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Synthesis of Glycidyl Methacrylate-Acrylic acid Copolymer Via Modified Microemulsion Polymerization and Using It As Textile Pigment Printing Binder

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ABSTRACT

Copolymerization of glycidyl methacrylate (GMA) and acrylic acid (AAC) was carried out via modified microemulsion polymerization process for textile pigment printing. Sodium dodecyl sulfate and Potassium persulfate/glucose were used as emulsifier and redox initiator, respectively. The prepared micro emulsion copolymer was characterized via spectroscopic measurements, FT-IR and transmission electron microscope (TEM), in addition to thermal analysis. Effects of polymerization parameters, such as monomer content ratio, initiator and emulsifier concentration on average particle size and size distribution have been studied. The prepared copolymer latex showed high performance physico-mechanical properties in addition TEM analysis showed that the polymer latex nano particle within rang of 35 – 74 nm. The study involved the application of the prepared micro-emulsion co-polymer as binder for pigment printing process onto cotton fabric by using a flat screen technique and the prints were dried and thermal cured. The optimum curing conditions were determined, color strength and fastness properties of pigment printed areas to light, washing, perspiration and crocking were evaluated. In addition stiffness of the prints was also determined

Key words: Micro-emulsion, co-polymer, nanotechnology, binder, pigment, textile printing.

Introduction

Emulsion polymerization is essentially a process in which an aqueous dispersion of a sparingly soluble monomer or a mixture of monomers is converted into a stable dispersion of polymer particles. The product of an emulsion polymerization is called latex (Guyot et al., 2007; Asua, 2004; Pelton and Hoare, 2011). Emulsion polymerization is an important industrial process that is used for the production of a wide range of polymer materials, e.g. paints, adhesives, coatings and binders (Chen and Wu, 2011; Arora et al., 2007; Dimitratos et al., 1994; Zhaoquan et al., 2010).

Nano-sized polymer particles have attracted great interest because of their excellent properties arising from their small size and high surface-to-volume ratio. Microemulsion Polymerization is a new polymerization technique which allows the preparation of stable ultrafine polymer particles in the nanosize range (20-100 nm) which exhibit very large specific areas and high surface functionality not attainable with classical emulsion polymerization process (Sawhney et al., 2008; He and Pan, 2004; Chern and Wu; 2001). Oil in water microemulsion polymerization involves the propagation reaction of free radicals with vinyl monomer in very fine oil droplets dispersed in the continuous aqueous phase (Sanghvi et al., 2002; Cannizzo et al., 2005). However, the microemulsion method requires a much higher amount of surfactant compared with conventional emulsion polymerization (monomer /surfactant weight ratios, usually < 1) which limited the application of microemulsion latexes in industries. Hence, in order to make microemulsion polymerization more practical, it was desirable to minimize the surfactant amount and maximize polymer content (Chang and Chao, 2011; He et al., 2003).

Ming et al. prepared micro latexes from styrene, methyl methacrylate, and butyl acrylate using modified microemulsion polymerization method, in which the monomers were continuously and slowly added into the pre-polymerized microemulsion, i.e. a small amount of monomer was added into the reactor first to prepare the microemulsion and then the remaining monomer was added drop wise with mild stirring to avoid disturbing the stability of the micro-emulsion (Zhang et al., 2007; Jiang et al., 2004; Ming et al., 1998).

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Glycidyl methacrylate (GMA) monomer has dual functionality, containing both methacrylic and epoxy groups. Both of these groups readily react with a wide range of monomers and functionalized molecules to provide the user with maximum freedom and flexibility in polymer design (Baldan, 2004).

Pigment printing is not only the oldest but also the easiest printing method as far as simplicity of application is concerned. Pigments are finely ground insoluble colored particles. They do not contain groups capable of interact with fibers so that their fixation is achieved by use of a binder which encloses them and provides a bond between them and the fiber (Bahmani et al., 2000; Teli, 2008). We report here a study on the synthesis of GMA-AAc copolymer with high monomer/surfactant ratio via modified microemulsion polymerization technique. Also the use of the prepared microemulsion as a binder in pigment print pastes for textiles was investigated.

