Synthesis and Characterization of Silicone Modified Acrylic Resin and its Uses in the Emulsion Paints

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Abstract

The acrylate-silicone emulsions were prepared by emulsion copolymerization of methylmethacrylate (MMA), butylacrylate (BA), methacrylic acid (MAA) with vinyltriethoxysilane (VTES), and auxiliary agents at 85°C in the presence of potassium persulphate (KPS) as initiator. Alkylphenol ethersulphate and Arkupal N-300 were used as anionic and non-ionic emulsifiers, respectively. The resulting copolymers were characterized by using Fourier transform infrared spectroscopy (FTIR). Thermal properties of the copolymers were studied by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The morphology of copolymers was also investigated by scanning electron microscopy (SEM) and then the effects of temperature, agitation speed, initiator and VTES concentrations on polymerization rate are discussed. The obtained polymers had high solid content (43%) and were used in the emulsion paints as a binder. The experimental results show that these polymers supply very useful properties such as excellent storage stability, UV light stability, washing and abrasion resistance with good brushing in the above mentioned paints. The calculations of monomer conversion versus time histories and monomer conversion to polymer indicate that by increasing the VTES concentration, the polymerization rate and the number of polymer particles decrease, respectively.

Introduction

In recent years acrylic emulsion copolymerization in the presence of silicone has received considerable attention as a industrial method [1-10]. In these processes polymerizations are achieved with the assistance of a water or oil-soluble initiator or catalyst, water with one or more monomers, which are not miscible with water and an oil in-water emulsifier. These emulsions are generally opaque, milky, and viscous solution, but they can also be translucent emulsions with particle sizes ranging...
from about 8-80 nm when very high surfactant concentration is employed [11-15]. When an aqueous acrylate polymer emulsion obtained by emulsion polymerization is dried at room temperature or under heated conditions, a coating is obtained which has a relatively good durability. Therefore, aqueous acrylate polymer emulsions have been widely used as a resin for aqueous paints. However, when a coating which is obtained from an acrylate polymer emulsion or for a paint comprised of acrylate polymer emulsion with a pigment, is exposed to outdoor conditions or UV light, not only is the luster of the coating likely to rapidly deteriorate, but also the gloss retentivity of the coating is poor.

In order to solve these problems, it was proposed to add silicone to an aqueous acrylate polymer emulsion to increase the coating resistance to UV light, oxygen, permeation of water and various types of solvents. These will improve the durability of the coating [16-29]. Also, Yamaya and coworkers [30] emphasized that silicone resins, resulting from hydrolytic condensation of silane compounds, could be used since they are able to form films having high hardness, water and heat resistance. In this paper we wish to elucidate the effects of VTES on the properties of acrylate emulsion polymerization and emulsion paints.

EXPERIMENTAL

Materials

The monomers MMA (Merck) and BA (Merck), were freed from the inhibitor by shaking with 10% aqueous NaOH, washing with water and drying over Na2SO4. They were then distilled under reduced pressure before use and stored at -15°C to avoid thermal polymerization. The MAA (Merck) was distilled directly under vacuum and stored at 0°C. VTES, (Merck) was analytical grades and used directly without further purification. The initiator KPS (Merck); buffer, NaHCO3 (Merck); complex emulsifier alkylphenol ether sulphate and Arkupal N-300 were purchased from Henkel, Germany and were used as received. Sodium benzoate, hydroxyethyl-cellulose, ammonia solution 25%, titanium dioxide, aluminium silicate, talc (325 mesh), calcium carbonate, formaldehyde, ethylene glycol, butyl glycol and mineral spirits were supplied from Fluka and used without further purification. The antifoam, EFKA-2526 was kindly supplied by EFKA, Holland. The dispersing agent, Disperse A was obtained from BASF, Germany and the softening agent dioctylphthalate was a commercial product. Water was double distilled and deionized.

