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Stabilizing Capability of Gum arabic on the Synthesis of Poly(Styrene-Methylmethacrylate-Acrylic Acid) Latex for the Generation of Colloidal Crystal Films

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Abstract

This article describes the generation and characterization of colloidal crystals from particles of gum arabic (GA) and sodium dodecylbenzene sulfate (SDBS) emulsified poly(styrene methylmethacrylate-acrylic acid) (P(St-MMA-AA) latex. The colloidal latex was synthesized using GA and SDBS as the emulsifying agents and then used to generate colloidal crystal films via the vertical deposition technique. Dynamic light scattering analysis placed the average particle diameter, polydispersity and Zeta potential at about 122 nm, 0.014 and –36.20 mV for the as-synthesized GA emulsified terpolymer latex and 213 nm, 0.006, –35.60 mV for the SDBS emulsified terpolymer latex, respectively. Thermo-gravimetric analysis and differential scanning calorimetry showed comparable thermal stability for both prepared terpolymer samples. Microscopic analysis showed that the latex particles possess a core-shell morphology which readily assembles into a well ordered hexagonal arrangement of spherical particles with manifold layers. This study, therefore, shows comparable properties of terpolymer prepared using gum arabic as emulsifier with terpolymer synthesized using SDBS which is a conventional emulsifier.

Keywords: Gum Arabic; sodium dodecylbenzene sulphate; colloidal crystal films; morphology; emulsifier

Introduction

Colloidal crystals can be defined as the arrangements of spherical colloidal particles into well-ordered morphologies (Pieranski and Pawel 1983). Several naturally occurring colloidal crystals have been shown to exist in nature. The fascinating, iridescent colour of an opal (synthetic or natural), for instance, is due to the Bragg diffraction of compact crystalline lattice arranged from silica colloidal particles that give out no colour on their own (Sanders 1968). A similar mechanism has also been used by a variety of insects like butterflies and beetles. Researchers used to think that the shiny colours displayed by these insects were due to pigmentation. It was later discovered that the beautiful colours emanating from the aforementioned insects are due to the structural arrangements of their wings. Colours of this sort are known as structural colours (Gu et al. 2015, Srinivasarao 1999). This finding led to the conclusion that, if naturally occurring materials can give

unique properties just by the periodic arrangements of their structures, it therefore means that, scientists can deliberately obtain numerous desired properties from myriad of materials by arranging their particles or atoms into periodic structural patterns rather than just arriving at these materials by an accidental process (Holtz and Asher 1997).

Presently, colloidal crystals have been established by several studies as one of the best systems for the formation of photonic band gaps that could be used to tune electromagnetic waves propagation in all three space directions (Ifijen et al. 2019a, Ifijen and Ikhuoria 2020). They have been applied as functional elements in generating diffractive optical devices for use in telecommunications, information processing, illumination, spectroscopy, holography, medicine (surgery, vision correction, endoscopy), military (guided missile) technology, agriculture and robotics (Cao et al. 2019).

Colloidal self-assembly has been established as the most promising for the low-cost production of 2-D and 3-D colloidal crystals over large areas or with various shapes (Galisteo- López et al. 2011, Marlow et al. 2009). Self-assembly (SA) in the classical sense can be defined as the spontaneous and reversible organization of molecular units into ordered structures by non-covalent interactions (Ikhuoria et al. 2018). Over the years, the primary focus has been to relate materials behaviour to the spatial arrangements of their fundamental building blocks. These building blocks may comprise atoms, molecules, macromolecules and colloidal particles. It is well known that the same chemical substance can have vastly different chemical properties depending on the ways its building blocks are arranged.

Materials like polymers and semiconductors have been used for the preparation of colloidal solutions for the fabrication of colloidal crystal films (Omorogbe et al. 2019). The stability of colloidal particles is a key factor that must be considered before the practical applications of any prepared colloids. It has been established that the selection of a correct emulsifier is very important in the development of polymer colloidal particles with a good level of stability (Ikhuoria et al. 2018). Also, the emulsifier is believed to enable fast polymerization rate, prevent the particles from coagulating with each other, high viscosity polymerization and maintains improved properties in the final products (Chern 2006). Ikhuoria et al. (2018) obtained unique morphologies from poly(styrene-methylmethacrylate-acrylic acid) latex synthesized using sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (C-tab) as emulsifiers. By altering the emulsifier type, differences in the particle morphology, colloidal stability and the particle sizes of the studied terpolymer were observed.