Experimental:

Chemicals:

The chemicals used in this study include glycidyl methacrylate (GMA, 99%, MW 128.17 g/mol, Merck Schuchardt OHG), Acrylic acid (AAc, 99.5%, MW 72.06 g/mol, Panreac Sintesis), Sodium dodecyl sulfate (SDS, 97%, MW 288.38 g/mol, Merck Schuchardt OHG, as the emulsifier), potassium persulfate (KPS, 98%, MW 270.33 g/mol, Merck Schuchardt OHG, as the initiator), and Glucose (95%, MW 198.17, RFCL Limited). Deionized water was used in all experiments. The monomers were distilled to remove inhibitors before use. All other chemicals were used as received.

Micro-emulsion polymerization procedure (Binder preparation):

- The micro-emulsion co-polymerizations process was carried out using mixtures of GMA and AAc comprising 0/100, 25/75, 50/50, 75/25, or 100/0 wt. % AAc/GMA (with a total monomers fraction of 20 wt % in the emulsion).
- A typical polymerization procedure was carried out in a 4-neck flask equipped with a reflux condenser, a thermometer, an addition funnel, a mechanical stirrer and N2 inlet and outlet.
- A solution of 2g wt. % GMA, 5g wt. % SDS, and 69.6 ml water were charged to the reactor to prepare the pre-microemulsion. N2 was bubbled through the micro-emulsion for 10 minutes. Then the flask was heated to 40°C with mild stirring (600 rpm) for 20 minutes.
- The flask was heated to 70°C and kept for 10 minutes. Then the monomers in the addition funnel were continuously and slowly added into the polymerizing micro-emulsion through 2 hrs with mild stirring (ca. 200 rpm) with a process can prevent coagulation and achieve a true emulsion.
- The flask was kept at 70°C for another 2 hrs.
- The slow addition of monomers avoids the bulk polymerization, especially along the flask wall. Also the mild stirring helps the homogeneity and stability of the micro-emulsion.

Printing paste:

The printing pastes were prepared according to the formulation given in Table 1. Ammonia, urea, diammonium phosphate and binder were mixed with water (68parts). The synthetic thickener PTP was then introduced and the paste was stirred using a high shear mixer for 10 minutes to allow full viscosity to develop. The pigment was then added to the mixture with stirring using a high shear mixer for 15 minutes. If the viscosity of the printing pastes decreases, a slight amount of the thickener is added to maintain consistent viscosity values of the pastes at 21,000 cps at rate of shear of 2.180.

Table1: Formulation of The printing paste

<table>
<thead>
<tr>
<th>Components</th>
<th>Weight (in grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>70</td>
</tr>
<tr>
<td>Ammonia (25 %)</td>
<td>0.5</td>
</tr>
<tr>
<td>Binder</td>
<td>18</td>
</tr>
<tr>
<td>Thickener ( Alcoprint PTP)</td>
<td>2</td>
</tr>
<tr>
<td>Diammonium phosphate</td>
<td>0.5</td>
</tr>
<tr>
<td>Urea</td>
<td>4</td>
</tr>
<tr>
<td>Pigment (Unisperse Red G)</td>
<td>5</td>
</tr>
<tr>
<td>Total</td>
<td>100 g</td>
</tr>
</tbody>
</table>

Printing technique:

All printing pastes were applied to 100% cotton fabrics using the flat screen printing technique.
Print fixation:

Prints were dried at room temperature, and then fixed at 150°C for 4 min in an automatic thermostatic oven (Wemer Mathis Co., Switzerland).

Characterization:

Particle size and particle size distribution:

Particle sizes of the polymerized micro-emulsion latex were determined using a JEOL-GEM transmission electron microscope and particle size distribution was determined using Leica Qwin 500 image analyzer.

FTIR Spectrum:

FTIR spectrum of the prepared co-polymer was recorded on Jasco FTIR – 6100 using the KBr pellet technique.

Glass transition temperature (T<sub>g</sub>):

the T<sub>g</sub> of the prepared binders were measured by differential scanning calorimetry (DSC) Shimadzu – 50

Color strength measurements:

the color strength of the printed samples expressed as K/S was evaluated by high reflectance technique (Judd and Wyszecki, 1975). Reflectance measurements of the printed fabrics were performed on PERKIN – ELMER Lambda 3B, UV/V Spectrophotometer.

Fastness properties:

fastness to light (AATCC 16A, 1993), washing (AATCC 36, 1993), rubbing (AATCC 8, 1993), and perspiration (AATCC 15, 1993) were determined according to the standard methods.