Polymerization Procedure

Continuous emulsion copolymerization was carried out using a 500-mL 5-necked round bottom flask equipped with a reflux condenser, stainless steel stirrer, sampling device and two separate feed streams. The first feed stream was a solution of MMA, BA, MAA, VTES and anionic surfactant. The other feed was the initiator solution 7.0 × 10⁻³ M. Before emulsion polymerization start-up, the reaction vessel was first charged with the desired amounts of water, emulsifier, NaHCO3 and initiator solution, respectively. During polymerization process the reaction mixture was stirred at a rate of 60 rpm and the temperature was maintained at 60°C. After 5 min a small portion of the monomer mixture was added to the flask at a period of 20 min. Then the temperature was kept at 85°C. The polymerization was performed under air atmosphere to investigate the effect of temperature, agitation speed, initiator and VTES concentration on monomer conversion. A typical recipe for the preparation of a 43% solid product is given in Table 1.

In order to determine the conversion percentage

<table>
<thead>
<tr>
<th>Compound</th>
<th>Initial charge</th>
<th>Feed</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA (g)</td>
<td>4.80</td>
<td>43.20</td>
<td>48</td>
</tr>
<tr>
<td>n-BA (g)</td>
<td>2.25</td>
<td>20.25</td>
<td>22.50</td>
</tr>
<tr>
<td>MAA (g)</td>
<td>0.025</td>
<td>0.225</td>
<td>0.25</td>
</tr>
<tr>
<td>VTES (g)</td>
<td>10% w</td>
<td>90% w</td>
<td>Variable (0-5)</td>
</tr>
<tr>
<td>Buffer: NaHCO3 (g)</td>
<td>0.75</td>
<td>-</td>
<td>0.75</td>
</tr>
<tr>
<td>Initiator: K₂S₂O₈ (g)</td>
<td>0.10</td>
<td>0.40</td>
<td>0.50</td>
</tr>
<tr>
<td>Demineralized water (g)</td>
<td>126</td>
<td>-</td>
<td>126</td>
</tr>
<tr>
<td>No-ionic emulsifier:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arkupal N-300 (g)</td>
<td>5.00</td>
<td>-</td>
<td>5.00</td>
</tr>
<tr>
<td>Anionic emulsifier:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkylphenol ethersulphate (g)</td>
<td>0.50</td>
<td>4.50</td>
<td>5.00</td>
</tr>
</tbody>
</table>
during the polymerization process, it was necessary to withdraw samples at various intervals from the reaction vessel. These samples are relatively small so that the overall composition in the reactor is not seriously affected. Once a sample is removed and put in a watch glass, polymerization is terminated by the addition of 7 ppm hydroquinone. Then 2 drops of ethanol is added to the sample as a coagulant agent and the contents of the watch glass were evaporated at room temperature, then dried to constant weight in vacuum oven. The conversion percentage was determined gravimetrically. The purification and precipitation of the polymer were done using Grassies method [31]. The number of polymer particles per unit volume of water \( N_T \) was calculated from the monomer conversion \( X_M \) and the volume average diameter of the polymer particles, \( d_v \), was determined by a scanning electron microscope, using the following equations:

\[
d_v^3 = \frac{\sum n_i d_i^3 v_i}{\sum n_i} \tag{1}
\]

\[
N_T = \frac{6M_o X_M}{\pi d_v^3 \rho p} \tag{2}
\]

Where \( M_o \) is the initial monomer concentration per mL, and \( \rho_p \) is the density of the polymer (g/mL) [32 - 34]. The volume average diameter of the latexes were found to be 1500, 6000, and 7000 nm for 0.00, 0.15 and 0.25 molar VTES containing copolymers, respectively. Although the produced copolymers have low solubility in various solvents such as toluene, benzene, acetic acid, xylene, \( N,N\text{-}d\text{imethylformamide} \) (DMF), dimethylsulphoxide (DMSO), \( N\text{-}methylpyrrolidine \) (NMP), acetone and dichloroethane which makes it difficult for their characterization, but their morphology as well as their thermal properties gave important information about their structure and property relation. On the other hand the appearance properties of the products such as adhesiveness, transparency of the film and elasticity are excellent and indicate the formation of copolymers. Also with the prepared copolymer, we made some different building paints which were under testing for eight months and during this time we did not observe any fluctuation such as decomposition, sedimentation and floating.