This study therefore, reports the synthesis and characterization of colloidal mono-dispersed poly(styrene-methyl-methacrylate-acrylic acid) colloidal latex (P(St-MMA-AA)) based on the templating effects of gum arabic (GA) and sodium benzene sulfate (SDBS) emulsifier with special emphasis on their colloidal stabilities, particle sizes and morphologies. For the first time, a comparative study on the properties of GA and SDBS emulsified P(St-MMA-AA) latex is reported.

Materials and Methods

Materials

Methyl methacrylate (MMA), styrene, acrylic acid (AA), pure nitrogen, ammonium bicarbonate, ammonium persulfate, sodium hydroxide, sodium dodecyl benzene sulfate (SDBS), and deionized water. All the chemicals were used without further purification and were of analytical grade obtained from Sigma-Aldrich. Purified gum arabic (GA) was obtained from the laboratory of Rubber Research Institute of Nigeria Iyanomo, Edo State, Nigeria.

Methods

Synthesis of monodispersed P(St-MMA-AA) colloidal latex

Monodispersed P(St-MMA-AA) colloidal particles were synthesized as detailed by a published procedure (Figure 1) (Wang et al.

2006). In a typical synthesis, methyl-methacrylate (0.179 mL), styrene (3.5 mL), acrylic acid (0.159 mL), ammonium carbonate buffer agent (0.085 g), ammonium per-sulfate (0.081 g) and gum arabic emulsifier (0.0042 g) were dispersed in a two-neck flask which contained de-ionized water (17 mL and then agitated at 410 rpm under nitrogen gas. The polymerization reaction was allowed to continue for 12 h under non-stop stirring and heating at a temperature of 80 °C. After the synthesis, the obtained colloidal particles were rinsed with distilled water using a centrifuge. The procedure was repeated with sodium dodecylbenzene sulfate.

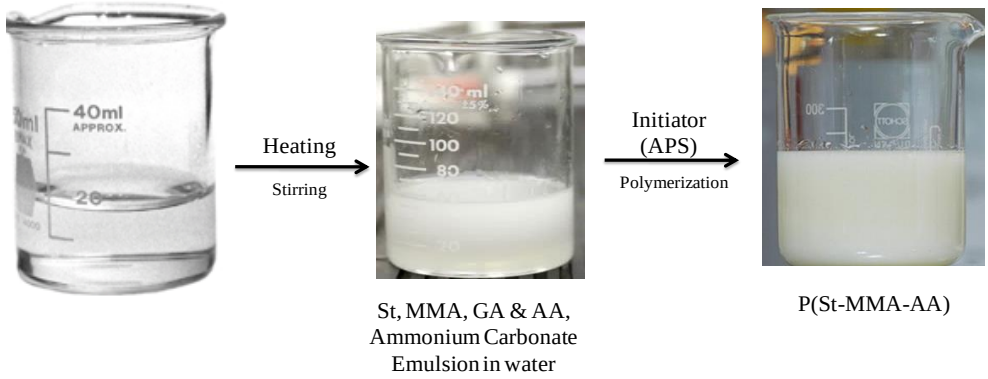

Figure 1: Synthesis scheme of GA emulsified P(St-MMA-AA).

Fabrication of colloidal crystals from GA and SDBS emulsified P(St-MMA-AA)

The colloidal crystals were generated as described in Figure 2. Here, the synthesized GA and SDBS emulsified P(St-MMA-AA) crystal films were used to generate colloidal crystal films via a technique known as vertical deposition on glass slides. The self-assembly of the latex particles was achieved after maintaining the deposition system at 60 °C in a water bath for 24 h. After the completion of the self-assembly process, the fabricated colloidal crystal films were oven-dried for 14 h.