Stiffness properties:

stiffness of printed and unprinted samples was determined according to ASTM test method D 1388 – 96 using the cantilever apparatus (ASTM 1388 – 96, 2002).

Rheological properties of the printing pastes:

the rheological properties of the pastes were measured using a rotary viscometer (Rheomat – 15, Zurich, Switzerland).

Results and Discussion

Effect of monomers content ratio on the properties of micro-emulsion binder:

According to Table 2 various micro-emulsion binders were prepared by different monomers composition using, 0/100, 25/75, 50/50, 75/25, or 100/0 wt. % AAc/GMA. From Table 2, it is clear that the average particle size of the micro-emulsions was increased by increasing the AAc content. This may be attributed to the surface modification of the latex particles by adding acrylic acid which increases the crosslinking and adhesion between latex particles. From table 2, it is also seen that the adhesive properties of the prepared microemulsions were improved by increasing the AAc/GMA ratio. So that microemulsions with low AAc content were seen to be homogeneous, compatible and stable (figure 1), while the micro-emulsion binders with high AAc content (75/25 or 100/0 wt. % AAc/GMA) show slight coagumulation (Figure 2).
Table 2: Effect of monomers content ratio on the properties of micro-emulsion polymer

<table>
<thead>
<tr>
<th>AAc/GMA ratio</th>
<th>Average particle size (nm)</th>
<th>Tg (°C)</th>
<th>Coagulation</th>
<th>Internal bond (Adhesive properties)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/100</td>
<td>38</td>
<td>-1.5</td>
<td>No</td>
<td>0.12</td>
</tr>
<tr>
<td>25/75</td>
<td>43</td>
<td>1.1</td>
<td>No</td>
<td>0.2</td>
</tr>
<tr>
<td>50/50</td>
<td>49</td>
<td>1.8</td>
<td>No</td>
<td>0.32</td>
</tr>
<tr>
<td>75/25</td>
<td>91</td>
<td>2.2</td>
<td>Some</td>
<td>0.38</td>
</tr>
<tr>
<td>100/0</td>
<td>110</td>
<td>2.45</td>
<td>Coagulate</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Glass transition temperature (Tg) is an important property of polymeric materials. Lower Tg improves the feel of the fabric, but too low Tg may lead to poor crock fastness. For a pigment printing binder, the Tg of the polymer can vary from -40°C (soft prints) to +15°C (tough prints). Table 2 shows that the prepared microemulsion binders have good Tg which lies between -2.44 and 2.39; enable it to used as binders for textile pigment printing. Also it was demonstrated that Tg value of the prepared microemulsions was increased by increasing the AAc content. This increase may be due to increasing the inter particles crosslinking with increasing AAc content in the co-polymer.

Fig. 1: TEM image of micro-emulsion binder of the composition 50/50 wt. % AAc/GMA

Fig. 2: TEM image of micro-emulsion binder of the composition 100/zero wt. % AAc/GMA (poly acrylic acid homopolymer)

Table 3 illustrates the effect of the monomers content ratio in the micro-emulsion binders on the color strength and fastness properties of pigment printed areas. These data indicate that the color strength (K/S) increased with the increase of AAc/GMA ratio. The dry and wet rubbing fastnesses of zero AAc content (poly
GMA homopolymer) are 2-3 and 2 respectively. On increasing AAc content in the co-polymer, the dry and wet rubbing fastnesses enhanced. It is hypothesized that the active carboxylic group of AAc can react with the function groups present on the fiber surface which strengthening the binder film. So that with increasing the AAc/GMA ratio the crosslinking and adhesion properties of the binder increased which lead to enhancing the adhesion between the binder film and the substrate or the pigment, and lead to enhancing the rubbing fastness properties of the prints.

All prints gave very good color strength and fastness to light, washing, and perspiration. Also all prints have good handle, except the sample of 100/0 wt. % AAc/ GMA (poly acrylic acid homopolymer) shows small increase in stiffness.

Out of results that are given in Tables 2 and 3, we can conclude that, the formulation which made use of the composition 50/50 wt. % AAc/GMA gives homogeneous micro-emulsion binder with small particle size and its prints have satisfactory fastnesses, good handle and high color yield.