Furthermore, the comparison of these paints with their available standard samples showed a very good maintenance time without any gelation. The repro-

<table>
<thead>
<tr>
<th>Compound</th>
<th>Functional</th>
<th>Amount (%)</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Solvent</td>
<td>28</td>
<td>279.5</td>
</tr>
<tr>
<td>Sodium benzoate</td>
<td>Softening agent</td>
<td>0.19</td>
<td>1.9</td>
</tr>
<tr>
<td>EFKA 2526</td>
<td>Antifoaming</td>
<td>0.36</td>
<td>3.58</td>
</tr>
<tr>
<td>Hydroxyethylcellulose</td>
<td>Thickening agent</td>
<td>0.6</td>
<td>6</td>
</tr>
<tr>
<td>Ammonia solution 25%</td>
<td>pH Adjustment</td>
<td>0.16</td>
<td>1.6</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>Opacifying white pigment</td>
<td>11.64</td>
<td>116.2</td>
</tr>
<tr>
<td>Aluminum silicate</td>
<td>Extender</td>
<td>2.54</td>
<td>25.4</td>
</tr>
<tr>
<td>Talc (325 mesh)</td>
<td>Extender</td>
<td>5.45</td>
<td>54.5</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>Extender</td>
<td>31.98</td>
<td>319.8</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Antibactericid</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>Co-solvent, antifreeze</td>
<td>1.07</td>
<td>10.7</td>
</tr>
<tr>
<td>Butyl glycol</td>
<td>Coalescence agent</td>
<td>0.93</td>
<td>9.3</td>
</tr>
<tr>
<td>Mineral spirits</td>
<td>Levelling agent</td>
<td>0.93</td>
<td>9.3</td>
</tr>
<tr>
<td>Disperse A</td>
<td>Dispersing agent</td>
<td>0.39</td>
<td>3.9</td>
</tr>
<tr>
<td>Dioctylphthalate</td>
<td>Softening agent</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>VTES Modified acrylic resin</td>
<td>Binder</td>
<td>15.06</td>
<td>150.6</td>
</tr>
</tbody>
</table>
ducibility of the kinetic data was checked by repeating the experiments and each monomer conversion considered in this paper is an average of at least four measurements and the deviation between four runs was always less than 5%.

**Polymer Characterization**

DSC Thermograms were taken on a Mettler TA 4000 Model apparatus at a heating rate of 10°C/min. The glass transition temperature ($T_g$) was taken at the onset of the corresponding heat capacity jump. TGA Measurements of copolymers were carried out by a Dupont TGA 951 under nitrogen atmosphere at a heating rate of 10°C/min. Scanning electron micrographs were taken on a Jeol-JXA 840 A SEM. The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying on a gold coating of approximately 300Å on an Edwards S 150 B sputter coater. FTIR Spectra of the copolymers were taken using a Nicolet Impact 400 D Model spectrophotometer.

**Preparation of Emulsion Paints by the Obtained Resin**

The preparation of emulsion paints was carried out using a 2000 mL round bottom metal vessel, equipped with a stainless steel stirrer. This vessel was first charged with water, sodium benzoate, dispersing agent, ammonia solution, defoamer, hydroxyethyl-cellulose and then the reaction mixture was stirred at a rate of 1600 rpm at room temperature. After 15 min alumini-um silicate, talc, titanium dioxide, calcium carbonate and dispersing agent were added, respectively and it was stirred for another 30 min with 2000 rpm. Then it cooled to 25-30°C and silicone modified acrylic resin was added to the mixture. After this, mineral spirits, ethylene glycol, butyl glycol and formaldehyde were added and stirred for 45 min which means the whole process took 90 min and then, the pH was adjusted with ammonia solution between 7.5-8.0. The amount of all ingredients [35,36] and general properties of this paint are summarized in Tables 2-4, respectively.

