Syntheses of crosslinked latex nanoparticles using differential microemulsion polymerization

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Abstract. The differential microemulsion polymerization was used to synthesize latex nanoparticles. In this paper, 1, 3-butylene glycol dimethacrylate (1, 3-BGDMA) was used as a crosslinker respectively 1-5 weight% of monomer total. Butyl acrylate (BA), butyl methacrylate (BMA), and methacrylic acid (MAA) was used as the monomer. The thin film of latex nanoparticles were prepared by using spin coating method and have been dried at 100°C for 5 minutes. The amount of the crosslinker added in the polymerization was optimized and we found that the particle sizes fall in the range of 30-60 nm. The structural morphology of the uncrosslinked latex represented the most homogeneous image compared to the crosslinked latex. The effect of the amount of crosslinker on the particle sizes investigated by the Zeta-sizer Nano series while Atomic Force microscopy (AFM) was used to study the structural properties of latex nanoparticles.

1. Introduction
Latex with size less than 100 nm have received an increasing attention due to the wide range of application such as coating, paint, adhesive, and textile [1,2]. The common method to prepare the latex nanoparticles are emulsion polymerization [3,4] and microemulsion polymerization. Microemulsion polymerization has been actively studied since 1980’s. It can produce stable dispersion of polymer latexes with particle sizes in nanosize range [5-7]. Latex nanoparticles have an extremely large specific surface area which can provide high smoothness, strong adhesion and lasting latex dispersion stability. Crosslinking technology has been introduced in the polymerization method since it can improve the stabilities of latex and extend their applications. Recently, a number of crosslinkers and crosslinking technologies have been reported elsewhere [8,9].

In the present work, 1,3-butylene glycol dimethacrylate (1,3-BGDMA) was used as a cross linker during the polymerization of the latex nanoparticles. 1,3-BGDMA are chosen since it has a good stain resistance and solvency. The objective of this study is to investigate the effect of the addition of crosslinker on particle sizes and surface morphology of latex nanoparticles via differential microemulsion polymerization through Zeta-sizer Nano series and Atomic Force microscopy (AFM).
2. Methodology

Figure 1 shows the flow chart of the research methodology.

![Flow chart of research methodology](image)

2.1. Materials

The crosslinking agent 1,3-butylene glycol dimethacrylate (1,3-BGDMA) was purchased from Sigma Aldrich. Butyl methacrylate (BMA), butyl acrylate (BA), methacrylate acid (MAA), N,N,N,N’,N’-tetramethylethylenediamine (TMEDA), 2-amino-2methyl-1propanol (AMP), and 1-pentanol were purchased from Merck without further purification. Ammonium persulfate (APS), sodium dodecyl sulphate (SDS) and ammonia solution 25 % brought from R&M chemical were used as received. Deionized water was used throughout the experimental work.

2.2. Polymerization

Detailed polymerization recipes and the characterization of the samples are summarized in Table 1. As the usual method of polymerization, all the reactions were carried out in a 500 cm\(^3\) three necked round bottom flask with a reflux condenser, a thermometer, a magnetic stirrer, and the nitrogen inlet to dissolve the oxygen [2]. Microemulsion composed of 0.3 g of monomer content, 1.0 g SDS, 0.1 g of 1-pentanol, and 78.0 g of de-ionized water was heated to 40 °C and stirred about 300 revolutions per minute (rpm) with a gentle flow of bubble nitrogen. Ammonia solution was used to adjust the pH in the range of 9 – 10. TMEDA and APS that was dissolved in water were added into the microemulsion. The rest of monomer was added drop wise into the microemulsion and stirring continue to 2 – 3 hours to complete the polymerization process. The microemulsion was cooled down at room temperature and the pH was adjusted using AMP solution to 9.2 – 9.5.