**Table 3: Effect of AAc/GMA content ratio on the color strength and fastness properties of the prints**

<table>
<thead>
<tr>
<th>AAc/GMA ratio</th>
<th>K/S</th>
<th>Light</th>
<th>Stiffness</th>
<th>Rubbing</th>
<th>Washing</th>
<th>Perspiration</th>
<th>Adhesive properties</th>
<th>Coagulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Dry</td>
<td>Wet</td>
<td>Acidic</td>
<td>Alkaline</td>
<td></td>
</tr>
<tr>
<td>0/100</td>
<td>9.3</td>
<td>7</td>
<td>1431</td>
<td>2-3</td>
<td>2</td>
<td>4-5</td>
<td>4-5</td>
<td>-</td>
</tr>
<tr>
<td>25/75</td>
<td>9.5</td>
<td>7</td>
<td>1450</td>
<td>3</td>
<td>2-3</td>
<td>4-5</td>
<td>4-5</td>
<td>-</td>
</tr>
<tr>
<td>50/50</td>
<td>9.8</td>
<td>7</td>
<td>1490</td>
<td>3-4</td>
<td>3</td>
<td>4-5</td>
<td>4-5</td>
<td>-</td>
</tr>
<tr>
<td>75/25</td>
<td>9.6</td>
<td>7</td>
<td>1547</td>
<td>3-4</td>
<td>3</td>
<td>4-5</td>
<td>4-5</td>
<td>-</td>
</tr>
<tr>
<td>100/0</td>
<td>8.3</td>
<td>7</td>
<td>1591</td>
<td>3-4</td>
<td>3</td>
<td>4-5</td>
<td>4-5</td>
<td>-</td>
</tr>
</tbody>
</table>

**Effect of emulsifier content on the properties micro-emulsion polymer:**

As seen from Table 4, the particle size of polymer particles decrease with increasing emulsifier concentration. Sodium dodecyl sulfate (SDS) influences the particle nucleation and thus the final latex size. The role of the SDS is to stabilize the primary particles so that they are smaller than those prepared without SDS. The smaller the primary particles, the higher the total number of primary particles that are initially formed, result in smaller particles for the same dose of monomer.

Also from table 4, it appears that the adhesive properties of the prepared microemulsion were increased with increasing the SDS. This may be due to the particle size in emulsions determines the area of the contact surface of the reactants. Also the cross-linking properties of the polymer chains increase with a decrease in particle size of the microemulsion. It was demonstrated that, as shown in table 4, at low emulsifier content, the prepared microemulsion are unstable to coalescence. This may be attributed to that the amount of emulsifier is inadequate to stabilize the micro latexes.

**Table 4: Effect of emulsifier content on properties of microemulsion binders**

<table>
<thead>
<tr>
<th>Emulsifier content</th>
<th>Particle size</th>
<th>Adhesive properties</th>
<th>Coagulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>150</td>
<td>0.1</td>
<td>coagulate</td>
</tr>
<tr>
<td>3</td>
<td>107</td>
<td>0.14</td>
<td>some</td>
</tr>
<tr>
<td>4</td>
<td>78</td>
<td>0.2</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td>49</td>
<td>0.32</td>
<td>No</td>
</tr>
<tr>
<td>6</td>
<td>46</td>
<td>0.33</td>
<td>No</td>
</tr>
</tbody>
</table>

3.3. Effect initiator concentration on the particle size of micro-emulsion binders:

According to Harkins’ scheme, initiator decomposes into free radicals in the aqueous phase and these radicals enter micelles to form polymer particles. These polymer particles grow absorbing monomer and emulsifier from the aqueous phase. Figure 3 shows the effect of initiator concentration on the particle size of micro-emulsion binders, it is clear that the particle size was increased by increasing initiator concentration. The increase in the initiator content causes an increase in the rate of polymerization which may be attributed to the increase of the number of growing particles or the particle rate formation (the nucleation activity). So that increasing the initiator concentration results in an increase in the size of the large particles and a delay in the birth of second generation particles. These two effects may be explained by the increase in radical flux into the seed particles.