**Preparation of Paint Films**

For making paint films a four-edge applicator 125 micron has been used. In order to do this, the paints were charged in to the empty bulk of apparatus, then it was applied on the plastic surface and removed from up to down direction slowly. After coating of the glass or

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**Table 3. Physical properties of emulsion paint.**

<table>
<thead>
<tr>
<th>VTES Concentration (molar)</th>
<th>Washing and abrasion resistance (cycles)</th>
<th>UV resistance</th>
<th>Brushing control</th>
<th>Drying time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5000</td>
<td>Turn yellowish</td>
<td>By painting-brush effect</td>
<td>60</td>
</tr>
<tr>
<td>0.05</td>
<td>5000</td>
<td>Turn yellowish</td>
<td>By painting-brush effect</td>
<td>60</td>
</tr>
<tr>
<td>0.10</td>
<td>6000</td>
<td>No yellowing</td>
<td>By painting-brush effect</td>
<td>60</td>
</tr>
<tr>
<td>0.15</td>
<td>7500</td>
<td>No yellowing</td>
<td>No brush marks can be seen</td>
<td>75</td>
</tr>
<tr>
<td>0.20</td>
<td>9000</td>
<td>No yellowing</td>
<td>No brush marks can be seen</td>
<td>75</td>
</tr>
</tbody>
</table>

Density: 1.35 g/mL, viscosity: 1600 cps

**Table 4. Morphologies of latex particles at different VTES concentrations.**

<table>
<thead>
<tr>
<th>[VTES]= 0.00</th>
<th>$X_M$</th>
<th>$X_T$</th>
<th>$X_T$</th>
<th>$X_T$</th>
<th>$X_T$</th>
<th>$X_T$</th>
<th>$X_T$</th>
<th>$X_T$</th>
<th>$X_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_n = 1.5 \times 10^3$ nm</td>
<td>0.00</td>
<td>0.05</td>
<td>0.10</td>
<td>0.15</td>
<td>0.20</td>
<td>0.25</td>
<td>0.30</td>
<td>0.35</td>
<td>0.40</td>
</tr>
<tr>
<td>$X_M$</td>
<td>50</td>
<td>55</td>
<td>65</td>
<td>69</td>
<td>75</td>
<td>86</td>
<td>95</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>$X_T$</td>
<td>838</td>
<td>922</td>
<td>1089</td>
<td>1157</td>
<td>1257</td>
<td>1442</td>
<td>1592</td>
<td>1676</td>
<td></td>
</tr>
<tr>
<td>$X_T$</td>
<td>45</td>
<td>52</td>
<td>63</td>
<td>65</td>
<td>86</td>
<td>94</td>
<td>25</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>$X_T$</td>
<td>45</td>
<td>52</td>
<td>63</td>
<td>65</td>
<td>86</td>
<td>94</td>
<td>25</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>$X_T$</td>
<td>5.3</td>
<td>44</td>
<td>51</td>
<td>60</td>
<td>75</td>
<td>90</td>
<td>92</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>$X_T$</td>
<td>12.3</td>
<td>16.5</td>
<td>17</td>
<td>22.5</td>
<td>24</td>
<td>25</td>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X_T$</td>
<td>12.3</td>
<td>16.5</td>
<td>17</td>
<td>22.5</td>
<td>24</td>
<td>25</td>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X_T$</td>
<td>12.3</td>
<td>16.5</td>
<td>17</td>
<td>22.5</td>
<td>24</td>
<td>25</td>
<td>26</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**[M]_0 = 4.0 M, \rho_p = 1.35 g/mL, 60 rpm, T= 85°C, [I]_0 = 7 \times 10^{-3}**
plastic surface the evaporation of solvent (water) resulted in the formation of paint films. In this order, the existence of some cosolvents such as white spirits act as a leveling agent and consequently an adequate film was supplied. This is a short description of film formation mechanism.