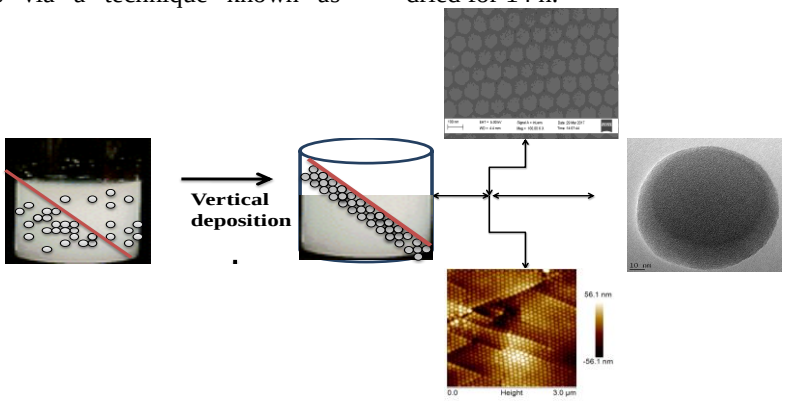

Figure 2: Fabrication of colloidal crystals.

Characterization techniques

The morphology of the latex powders was viewed using an Auriga scanning electron microscope (SEM), transmission electron microscopy (TEM) (TECNAI F2 G20 HR-TEM) and atomic force microscope (Bruker Dimension Icon). The functional groups present in the terpolymer samples were examined using Perkin-Elmer Spectrum One FTIR spectrometer operating between 4500 and 400 cm^{-1}. The average particle size and polydispersity index (PDI) were obtained

using dynamic light scattering (DLS) (Nano-Zetasizer, Malvern Instruments). Thermogravimetric analytical (Rheometric Scientific TGA 1000M+ apparatus) and differential scanning calorimetry instruments were used to carry out the thermal stability studies.

Results and Discussions

Chemical components and particle sizes of colloidal crystals

Figure 3 shows the functional groups of the as-synthesized GA and SDBS emulsified P(St-MMA-AA) latexes with variable intensities. Both spectra show identical absorbance peaks. The peaks from GA emulsified Ter-P (GA) were observed to be more intense than the SDBS emulsified terpolymer sample. The peaks at 748 cm^{-1} and 704 cm^{-1} are attributed to C-H (out-of-plane bending vibration in an aromatic ring). The wavenumbers at 1451 cm^{-1} and 1497 cm^{-1} can be ascribed to stretching vibration in aromatic C=C-C. The peaks at 2914 cm^{-1} and 3029 cm^{-1} are due to the presence of methylene groups and aromatic C-H, respectively (Wu et al. 2001). The peaks at 1204 cm^{-1} and 1729 cm^{-1} are due to C-O stretching vibration in ester bond and carboxylic acid (C=O stretch), respectively (Ifijen and Ikhuoria 2019). Finally, the peak at 3446 cm^{-1} can be ascribed to a water molecule which may have been absorbed from the environment. The FTIR results confirm the incorporation of styrene, MMA and AA monomers.

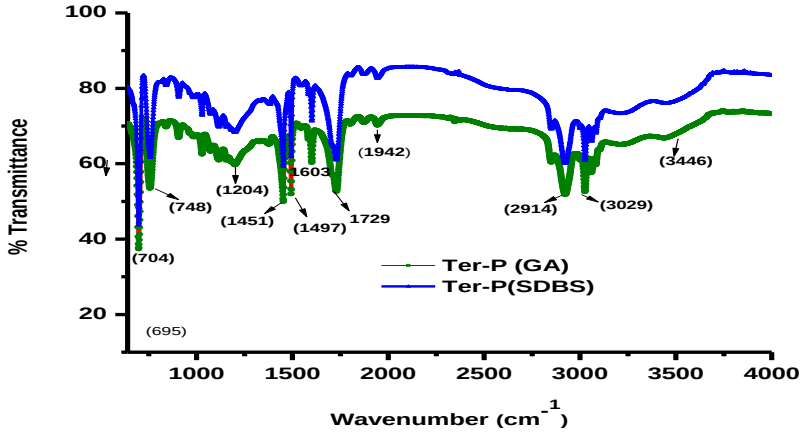

Figure 3: FTIR spectra of GA and SDBS emulsified P(St-MMA-AA) latex.