| Sample | BMA (g) | 1,3-BGDMA (g) | Particle Size (nm) | Surface roughness (nm) |
|--------|---------|---------------|--------------------|------------------------|
| IC0    | 7.7     |               | 37.07              | 3.78                   |
| IC1    | 7.6     | 0.1           | 39.29              | 6.99                   |
| IC2    | 7.5     | 0.2           | 47.50              | 3.52                   |
| IC3    | 7.4     | 0.3           | 47.37              | 11.24                  |
| IC4    | 7.3     | 0.4           | 57.13              | 6.41                   |
| IC5    | 7.2     | 0.5           | 37.66              | 5.81                   |
2.3 Thin Film
Glass substrate (2 cm x 2 cm) was cleaned to get a good adhesion of coating. The substrates were cleaned using acetone and methanol. The latex nanoparticles solution was coated onto the glass substrate using spin coating method. The spin coating was done in 3000 rpm at 30 seconds. Each sample was dried at 100°C for 5 minutes to vaporize the solvent and removed the contamination.

3. Results and discussion

3.1. Particle sizer
Particles size measurement was carried out using Zeta-sizer Nano series at 25°C and the reading was taken triplicate at 173° scattering angle. Figure 2 shows the average particle sizes of latex nanoparticles with various amount of crosslinker. The results revealed that particle sizes changed when the amount of 1,3-BGDMA was increased. Without crosslinking the average particle sizes is 37.07 nm. As the crosslinking agent was introduced into the polymerization the particle sizes increased to 39.29 nm at 0.1 g of 1,3-BGDMA. The average particle sizes for 0.2 g, 0.3 g, and 0.4 g, are 47.50 nm, 47.37 nm, and 57.13 nm respectively. The particle sizes for 0.5 g of 1,3-BDGMA was reduced to 37.66 nm and this might be due to the increasing number of primary particles. As the crosslinker increased, the rate of nucleation increased and thus increased the number of primary particles, which lead to decreased in the diameter of the latex nanoparticles [10].

![Figure 2. Average particle size of latex nanoparticles at different amount of 1,3-BGDMA](image)

3.2. Atomic Force Microscopy (AFM)
AFM XE-100 Park System was used to capture the image morphology and topography of the surface latex nanoparticles and to obtain detailed information about the structure of the latex film. Figure 3(a) shown the three dimensional image of uncrosslinked latex with surface roughness 3.78 nm. The uncrosslinked latex represented the most homogeneous structure compare to the others image. The image totally change when the crosslinking agent were introduced into the polymerization as shown in Figure 3(b-e) and the surface roughness are 6.99, 3.52, 11.24, 6.41, and 5.81 nm respectively. Figure 3(d) gives a higher surface roughness and from the image the peak and the valley are bigger compare to the others. This observation suggests that the addition of crosslinking agent was fast enough to significantly inhibit the homogenization of the film [11, 12].
4. Conclusion

As a conclusion, crosslinked latex nanoparticles were successfully prepared via differential microemulsion polymerization with particle sizes in the range of 30-60 nm. The 1,3-butyleneglycol dimethacrylate (1,3-BDGMA) was used as a crosslinker and the amount was varied from 1-5 weight% of monomer total. The average particle sizes increased as the crosslinker were added from 0-4 weight% of monomer total. The particle sizes reduced to 37.66 nm at the 0.5 g of 1,3-BDGMA and this might due the increasing number of primary particles. The structural morphology of the uncrosslinked represented the most homogeneous image. The addition of crosslinking agent was significantly retarding the homogenization of the film. Therefore, we have found that the addition of crosslinking agent has sensitively effect the particle sizes and the surface morphology of latex nanoparticles.

Figure 3. AFM image of (a) IC0, (b) IC1, (c) IC2, (d) IC3, (e) IC4, and (f) IC5
Acknowledgement

Authors are gratefully acknowledged for the financial support to the MyBrain15 Sponsorship Programme, Malaysian Government and also to the Research Management Institute, Universiti Teknologi MARA (UiTM), Shah Alam, Selangor, Malaysia.

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