RESULTS AND DISCUSSION

Agitation Effect

In heterogeneous reaction systems, mass transfer is one of the important factor that affects polymerization rate. In order to investigate the mass transfer effect on the polymerization rate, experiments were carried out under conditions of different impeller speeds [37]. Experimental results are presented in Figures 1 and 2 where the conversion of monomer to polymer are plotted against reaction time and impeller speeds at different agitation speeds. In these experiments, initiator concentration, was $7.0 \times 10^{-3} \text{ M}$ in H$_2$O and the concentration of total monomer added per unit volume of aqueous phase, $M_0$ was $4.0 \text{ M}$ in H$_2$O. In Figure 1 agitation speeds show the highest polymerization rate at 60 rpm and lowest polymerization rate at 300 rpm. Figure 2 confirms a decrease in the polymerization rate by increasing the agitation speed and also the experimental results at agitation speeds between 72 and 100 rpm do not show any difference in polymerization rate. It is worth to be mentioned that Peng et al. [38] have reported the same variation in the organosilicon composite emulsion polymerization. However, a reduction in impeller speed to 60 rpm leads to earlier attainment of an acceleration in the polymerization rate. Accordingly, the reaction time required to attain high conversion is shorter at 60 rpm than at the other impeller speeds. Arai and coworkers [39] observed a similar tendency for emulsion polymerization in the absence of a solid phase and were explained by a consideration of monomer mass transfer from monomer droplets to the polymer particles formed in the aqueous phase.

Effect of Initiator Concentration

Figure 3 shows the results of different initiator concentrations on the polymerization reaction rate. Upon increase in initiator concentrations at both the initial

Figure 1. The effect of agitation speed on monomer conversion vs. polymerization time at (●) 100; (+) 200; and (▲) 300 rpm. $[M]_0 = 4.0 \text{ M, } [\text{VTES}] = 0.05 \text{ M, } T = 85^\circ\text{C, } [I]_0 = 7.0 \times 10^{-3} \text{ M.}$

Figure 2. The effect of agitation speed on monomer conversion vs. impeller speed at (●) 15; (●) 60; and (+) 90 min. Min $[M]_0 = 4.0 \text{ M, } [\text{VTES}] = 0.05 \text{ M, } T = 85^\circ\text{C, } [I]_0 = 7.0 \times 10^{-3} \text{ M.}$

Figure 3. The effect of initial initiator concentration on monomer conversion vs. time at $[\text{K}_2\text{S}_2\text{O}_8] \times 10^{-3} = (●) 3; (●) 7; \text{ and (+) } 14 \text{ M}; [M]_0 = 4.0 \text{ M, } [\text{VTES}] = 0.05 \text{ M, } 60 \text{ rpm, } T = 85^\circ\text{C.}$
and intermediate stages of reaction leads to an enhancement of the polymerization rate. The rate increase at the intermediate stage suggests the existence of more than one radical in a polymerization locus. Thus the polymerization mechanism is different from that of an ideal emulsion polymerization, [40, 41], in which only one radical can exist and no gel effect appears.

**Effect of Temperature**

The effects of temperature of maximum conversion and the initial rate of emulsion copolymerization of silicone modified acrylic are represented in Figure 4. The temperature range studied at fixed concentration of monomers and initiator was between 60 to 90°C. It was observed that both initial rate of polymerization and maximum conversion increased with increasing temperature. Figure 4 also shows that there is no any polymerization onset at 75°C. After this temperature it has been observed that there is an increase in the polymerization rate by increasing temperature. The temperatures 85 and 90°C are suitable for these systems but at 85°C the highest conversion percentage is noticed others. Actually very high temperature such as 90°C and more is dangerous for these systems, because the polymer may turn to gel point.

