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Effect of pH on The Dispersion Property of Sulphur Nanoparticles in Natural Rubber

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Sulphur nanoparticles (NPs) have attracted significant research and industry interests, especially in the rubber industry as a vulcanisation agent that is responsible to form cross-links between the rubber chains in the vulcanisation process which will make the natural rubber more flexible and durable. Unfortunately, the main obstacle of direct incorporating sulphur NPs into natural rubber is the agglomeration of sulphur NPs attributed to its high surface energy. The objective of this study is to evaluate the dispersibility and stability of sulphur NPs in natural rubber based on the solution pH 1.5 wt% and 3.0 wt% sulphur NPs were dispersed in natural rubber. The sulphur suspensions were subjected to ultrasonication for 2 minutes in which the pH of homogenised sulphur suspensions was adjusted to the range 6.0-10.0. The results revealed that ultrasonic irradiation was successfully broken the agglomerated rubber particle and produced smaller mean particle size for 1.5 wt% sulphur NPs at pH 8 and 3.0 wt% sulphur NPs at pH 7 with the mean particle size of 366.2 nm and 384.9 nm, respectively. Between both concentrations, natural rubber loaded with 1.5 w% sulphur NPs is a better formulation with better dispersibility of sulphur NPs and smaller mean particle size distribution at pH 8.

Keywords: sulphur nanoparticles; natural rubber; pH; zeta potential; particle size distribution

I. INTRODUCTION

Natural rubber is the white sap obtained from the rubber plant, Hevea brasiliensis. It is a polymer matrix material that possesses high elongation at break and tensile strength attribute to strain-induced crystallisation (Nair & Joseph, 2014). These characteristics display excellent building tackiness, which is crucial in many rubber-based products such as gloves, footwear, elastic bands, and hoses. Natural rubber was first mentioned in literature as early as in the sixteenth century and it was used in the natural state at that time – latex (Nair & Joseph, 2014).

The significant breakthrough for the application of natural rubber occurred in 1820 where the vulcanisation process was discovered in altering the mechanical stress of natural rubber with the addition of sulphur with heating (Kruželák *et al.,* 2016). Today, the vulcanisation of natural rubber remains a crucial process in rubber technology. Vulcanisation is a chemical process that involves the formation of a chemical crosslink to convert linear rubber molecules into a network for better tensile strength, viscosity, hardness, and elasticity (Nair & Joseph, 2014). The oldest and most commonly used method for cross-linking natural rubber is sulphur vulcanisation (Kruželák *et al.,* 2016). The changes in the amount of sulphur in the vulcanisation process can lead to diverse network structures, both types of crosslinks, and the crosslink density which will result in changes of both thermal properties and mechanical of vulcanisates (Zhao *et al.,* 2011). However, direct incorporating of sulphur into natural rubber often caused agglomeration, where uniformly dispersed sulphur in natural rubber is not able to obtain and this will affect the effectiveness of the vulcanisation process. On the

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other hand, sulphur has bigger particle size than sulphur NPs. Sulphur NPs with particle size of 1 to 100 nm have larger effective surface area which would help in enhancing good structural and textural properties of the latex suspension owing to the well-dispersed of the sulphur NPs (Yousatit *et al.*, 2020).

Agglomeration of NPs in a liquid medium often occurs attribute to their high surface energy due to their extremely small particle size (Teow *et. al.*, 2012; Shao *et al.*, 2015). It would restrict the interfacial area and lead to thermodynamic instability (Ashraf *et al.*, 2018). Ultrasonication is one of the most commonly used methods for dispersing agglomerates of NPs. Ultrasonication takes place by oscillating the liquid medium or suspension, leading to nucleation and collapse of the bubbles of the liquid medium. The repeating process of initiating and collapsing the bubbles on the solid surfaces is very powerful in breaking the agglomerates of NPs (Mandzy *et al.*, 2005). The most common method to evaluate the stability of NPs in a liquid medium is by determining the zeta potential value.

Zeta potential value represents the surface charge of the NPs which indicates their stability and surface interactions with other molecules. NPs tend to agglomerate if the zeta potential value is near zero, while at a higher zeta potential value (above +30 mV or less than -30 mV), no agglomeration happens as NPs in the liquid medium tend to repel each other (Manzdy *et. al.*, 2005; Mahmoudi *et al.*, 2019). Long-term stability of sulphur NPs is crucial to produce a uniformly dispersed sulphur in natural rubber, hence can maximise the effectiveness of the vulcanisation process. The objective of this study is to evaluate the dispersibility and stability of sulphur NPs in natural rubber based on the solution pH.