Also increasing the initiator concentration causes the increase in the instantaneous concentration of the oligomeric radicals, which in turn increase the rate of association of the oligomers and/or the coagulation rate of the unstable nuclei to form larger permanent particle nuclei, and therefore, larger final particle size.
Effect of initiator content on particle size of binder

**FTIR analysis for prepared micro-emulsion co-polymer:**

The FTIR spectrum of AAc/GMA micro-emulsion binder synthesized under optimum condition is shown in figure 4. The absence of characteristic vinyl group absorption at 1640 cm⁻¹ confirms the formation of co-polymerization process. The broad peak at 3495 cm⁻¹ was associated with the (-OH) of carboxylic group. The symmetrical and asymmetrical stretching due to the methyl and methylene groups are observed at 2970, 2930 and 2890 cm⁻¹. The symmetrical stretching of the epoxy group is observed at 1242 and 974 cm⁻¹. The peak detected at 1730 cm⁻¹ belongs to the extending vibration of carbonyl groups (C=O). The stretching absorption of C-O (of carboxylic group) and that of C-O (of ester group) were appeared at 1116 cm⁻¹ and 1059 cm⁻¹ respectively.

**Effect of curing conditions on the color strength of the prints:**

Eight cotton samples were printed with one printing paste which prepared according to the formulation listed in Table 1, using micro-emulsion binder synthesized under optimum condition. Four samples cured at 130, 140, 150 and 160°C, respectively, while curing time fixed at 4 minutes. Other four samples cured at 150°C while curing time varied from 2 to 5 minutes. The color strength of printed samples were measured, results are shown in Figures 5 and 6 to evaluate the effect of curing conditions on the color strength of the prints. It is obvious from Figure 5 that the color strength increases with increasing the temperature of fixation; and the optimum of fixation curing temperature is 150°C.

Figure 6 shows that the color strength of printed areas increases as the time of fixation increases. From the previous results, it can be noted that the optimum conditions of curing samples printed with the prepared micro-emulsion binder were 150°C for 4 min.
Fig. 5: Effect of fixation temperature on the color strength of the printed areas (Curing time fixed at 4 minute)

Fig. 6: Effect of fixation time on the color strength of the printed areas (Curing temperature fixed at 150°C)

Effect of prepared binder concentration in the printing paste on properties of the pigment prints:

Micro-emulsion binder synthesized under optimum condition (50/50 wt. % AAc/GMA, 5g wt. %SDS and 0.2 g wt. % KPS) was used to prepare series of printing pastes. These pastes were prepared according to the formulation and method was shown in experimental section except that the binder content was varied from 15 to 20 % based on the total paste. Cotton fabrics were printed using these pastes, dried, and then thermo fixed at 150°C for 4 minutes. The properties of the prints were listed in Table 5.

From the results in Table 5, it could be noticed that the color strength and rubbing fastnesses of the prints were enhanced as the binder content increased. All the prints gave satisfactory light, washing and perspiration, except sample of 15 % binder content which shows poor washing fastness. All printed areas have good handle except the sample printed with 20 % binder content which shows an increase in stiffness. From previous data we can say that the optimum concentration of the binder that gave satisfactory fastnesses, good handle and high color yield was 18%.

Table 5: Effect of prepared binder content in the printing paste on properties of the pigment prints

<table>
<thead>
<tr>
<th>Binder content (%)</th>
<th>K/S</th>
<th>light</th>
<th>Stiffness</th>
<th>Rubbing</th>
<th>Washing</th>
<th>Perspiration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Acetic</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Dry</td>
<td>Wet</td>
<td>Alt</td>
</tr>
<tr>
<td>15</td>
<td>8.1</td>
<td>7</td>
<td>1300</td>
<td>2</td>
<td>2</td>
<td>3-4</td>
</tr>
<tr>
<td>18</td>
<td>9.8</td>
<td>7</td>
<td>1410</td>
<td>3-4</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>20</td>
<td>9.86</td>
<td>7</td>
<td>1460</td>
<td>3-4</td>
<td>3</td>
<td>4-5</td>
</tr>
</tbody>
</table>

Conclusion:

Modified microemulsion polymerizations of glycidyl methacrylate (GMA) and acrylic acid (AAC) were investigated. Sodium dodecyl sulfate and Potassium persulfate/glucose were used as emulsifier and redox initiator, respectively. The prepared micro-emulsion co-polymers were used as binders for pigment printing process onto cotton fabric. The presence of active epoxy groups of GMA and carboxylic groups of AAc enhance the adhesive properties and crosslinking of the prepared binders, hence color strength and fastness properties of
the printed fabrics were enhanced. Preparation of binder with fine particles including active sites help in decreasing the amount of binder used in the printing paste and curing temperature.

References