA, styrene based on BA, styrene



**Figure 3.** The effect of the type of binders used on the color strength of screen printed cotton fabrics using 3% Imperon Brilliant red B, the time of fixation is 2 min.



**Figure 4.** The effect of the type of binders used on the color strength of screen printed cotton fabrics using 5% Imperon brilliant red B, the time of fixation is 2 min.



**Figure 5.** The effect of the type of binders used on the color strength of screen printed cotton fabrics using 3% Imperon Brilliant red B, the time of fixation is 2 min.

**Table 2** Color strength and overall fastness properties of screen printed synthetic fabrics using prepared polyurethane acrylate based on either polyethylene glycol or glycerol ethoxylate-co-propoxylate and/or Ebecryl 2002 as a thermal curable binders in printing paste using 3% Imperon Brilliant red B, the time of fixation is 2 min.

Polyester				Cotton				Binder
Washing fastness		Robbing fastness		Washing fastness		Robbing fastness		
Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	
3-4	3-4	3-4	3-4	4	3-4	4	3-4	EA
4	4	4	3-4	4-5	4	4-5	4	2-EHA
3	3-4	3-4	3	4	3-4	4	3-4	BA
3	3-4	3-4	3	4	3-4	3-4	3	MMA

based on MMA a binder in printing paste containing 3% Imperon red B, respectively. This may be due to either the difference in the structure of the binder used or the amount of unsaturation groups found in the binders which is responsible for fixation of the dye through the polymerization process that happened to these oligomers that is, binders.

### Fastness properties

Table 2 show the color strength and overall fastness properties of screen printed natural and synthetic fabrics using synthesis styrene acrylate based on EA as a thermal curable binder used in prepared printing paste containing 3% Imperon brilliant red B. It is clear from the

data in Tables 2 that the K/S and overall fastness properties not only depend on the type of binder used in printing paste but also on the type of textile fabric printed. The highest color strength for cotton and polyester of printed fabric was obtained upon using MMA as a binder in printing paste and the fixation temperature was 160°C for 2 min, and the lowest color strength in case of cotton and polyester printed fabrics upon using EA the change in color due to washing ranged from poor to good for all printed fabrics. The rubbing, washing and perspiration fastness ranged from good to excellent in case of using prepared binder. This was true irrespective of the nature of the binder used and/or the type of fabric printed. The lowest K/S is obtained in case of using Ethyl acrylate styrene (EA) as a commercial binder. The binder of 2-Ethylhexylacrylate (2-EHA) gives K/S better than the

binder of Butyl acrylate styrene (BA) for two the types of printed fabrics.

## Conclusions

These results show that some novel prepared aqueous binder of styrene acrylate based on having zero volatile organic compounds can be used safely for preparing printing paste for screen printing of cotton and polyester types of textile fabrics using pigment dyes.

The highest K/S is obtained and the fastness properties range between good and excellent for samples printed using MMA based, this is true irrespective of the type of printed fabric. The lowest K/S is obtained in case of using EA as a commercial binder. The binder of 2-EHA gives K/S better than the binder of BA for two the types of printed fabrics.

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