Figure 4 depicts the thermogravimetric analysis (TGA) of the as-synthesized latexes (GA and SDBS emulsified terpolymer samples) at a ramp rate of 10 °C/min. The result revealed a stable degradation rate from 0 °C to 100 °C for both terpolymer latex samples. A small decrease in weight was observed for both terpolymer samples as the temperature exceeded 100 °C. The observed decrease could be due to the loss of carbon (IV) oxide and loss of water from the acrylate and the acrylic portion of the terpolymer samples. Beyond heating temperature of 356 °C, there was an elevation in the rate of degradation for both synthesized terpolymer samples until the temperature gets to 442 °C. The TGA result therefore, showed that the synthesized GA and SDBS emulsified terpolymer samples degraded completely at 444 °C. Besides, the impact of heating temperature on the rate of terpolymer degradation for both samples was seen to be similar signifying that emulsifier types do not affect the thermal stability of the prepared terpolymer samples.

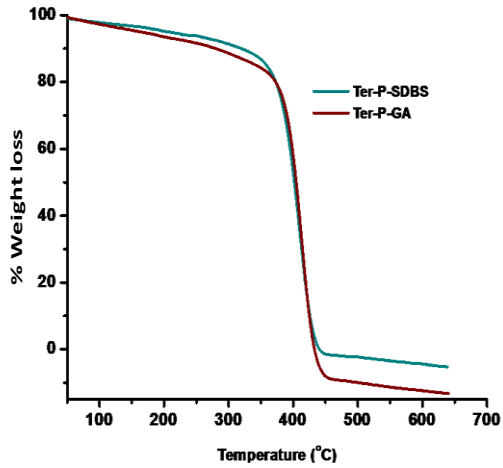

Figure 4: Thermogravimetric analysis (TGA) of GA and SDBS emulsified P(St-MMA-AA).

Figure 5 shows the DSC spectra of SDBS and GA emulsified P(St-MMA-AA) latex. The thermal stability of polymer colloidal latex is an important factor that must be examined in order to adopt polymers for applications that are temperature-dependent. The obtained result placed the glass transition temperature (Tg) of the prepared SDDS and GA emulsified terpolymer microspheres at about 108.4 °C and 108 °C, respectively. This shows that the emulsifier type adopted during the synthesis stage of the latex did not affect the glass transition temperature of the synthesized terpolymer. This Tg implies that the glassy and rigid nature of both terpolymer samples will be maintained provided the latexes are used below 108.4 °C and 108 °C, respectively. However, when the aforementioned Tg is exceeded, the rigid and glassy nature of both terpolymers will become rubbery like or viscous.

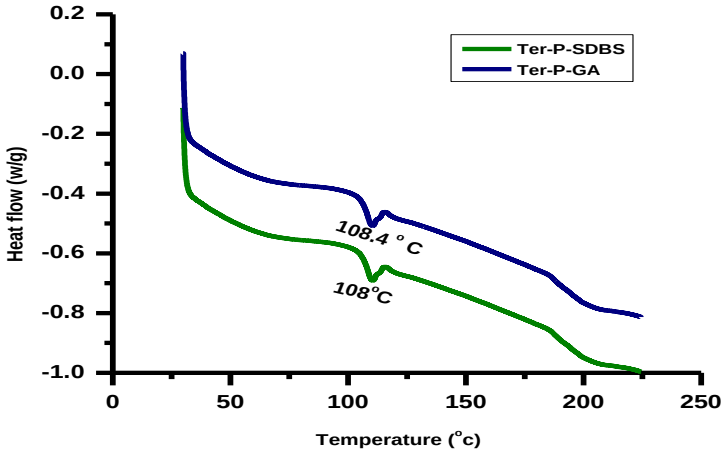

Figure 5: Differential scanning calorimetry (DSC) analysis of SDBS and GA emulsified P(St-MMA-AA) latex.