II. MATERIALS AND METHOD

A. Materials

Natural rubber was obtained from the Rubber Research Institute of Malaysia (RRIM), while powdered sulphur with ~80 nm of particle size and sodium hydroxide (NaOH) were purchased from Systerm, Malaysia. Hydrochloric acid (HCL) (purity: 38%) was received from Macron Fine Chemical, US.

B. Preparation of Sulphur NPs Suspension in Natural Rubber

Powdered sulphur at different concentrations (1.5 wt% and 3.0 wt%) was dispersed in 20 mL natural rubber. The sulphur suspensions were then homogenised using a homogeniser, WT500 (Dynaken, Kenya) for 2 minutes. The pH of homogenised sulphur suspensions was then adjusted at the range 6.0-10.0 by using HCL or NaOH. HCL or NaOH was added drop-wise to the sulphur suspensions under slow stirring until an equilibrium pH value was obtained. The pH value of the sulphur suspensions was measured using litmus papers, Universal Test Paper (HmbG, Malaysia).

C. Zeta potential and Mean Hydrodymanic Particle Size of Sulphur NPs Suspension in Natural Rubber

10 mL of sulphur suspension was diluted in 100 mL distilled water and was sonicated for 30 minutes using an ultrasonicator, WUC-A03H (Wisd, Korea) before analysis. The zeta potential and the mean hydrodynamic particle size of sulphur NPs in natural rubber at various pH were assessed using Malvern Zetasizer Nano ZS90 (Malvern Instruments Ltd., UK). The zeta potential reading indicates the electrostatic stability of sulphur NPs which was analysed using laser doppler electrophoresis, whereas the mean hydrodynamic particle size of sulphur NPs was measured using dynamic light scattering (DSL) mode.

III. RESULT AND DISCUSSION

A. Effect of pH on the Electrostatic Stability and Mean Hydrodynamic Particle Size of Sulphur NPs Suspension in Natural Rubber

The electrostatic stability of sulphur NPs suspension in natural rubber was indicated by the zeta potential value assessed using Malvern Zetasizer Nano ZS90. The distribution of ions in the surrounding interfacial area is affected by the development of net charge at the particle surface, causing the concentration of counter ions (ions with opposite charge to the particle) near the particle's surface to increase. Hence, a double electrical layer would form around each particle (Fernandes *et al.*, 2011). The liquid layer surrounds the particle is divided into two parts; an inner region, known as the Stern layer, where the ions are tightly bound, and an outer region where the ions are loosely bound.

There is a notional boundary within the diffuse layer where the particles and ions form a firm entity. When a particle moves, ions within the boundary move with it, but any ions beyond the boundary do not travel with the particle, and this boundary is called a slipping plane (Willams, 2016). Zeta potential is the potential that occurs at this boundary and the magnitude of zeta potential serves as an indicator in determining the potential stability in a colloidal system and it denoted the particles' surface charge (Teow *et al.*, 2018). Figure 1 illustrates the schematic representation of zeta potential.,

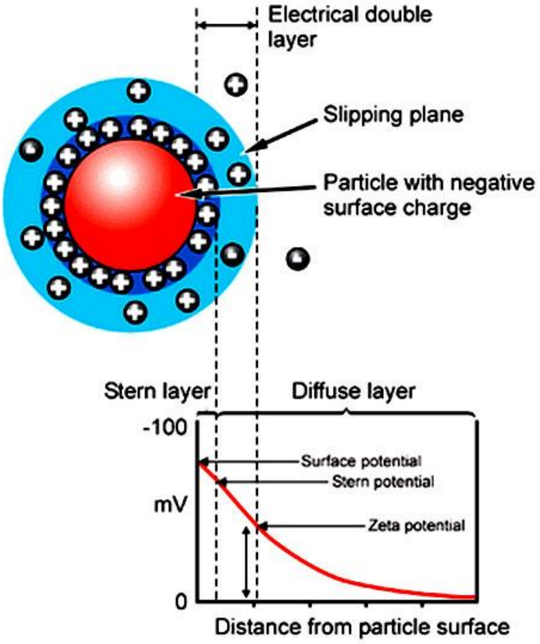

Figure 1. Schematic representation of zeta potential (Willams, 2016)

Particles tend to repel one another where no coagulation will occur if the colloidal system has either a high positive or high negative zeta potential value. Conversely, there is no force present to keep the particles apart from colliding and forms aggregate if the colloidal system has a low positive or low negative zeta potential value (Panatarani *et al.*, 2020). The general dividing line between stable and unstable suspensions is taken at +30 mV or -30 mV. A colloidal system with a zeta potential value more positive than +30 mV or more negative than -30 mV is considered stable due to high electrostatic repulsion which results in particles repelling (Teow, 2012; Ho *et. al.*, 2017; Mahmoudi *et al.*, 2019).