**Effects of the VTES Concentration**

Addition of VTES in acrylic emulsion provides beneficial effects by improving various mechanical properties such as water and weatherability and good acid and alkali resistance [24,27,43]. In addition to this, the incorporation of silicone plays the roles of coupling agent and softener [42] and it is enriched on surface of the film [27]. On the other hand You et al. [28] demonstrated that silanes can be bonded with hydroxyl groups on the surface of substrate to increase the adhesion and also FTIR analysis indicated that organic functional silanes can be polymerized with other monomers. Figure 5 shows the effect of VTES concentration on the conversion versus time histories where the initial initiator and total monomer concentrations were constant at [I]₀ = 7.0 × 10⁻³ M and [M]₀ = 4.0 M. It has been observed that the rate of reaction decreases with increase the amount of VTES. Figure 6 confirms a decreasing in the reaction rate with increasing VTES concentration. Kan et al. [44] also observed the same
behaviour in the acrylate-silicone emulsion.

It is known that the rate of propagation and consequently the rate of copolymerization in a radical copolymerization reaction is inversely related to the termination rate constant. As the amount of VTES increases it can act as a chain transfer agent and decreases the rate of polymerization reaction.

**Studies of Paints Properties**

The obtained paints have acceptable results such as excellent storage stability, great surface coating, good brushing, UV light stability, washing and abrasion resistance. Among these properties, the surface coating, washing and UV resistance have been shown in Figures 7-9, respectively. Figure 7 shows that excellent surface coating by using white paints by considering Table 2 recipe of emulsion paint on the dark background, and the disappearance of the black fraction after coating could be obtained. As Figure 8 (A-D) reveals some differences between the samples which contained 0.00, 0.10, 0.15 and 0.20 molar VTES can be clearly observed. In this relation it is worth mentioning that the washing and abrasion resistance tests were done by making films on a plastic surface of 10 cm width and 30 cm length with an applicator 125 micron. Then they were settled on the tester apparatus for 48 h. The velocity of this apparatus is 37±1 rpm and it works until no abrasion is seen in the films. The measure of washing apparatus is the round of brush on the film of paint. Generally it has been measured around 1000 round for the paints which their binder is a homopolymer and 5000-7000 round for copolymers, respectively. Table 3 shows the stabilities of these paints until 9000 round that it is belong to the existence of VTES and Figure 8 shows that by increasing the VTES concentration the washing and abrasion resistance increase as well. The UV resistance of these paints has been shown in Figure 9 (A with 0.25 molar and B without VTES). The comparison of two film samples shows that the colour of B has a tendency to become yellowish while A is stable.

![Figure 7](image)

*Figure 7.* The photograph of surface coating of sample paints with (A) 0.15, (B) 0.20 and (C) 0.25 M VTES.
and this is another important improvement because of the presence of VTES. Brushing control studies have been done by dissolving the paint in the determined amount of water, then it has been applied on the surface of chalk by a painting brush. Basically no painting brush effect must be observed during the painting. According to the results of brushing control which is shown in Table 3, it has been observed that the effect of painting brush at low VTES concentration is being observed but it is improved by increasing the VTES concentration.

**Solubility and FTIR Studies**

The emulsion copolymers basically have low solubility or show no solubility in any solvents at all.

These copolymers which have been synthesized from MMA, BA and MAA with or without VTES are not exceptions. They are not soluble even in aprotic polar solvents such as NMP, DMSO, DMF or dimethylacetamide (DMAC). This insolubility could be due to conversion of the polymer samples to gelation immediately during drying under atmospheric air or vacuum. Different procedures for the preparation, purification and drying of the polymer samples were carried out. 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 these copolymers will turn to gel in ethanol after dissolving in little water. Anyway, the characterization of these copolymers is very difficult with the aim of their solubilities. For example NMR study of these copolymers is nearly impossible to perform, but FTIR spectra in the region from 4000 to 500 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 10 shows the FTIR spectra of (A) MMA, BA, MAA, ...
(B) with 0.15 and (C) with 0.25 molar VTES-added copolymers, respectively. The comparison of A spectra with B or C has not shown any differences between two different samples of copolymers. The same analyses were repeated for each sample three times and from the FTIR data it was concluded that this method is not able to show the presence of VTES moiety in these copolymers.