Table 1 shows the impact of GA and SDBS emulsifier type on the particle sizes, colloidal stability and dispersity of P(St-MMA-AA) latex. The function of emulsifier during synthesis that is emulsion polymerization based is basically to decrease the interfacial tension existing between the aqueous phase and organic phase. This facilitates monomer emulsification and also promotes the formation of stable polymeric particles (Fan et al. 2013, Minami et al. 2013). Dynamic light scattering analysis shows that a variation in emulsifier types resulted in a slight change in the particles sizes, dispersity and change in the colloidal stability of the as-synthesized GA and SDBS emulsified P(St-MMA-AA) latex. This we assumed to be due to the differences in the intrinsic properties of the studied emulsifier types used during the synthesis of the terpolymer samples. The average particle sizes of the prepared GA and SDBS

emulsified P(St-MMA-AA) latexes as depicted in Table 1 were observed to be around 122 nm and 213 nm, respectively. The synthesized GA and SDBS emulsified P(St-MMA-AA) latex revealed polydispersity index (PDI) of 0.014 and 0.006 which indicated a high level of monodispersity (Ifijen et al. 2019a). The obtained Zeta potentials (–36.2 mV and –35.60 mV) showed that both emulsifiers (GA and SDBS) produced terpolymers that have good stable colloidal dispersion (Table 1). It has been established by a previous study that the more positive or negative the zeta potential is, the greater the colloidal stability becomes as it promotes minimal particle aggregation and agglomeration (Ikhuoria et al. 2018).

Table 1: Effect of surfactant types on the particle sizes of SDBS and GA emulsified P(St-MMA-AA) latex

	Ter-pSDBS	**Ter-pGA**
Average particle diameter (nm)	122	213
Polydispersity	0.014	0.006
Zeta-potential (mV)	–36.20	–35.60

Figures 6 (a) & (b) show the TEM micrographs of the as-synthesized GA and SDBS emulsified P(St-MMA-AA) particles. The TEM analysis shows that the obtained terpolymers have spherically shaped particles with two well-defined layers (Figures 6 (a & b)), affirming a morphology that is core-shell in nature. The light regions which can also be regarded as the shell portion of the particle are composed of poly (acrylic acid) and (methyl methacrylate), while the dark region (core portion of the particle), is polystyrene portion of the terpolymer particle (Ifijen et al. 2019b, Ifijen et al. 2019c) The distance of the core from the shell portion of the GA emulsified terpolymer particle appeared to be less uniform when compared to the SDBS emulsified terpolymer particle. The particle diameters of a particle viewed from the synthesized P(St-MMA-AA) are estimated to be about 93.33 nm and 86.67 nm (Figures 6(a & b)). These diameters are different from the results obtained by the dynamic light scattering analysis (DLS) because DLS measures the hydrodynamic diameter of a particle.

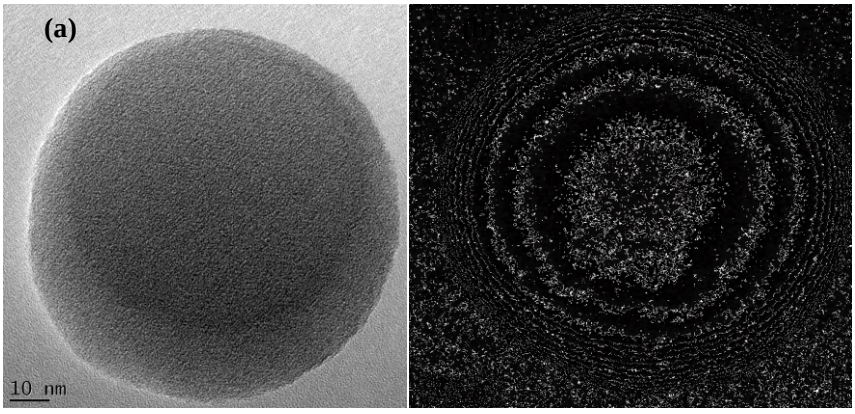

Figure 6: Transmission electron micrograph of (a) GA emulsified and (b) SDBS emulsified P(St-MMA-AA) latex.

Figures 7 (a) & (b) show the scanning electron micrographs (SEM) of the fabricated colloidal crystal particles. The SEM micrographs revealed a highly ordered hexagonal compact arrangement of spherical particles with manifold layers (Figures 7(a)

& (b)). Since this type of structures has the needed Gibbs free energy that can be possessed by colloidal crystals, the hexagonal compact arrangement is thermodynamically favoured by the generated crystal films (Su et al. 2009).