Parameters that affect the zeta potential value of a colloidal system include the temperature and pH of the colloidal system as well as the type of solvent used. Small adjustments to each of these parameters can give a big impact on the zeta potential value (Smith *et al.*, 2017). This study focuses on investigating the effect of pH on the zeta potential value of the natural rubber colloidal system. Figure 3 and Figure 4 show the zeta potential value and mean hydrodynamic particle size of sulphur NPs suspension in natural rubber at different pH values, respectively. The type of natural rubber used in this study was low ammonia natural rubber latex with a pH close to 10. Meanwhile, the initial pH of sulphur NPs is 8.5. The isoelectric point of low sulphur proteins is at range of pH 4.9-5.4. Meanwhile, for natural rubber latex is at pH 4.2. Referring to Figure 3, the zeta potential value of natural rubber loaded with 1.5 wt% sulphur NPs was decreased drastically from pH 8 (-11.6 mV) to pH 9 (-0.5 mV) and remains unchanged at -0.5 mV for pH 10. However, the zeta potential value at pH 6 and pH 7 for natural rubber loaded with 1.5 wt% sulphur NPs could not be obtained due to the critical agglomeration that occurred to the natural rubber. Meanwhile, the zeta potential value for natural rubber loaded with 3.0 wt% of sulphur NPs was continued to decrease from pH 6 (+6.2 mV) to pH 10 (-0.5 mV).

For both concentrations of sulphur NPs, critical agglomeration occurred at pH 5 and below (acidic pH). The critical agglomeration makes it impossible for zeta potential analysis assessment. The addition of acid caused the positive charge of hydrogen ions from acid to be in touch with the negative charge protein-membrane the rubber particles, thus reducing the negative charge of the rubber particles' surface. Rubber particles which close to neutral charge when electrons and protons balance each other would present neither positively charge nor negatively charged. These neutral charge rubber particles will then move freely and start to collide with one another as charge repulsion between one rubber particle to another rubber particle does not occur. The collision between the rubber particles results in the breaking up of the protein-membrane hence the rubber polymers are set free. The free rubber polymers begin to coagulate forming large lumps (Reis, 2015). Figure 2 illustrates the collision between two rubber particles of neutralised rubber particles leading to rubber particles agglomerate.

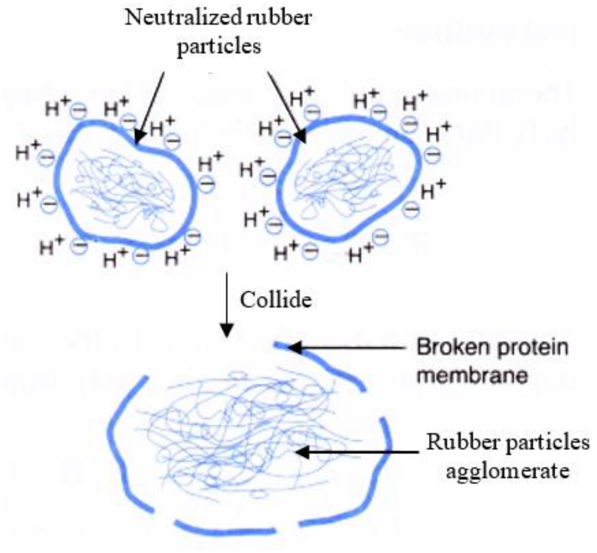

Figure 2. The collision between two rubber particles of neutralised rubber particles leading to rubber particles agglomerate (Veerenda, 2020)

