Synthesis and Characterization of Butyl Acrylate, Acrylic Acid and Vinyl Acetate Emulsions for Water born Pressure Sensitive Adhesives

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Abstract

Emulsion based pressure-sensitive adhesives (PSAs) are prepared with different monomer composition which are gaining importance due to their improved performance as well as lower environmental impact of the aqueous emulsion polymerization process. In this study the monomers used are butyl acrylate (BA), vinyl acetate (VAc) and acrylic acid (AAcid). The adhesive performance was studied with varying amounts of viz., 0, 5, 10 and 15 wt% VAM content based on total monomer composition. Final performance properties such as peel strength and shear strength were investigated on two different substrates such as stainless steel test plate to bi axially oriented polypropylene (BOPP). The adhesive property ranges from very good to poor PSA performance. As the VAM content increased in BA formulation, shear strength, and peel strength were found to increase. The effect of particle size of latexes on PSA performances have been studied using varying amounts of surfactant content. The effect of monomer compositions on glass transition temperature (Tg) of the BA/VAM formulation have been investigated.

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Key Words: Butyl acrylate, emulsion polymerization, pressure sensitive adhesives, peel strength, particle size.

1. INTRODUCTION

The emulsion polymerization is used to obtained number of products such as adhesives, paints, drug delivery, etc. Among the pressure sensitive adhesives (PSAs) are visco-elastic materials that adhere upon application of light pressure [1]. Different technologies can be used for the production of PSAs. Increasingly the interest is to utilize environmentally friendly process, such as water borne and curing technologies, without use of organic solvents [2]. For this reason, PSAs are polymerized with a low glass transition temperature (Tg) monomer usually butyl acrylate (Tg = -54 °C). The low Tg component enables the PSA to flow and wet substrate surface [1]. Thus, they polymerized with high Tg acrylic acid and vinyl acetate (VAM). The aim of the study is to investigate the effect of vinyl acetate content on the adhesive performance of the resultant polymers through measurement of shear strength and peel strength. In this work peel strength and shear strength was studied with bonding on two different surfaces namely stainless steel and BOPP tape. Acrylic based pressure-sensitive adhesives (PSAs) obtained by emulsion polymerization using water as solvent and are characterized as adhesive which can adhere strongly to solid surfaces upon application of light contact pressure and short contact time. It is used in pressure sensitive tapes, labels, note pads, automobile and a wide variety of other products [3].

Now a days, increasing social awareness, coupled with the tightening of worldwide environmental legislation such as strict volatile organic compound (VOC) level reduction as required by the EPA Clean Air Act, has forced coating industries to decrease the levels of pollutant substances released to the atmosphere. Solvents from the coating industry are considered to be volatile organic substances. Hence, there is an increasing tendency to move away from solvent-borne PSAs [3]. In the curing process, the largest particle sizes imparted some inherent weakness to the peel strength property. However, as the particle size decreases, the peel strength will increase [4].

The emulsions are obtained by using anionic surfactant sodium alkyl benzene. The monomer was butyl acrylate (BAM), vinyl acetate (VAc) and acrylic acid (AA), and initiators potassium per sulfate, NaHCO₃ and doubly de-ionized water is used. The proportion of VAM content was studied at 0, 5, 10 and 15 wt% based on total monomer composition.
2. EXPERIMENTAL

2.1 Materials
Butyl acrylate (BA) monomer (Industrial grade) was obtained from Sahngha Jundan Industrial Co. Ltd., China, vinyl acetate monomer (VAM) purchased from Visen Industries, India. Acrylic acid (AA), sodium bicarbonate and potassium per sulfate were purchased from Merck labs, India. Emulsifier (sodium alkyl benene sulfonate) was obtained from Diachi Karkaria Ltd., India.

2.2 Synthesis of butyl acrylate and vinyl acetate emulsions
The emulsions were prepared by free radical polymerization. The polymerization was carried out in a 1000 ml four necked round bottom flask immersed in a constant temperature water bath at 80 °C, equipped with a reflux condenser, stirrer, dropping funnel and a nitrogen inlet. 4.86 g surfactant was dissolved in de-ionized water and buffers were initially charge and maintained 100 rpm.

2.3 Particle size characterization
The particle size was determined by using dynamic light scattering Particle Size Analyzer. Samples for particle size analysis were prepared by diluting PSA obtained from de-ionize water. After dilution, the latex samples were injected into the instrument.

2.4 Peel strength test
The peel strength (ASTM D330) is the measure of the average force to delaminate the two bonded materials like tape, labels, textile or plastic films. The strength is calculated during a peel test at a constant speed rate divided by the average force required during the test by the unit width of the bonded samples. Depending on nature of materials and products, the tests was conducted with different angles: 90° and 180° [9]. Peel test is carried out at 45 °C.

All PSAS latex obtained was coated on BOPP by using a micron rod. The adhesive coated tape was dried at 100°C for 10 min. To measure the adhesive coating weight, first take a BOPP sheet 200 mm × 75 mm weighted without adhesive. The coating weight was calculated from the average force to peel the specimen from test plate was recorded at angle 180°. The testing speed of Universal Material Testing Machine (UTM) was 300 mm/min.