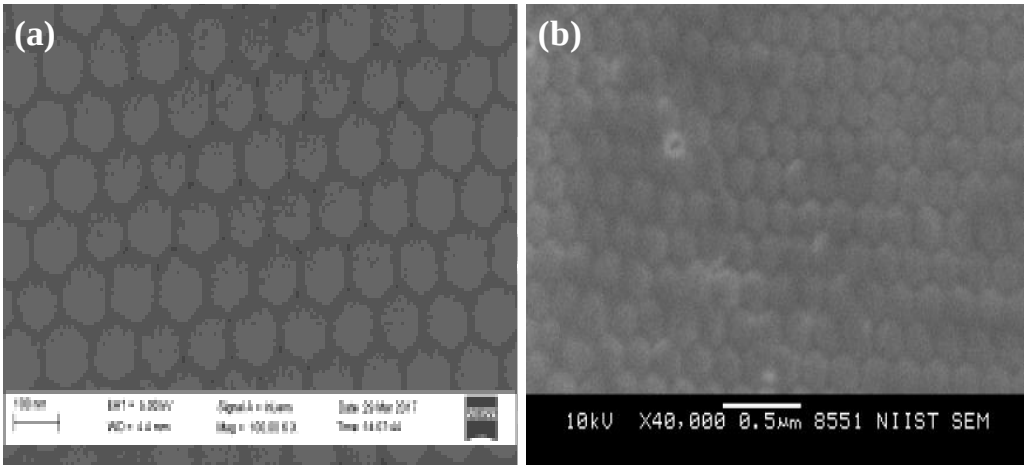

Figure 7: Scanning electron micrographs of (a) GA and (b) SDBS emulsified P(St-MMA-AA) particles.

Figures 8(a) & (b) show atomic force microscopic images of colloidal crystals fabricated from GA and SDBS emulsified P(St-MMA-AA) latexes. The micrographs revealed a well-ordered morphology that is in agreement with the results obtained by the scanning electron microscopic analysis (SEM) in Figures 7 (a) & (b).

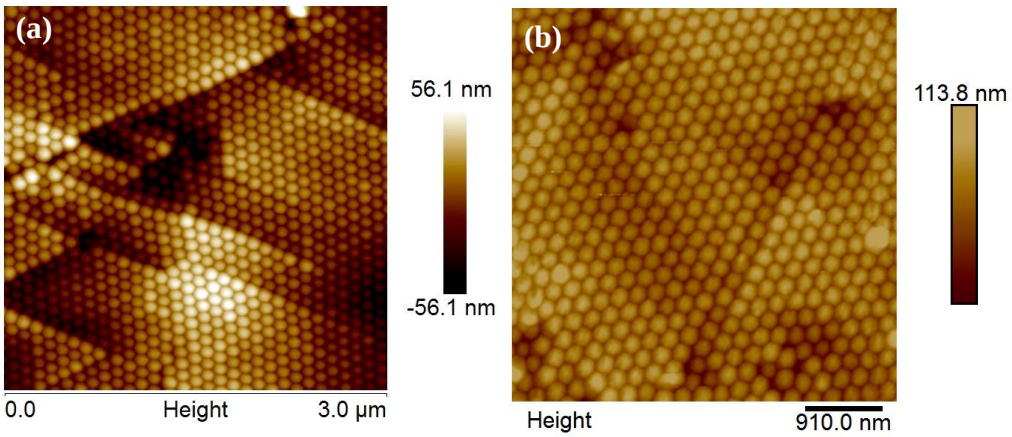

Figure 8: Atomic force micrographs of (a) GA (b) SDBS emulsified P(St-MMA-AA) latexes.

Conclusion

The use of gum arabic as an emulsifier in the synthesis of poly (styrene-methylmethacrylate-acrylic acid) P(St-MMA-AA) latex for the generation of colloidal crystals was investigated. Experimental analyses showed that the as-synthesized GA emulsified latex have properties that are very comparable to SDBS emulsified P(St-MMA-AA) latex as both synthesized terpolymer samples show good stable colloidal dispersion. Also, both latex

particles readily assemble into a well ordered hexagonal arrangement of spherical particles with manifold layers known as colloidal crystals after the completion of the self-assembly process. This study therefore, shows that the use of gum arabic as an emulsifying agent can be used to produce monodisperse terpolymers whose properties are comparable to conventional emulsified terpolymers.

Conflict of interest

The authors declare no conflict of interest.

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