Most of the zeta potential values obtained for both natural rubber loaded with 1.5 wt% sulphur NPs and 3.0 wt% sulphur NPs are less than 5 mV. Low zeta potential value may lead to particle agglomeration due to the van der Waals attractive forces act upon the particles (Gumustas *et al.*, 2017). Initially, the attractive force between sulphur NPs was stronger than the repulsive force. Therefore, sulphur NPs in natural rubber tend to agglomerate and the agglomeration size was massive. However, natural rubber loaded with 1.5 wt% sulphur NPs at pH 8 and 3.0 wt% sulphur NPs at pH 6 had recorded the highest zeta potential value, indicating that the optimum stability of natural rubber with a certain concentration at the specific pH. As the pH value was further increased, natural rubber loaded with 1.5 wt% sulphur NPs and 3.0 wt% sulphur NPs showed a significant decrease in its zeta potential value, meaning the sulphur NPs were having a high tendency for agglomeration at high alkaline pH. Among both concentrations, natural rubber loaded with 1.5 wt% sulphur NPs is the better formulation for better dispersibility of sulphur NPs. This is due to the highest zeta potential value obtained at pH 8 for natural rubber loaded with 1.5 wt% sulphur NPs.

As for mean particle size distribution, ultrasonication helped in breaking the agglomeration of sulphur NPs in natural rubber. Figure 4 revealed that the mean particle size distribution for natural rubber loaded with 1.5 wt% sulphur NPs after sonication for 30 minutes had no significant change from pH 8 and pH 9 but a slight increase at pH 10. This could be related to the low zeta potential value of the suspension. As the zeta potential is close to zero, sulphur NPs will remain stationary and exhibit minimum stability. When ultrasonication was applied to it, the compressive force exerted onto rubber particles will push the particles to colloid and agglomerate. On the other hand, the mean particle size distribution of natural rubber loaded with 3.0 wt% sulphur NPs was reduced drastically from pH 6 (662.50 nm) to pH 7 (384.49 nm) and keep increased until pH 10. In short, natural rubber loaded with 1.5 wt% sulphur NPs is the better formulation for small mean particle size distribution.

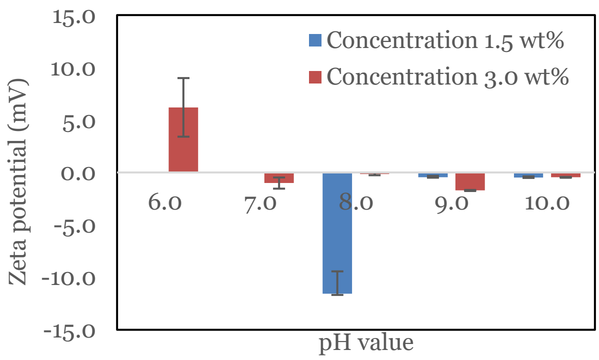

Figure 3. Zeta potential value of sulphur NPs suspension in natural rubber at different pH

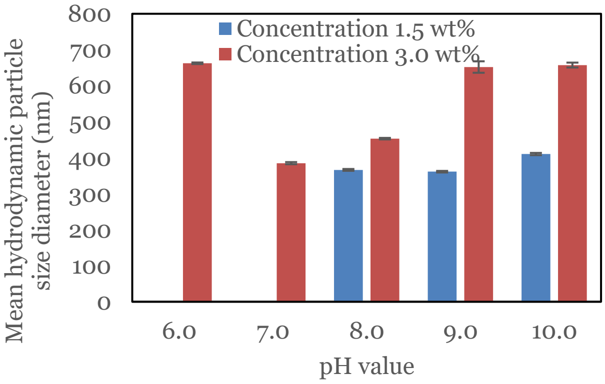

Figure 4. Mean hydrodynamic particle size diameter of sulphur NPs suspension in natural rubber at different pH

IV. CONCLUSION

Natural rubber loaded with 1.5 wt% and 3.0 wt% sulphur NPs resulted a low zeta potential value, indicates low stability of sulphur NPs in natural rubber. Both acidic and alkali environments did not give huge change to the zeta potential value of natural rubber for both concentrations. The natural rubber loaded with both 1.5 wt% and 3.0 wt% NPs faced critical agglomeration and produced massive lumps when the pH of the suspension was adjusted to below pH 6 and below which is in the range of acidic pH. Ultrasonic irradiation successfully break the agglomerated rubber particle and produced smaller mean particle size for 1.5 wt% sulphur NPs at pH 8 and 3.0 wt% sulphur NPs at pH 7 with the mean particle size of 366.2 nm and 384.9 nm, respectively. Between both concentrations, natural rubber loaded with 1.5 w% sulphur NPs is a better formulation with better dispersibility of sulphur NPs and smaller mean particle size distribution at pH 8.

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