**Morphologies of Latex Particles at Different VTES Concentrations**

The particle morphologies of the VTES modified acrylic copolymers were examined by SEM, and the data are given in Table 4. Figure 11A-11C are electron micrographs of the latex particles of samples that contain 0.00, 0.15 and 0.25 molar VTES and the number average particle diameters were found to be 1500, 6000 and 7000 nm, respectively. According to these micrographs the acrylic copolymers have very low particle size compared to VTES modified samples and by increasing the VTES concentration the particle size increases and their size distributions become narrower. On the other hand from the date of the Table 4 it is observed that the number of polymer particles decreases by increasing the VTES concentration. In addition it is obvious that the number of polymer particles for the emulsions obtained increases by increasing the time and conversion monomers to copolymers. These results suggest that MMA, BA, and MAA monomers were completely polymerized in the presence VTES.

**Thermal Properties**

The thermal properties of acrylic and VTES modified acrylic copolymers were evaluated by means of TGA/DTG and DSC under nitrogen atmosphere and are shown in Figures 12 and 13. The acrylic emulsion of Figure 12a shows some weight loss between 50-130°C which is due to loss of solvent. Then it is stable up to 280°C. The chemical decomposition will start after this temperature and the maximum decomposition is around 370°C. On the other hand VTES modified acrylic copolymers exhibited thermal decomposition similar to the above, but the maximum decomposition was around 380°C. The results are represented in Figures 12b and c for 0.15 and 0.25 molar VTES, respectively. According to these results it is concluded that the existence of VTES moiety in the copolymers causes some thermal stability and by increasing the amount of

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**Figure 11.** SEM Pictures of (a) MMA, BA, MAA copolymer, (b) with 0.15 and (c) 0.25 molar VTES [M]₀ = 4.0 M, 60 rpm [I] = 7.0 × 10⁻³ M, T = 85°C.
silicone thermal stability increases. The DSC curve of the copolymers is shown in Figure 13 A-C for 0.00, 0.15 and 0.25 molar ratio VTES, respectively. Curve A in Figure 13 reveals an endothermic shift around 50°C which corresponds to T_g without VTES. The T_g is around -85 and -100°C for (B) and (C), respectively. On the other hand all of these copolymers (A-C) show very sharp endothermic peak with a maximum of 380°C which corresponds to the T_m. From these data it is very interesting to mention that without VTES the resulting copolymer is thermoplastic, while by addition of VTES the T_g of copolymer will be drastically lowered and it shifts to the elastomeric materials while its T_m remains unchanged. According to these results it is found that the presence of VTES moiety causes the change in thermal behaviour and it particularly affects T_g.

**CONCLUSION**

Continuous emulsion copolymerization of VTES modified acrylic resin, initiated by K_2S_2O_8, was evaluated.
The experimental conditions of impeller speed, initiator concentration, temperature, and VTES concentration were varied and the following results were obtained:

- The obtained copolymers have high solid content (43%) and are used in the emulsion paints as a binder.
- An increase in VTES concentration causes an increase in heat stability and particle size, while the $T_g$, number of polymer particles and polymerization rate decrease and also particle size distributions became narrower.
- The presence of VTES moiety in the copolymers causes conversion of thermoplastic structure to elastomeric property.
- An increase in initiator concentration at both initial and intermediate stages of polymerization resulted in an increase in polymerization rate.
- In the region of relatively low impeller speed, a reduction in impeller speed shortens the reaction time required to attain high conversion.
- It is observed that both initial rate of polymerization and maximum conversion are increased by increasing the temperature.

REFERENCES