Table 1. Typical formulation of Pressure sensitive adhesives

<table>
<thead>
<tr>
<th>Sample</th>
<th>BA (%</th>
<th>AA (%)</th>
<th>VAM (%)</th>
<th>Surfactant (%)</th>
<th>Total solid (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
<td>94</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>89</td>
<td>1</td>
<td>10</td>
<td>1</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>84</td>
<td>1</td>
<td>15</td>
<td>1</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>99</td>
<td>1</td>
<td>0</td>
<td>1.5</td>
<td>55</td>
</tr>
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<td>99</td>
<td>1</td>
<td>0</td>
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<tr>
<td>7</td>
<td>99</td>
<td>1</td>
<td>0</td>
<td>3</td>
<td>55</td>
</tr>
</tbody>
</table>

Separately 320.9 g of butyl acrylate monomer (BAM), 3.24 g of acrylic acid (AA) and calculated amounts of VAM as per composition mentioned in Table 1 were mixed. Then initiator was prepared by adding 0.75 g of potassium per sulfate into 35 g of de-ionized water and stirred by using a magnetic bar. Approximately 25% initiators was added and followed by the delayed addition of 5% of the total monomer mixture. The initiation occurred after 10 min with the appearance of a light blue color. Then 75% of the monomer was added drop wise over a period of 4 hrs. At the end remaining mixture was added drop wise over a period of 1 hr. The remaining initiator was added equal parts during the reaction at regular intervals continuously. Then bath temperature was increased to 90°C and stirring was continued for another 1 hr. The mass ratio of monomers and surfactant were varied as summarized in Table 1. The reaction mixture then cooled below 40 °C and filtered.

2.5 Shear strength Test
Shear strength was the resistance of an adhesive coated label stock on a standardized surface to shear at a constant rate [7]. To measure the adhesive dynamic shear resistance first a 150 × 12.7 mm strip of adhesive laminate was prepared. One end of the adhesive laminate was adhered to a clean stainless steel test plate with a 12.7 × 12.7 mm contact area. A standard pressure roller was rolled across the bonded area, which formed an adhesive bond. Dwell time between roll down and testing was 20 min. Gripping separation speed at 5 mm/min was applied to the free end of the test piece in the length direction. The adhesive layer resists the deformation. The maximum shear force have been reported [5].

2.6 Thermal method
The glass transition temperature (Tg) of the pressure sensitive adhesives was determined by a differential scanning calorimetry (DSC) with TA instrument Q-1000 with a scan rate of 10 °C over a temperature range of -60 °C to 100 °C.

2.7 Fourier-transform Infrared Spectroscopy
The FTIR spectra were recorded on a Nicolet 940 Fourier transform Infrared (FTIR) spectrometer. About 0.5 g of sample is dissolved in chloroform of HPLC grade and made into a thin transparent film and subjected to IR measurements in the wave number range 4000 - 400 cm⁻¹. The attenuated total reflection (ATR) infrared spectroscopy
was used to record the spectra of the PSA films.

3. RESULTS AND DISCUSSION

3.1 Surfactant content effect on Particle Size of adhesives

Surface active agent was added for a stable monomer emulsion in water. The effect of emulsifier or surfactant (BOTM) content in the PSA formulations on the particle size and solid content have been measured and obtained results is tabulated in Table 2. From the table it is noticed that as the surfactant content increased from 1 to 3 % based on total monomer content a significant reduction particle size and a slight increase in solid content of the PSA. In conventional emulsion polymerization, when the concentration of surfactant exceeds its critical micelle concentration (CMC), the excess surfactant molecules aggregate to form small colloidal clusters referred to as micelles. In principle, polymer particles can be formed by the entry of monomer radicals into the micelles, precipitation of growing oligomers in the aqueous phase and radical entry in monomer droplets. As the amount of monomers was kept constant, the number of micelles increased with the increasing surfactant content, therefore more sites for polymerization occurred and smaller particle size of latexes formed. The surfactant was useful to control the particle size of latexes. Furthermore, the total solid content results indicated that the maximum conversion of all monomer into polymer.

Table 2: The effect of surfactant content on (Butylacrylate/Acrylic acid/Vinyl acetate monomer) Based on total monomer (BOTM).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Butylacrylate Monomer (BAM)</th>
<th>Acrylic acid (AAcid)</th>
<th>Vinylacetate monomer (VAM)</th>
<th>Surfactant (sodium alkylbenzene sulfonate)</th>
<th>Particle size (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99</td>
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<td>0.30</td>
</tr>
<tr>
<td>7</td>
<td>99</td>
<td>1</td>
<td>0</td>
<td>3</td>
<td>0.21</td>
</tr>
</tbody>
</table>

3.2 Effect of Particle Size on Adhesive Performance

The effect of particle size of on the adhesive performances such as peel strength and shear strength of emulsion BA/VAM PSA is shown in Figures 1 and 2 respectively. It can be observed that the peel strength and shear strength decreased with increase in the particle size of BAM/VAM latexes [6]. During the drying process, the largest particle sizes imparted some inherent weakness to the peel strength property. A possible explanation for the positive effect of smaller particles on shear strength relates to the ability of these smaller particles to pack more tightly together during the drying process, so that increasing the area of contact between the substrate and the adhesive.

3.3 Vinyl Acetate Monomer Composition on Adhesive Performance

The effect of monomer compositions on the peel strength and the shear strength of the BAM/VAM pressure sensitive adhesives is plotted in Figures 3 and 4 respectively. From the figure it was noticed that as increase in VAM content in BA latex, exhibited the higher peel and shear strength as compared to formulation without VAM composition. The peel stress was sensitive to monomer content. Low BA or high VAM content provided the highest peel stress. A similar kind of research work i.e., effect of incorporating VAM on peel strength on PSAs have been reported by Gower and Shanks [8]. The results showed an increase in gel content as the weight fraction of VAM increased. Tobing and Klein have been investigated that as gel content of the formulations increased, peel strength also increased [10]. Figure 4 indicates that the shear strength strongly depends on the VAM content. The flow of adhesive or wetting of the substrate, must be dominated by the VAM/BAM formulations. The higher shear strength with increasing of VAM content was due to entanglements of the vinyl side groups [8].
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3.4 FTIR Spectroscopy

The obtained FTIR spectra of BA/VAM PSA with different surfactant are shown in Fig 6. The characteristic absorption bands at 2956, 2940 and 2875 cm\(^{-1}\) were due to C-H strong bonding butyl acrylate and vinyl acetate copolymer were characterized The absorption peak at 990 cm\(^{-1}\) showed the presence of vinyl group. The peak at 1065 cm\(^{-1}\) showed primary alcohol bonding vinyl in it backbone structure. The peak at 1740 cm\(^{-1}\) indicates the presence of acetate and ester functional groups.

3.5 Scanning Electron microscopy (SEM)

The SEM images reveal the different particle size of Pressure sensitives adhesives reduced from sample1 to sample 7 with increasing of surfactant (sodium alkyl benzene sulfonate) content in sample1, sample5, sample 6 and sample7. The excess surfactant molecules aggregate to form small colloidal clusters referred to as micelles. In principle, polymer particles can be formed by the entry of radicals into the micelles, precipitation of growing oligomers in the aqueous phase and radical entry in monomer droplets. As the amount of monomers (BAM/VAM/AAcid) (99/1/0) was kept constant, the number of micelles increased with the increasing surfactant content, therefore more sites for polymerization occurred and smaller particle size of

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**Figure 3.** The effect of VAM/BAM composition on peel strength of Pressure sensitive adhesives.

**Figure 4.** The effect of VAM/BAM compositions on shear strength of Pressure sensitive adhesives.

**Figure 5.** The effect of VAM/BAM composition on glass transition temperature of Pressure sensitive adhesives (PSA).

The effect of monomer compositions on \(T_g\) of the PSA is plotted in Figure 5. From the figure it was noticed that \(T_g\) decreases with increase in rubber phase (BAM) in the formulations as expected. This is due to BAM has low \(T_g\) whereas VAM has high \(T_g\); hence, \(T_g\) decrease with increase in BAM content in BAM/VAM formulations.

**Figure 6.** FTIR spectra of Pressure sensitive adhesives (BAM/VAM/AAcid).

**Figure 7.** Scanning electron microscope particle size images of sample 1 sample 5 sample 6 and sample 7

The SEM images reveal the different particle size of Pressure sensitives adhesives reduced from sample1 to sample 7 with increasing of surfactant (sodium alkyl benzene sulfonate) content in sample1, sample5, sample 6 and sample7. The excess surfactant molecules aggregate to form small colloidal clusters referred to as micelles. In principle, polymer particles can be formed by the entry of radicals into the micelles, precipitation of growing oligomers in the aqueous phase and radical entry in monomer droplets. As the amount of monomers (BAM/VAM/AAcid) (99/1/0) was kept constant, the number of micelles increased with the increasing surfactant content, therefore more sites for polymerization occurred and smaller particle size of
latexes formed.

4. CONCLUSION

In this work, pressure-sensitive adhesives (PSAs) were prepared from monomers (BA, VAM and AA) by emulsion polymerization method. The effect of VAM content on the PSA performances have been investigated. The particle size of the latex is depends on the surfactant (sodium alkyl benzene sulfonate) in the polymerization. PSAs performances strongly depend on the particle size of the latex and monomer compositions. Lower the particles size of the latex and higher VAM content in BA/VAM formulations exhibit higher peel strength and shear strength. The glass transition temperature was strongly depends on BA content in the PSA formulations. Tg increase with increase in VAM content in the PSA. From the results it was noticed that BA/VAM/AA copolymers gave good PSA tapes for BOPP. These PSAs will belong to eco-friendly high performance adhesives and that are multi-functional.

5. REFERENCES


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