

2-[(Hydroxymethyl)amino]ethanol in water as a preservative: Study of formaldehyde released by Taguchi's method

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Abstract. This research studied the quantity of free formaldehyde released from 2-[(hydroxymethyl)amino]ethanol (HAE) in DI water and natural rubber latex mixture using high-performance liquid chromatography (HPLC) technique. The quantity of formaldehyde retained in the solution was cross-checked by using titration technique. The investigated factors were the concentration of preservative (HAE), pH, and temperature. Taguchi's method was used to design the experiments. The number of experiments was reduced to 16 experiments from all possible experiments by orthogonal arrays (3 factors and 4 levels in each factor). Minitab program was used as a tool for statistical calculation and for finding the suitable condition for the preservative system. HPLC studies showed that higher temperature and higher concentration of the preservative influence the amount of formaldehyde released. It was found that conditions at which formaldehyde was released in the lowest amount were 1.6 %w/v HAE, 4 to 40 °C, and the original pH. Nevertheless, the pH value of NR latex should be more than 10 (the suitable pH value was found to be 13). This preservative can be used to replace current preservative systems and can maintain the quality of latex for long-term storage. Use of the proposed preservative system was also shown to have reduced impact on the toxicity of the environment.

1. Introduction

Thailand is a manufacturer and exporter of natural rubber (NR), making the latter one of the plants important to the country's economy [1]. NR is an elastomer or elastic hydrocarbon polymer that can

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be used for processing in manufacturing centres, with the associated NR industries being highly competitive in domestic and overseas markets. Most NR is exported as crude rubber and NR latex, which can be transformed into concentrated latex that can itself be prepared for market by rolling slabs of latex for continuous use in many products such as rubber gloves and tires.

NR liquid from rubber trees is called latex. It is a sticky and milky colloid which is drawn off by making a tap and collecting it in vessels. Then the latex is prepared by refining it into rubber ready for processing. Since NR latex putrefies within 6 hours after it is incised from the rubber tree due to natural destabilization by heavy microbial contamination [2], preservation of the latex is necessary. A suitable preservative is used to maintain the quality of latex and to allow long-term storage. The preservative substances can be either a sterilizer or a stabilizer.

Currently, an ammonia system is widely used as a standard preservative for NR latex. Ammonia is used with tetramethylthiuram disulfide (TMTD) and zinc oxide (ZnO) for reducing the harmful effects of ammonia toxicity [3]. However, there are several disadvantages related to environmental pollution and health. Ammonia imparts a strong odor and is easy to evaporate. Its emitted fumes cause corrosion of factory buildings and roofs. The amount of ammonia in latex that affects the qualities of latex and makes unstable the properties of latex is difficult to control [4]. Moreover, TMTD produces carcinogenic nitrosamines and allergens in rubber products which cause contact dermatitis, while ZnO is a source of heavy metal in waste sludge and effluent water.

As a result of the preceding consideration, it has been proposed to used 2-[(hydroxymethyl)amino]ethanol (HAE) as a sterilizing and preserving solution. It is a formaldehyde-releaser with respect to free formaldehyde. This formaldehyde is used as preservative to prevent bacterial and disinfectant [5, 6], making HAE a good choice as a preservative for NR latex, instead of the ammonia system which widely used as the standard. HAE also reduces the environment toxic, thereby opening up potential applications in agriculture. This research focussed on the quantities of free formaldehyde released from HAE in DI water and in NR latex mixture with different ratios of preservative systems in order to investigate the latex quality deterioration and study the effects of various parameters on the amount of formaldehyde released: concentration of formaldehyde releaser, pH, and temperature.

2. Material and Methods

2.1. Design of experiments

Taguchi method was used in the form of orthogonal array of three factors and four levels in each factor to reduce the number of experiments from a full factorial [7] (64 experiments) to sufficient, but lower, number of experiments (16 sampling experiments). The concentration of HAE was varied as 0.1, 0.2, 0.8, and 1.6 %w/v, while the pH was either kept at the original condition or adjusted to 11, 12 or 13. The temperature was chosen as either 4, 28, 40 or 90 degrees Celsius, and the storage time was set as 24 hours. Minitab program was used as a device for statistical calculation and finding the suitable conditions for using NR preservative system. The signal-to-noise ratio (SN ratio) characteristic is a number used to improve quality through variability reduction. The concept of SN ratio for this study is “smaller is better” [8], with the actual ratio given by equation (1):

$$S/N = -10\log_{10}\left(\frac{1}{n}\sum y^2\right) \quad (1)$$

where n is the number of the tests in a trial and y is the value of the quality characteristic measured from the test.

2.2. Sample preparation

Samples of 0.2, 0.4, 1.6 and 3.2 mL of HAE were diluted into 200 mL DI water or 200 mL NR latex, and 0.1 mL of EDTA was added. The pH was adjusted with KOH; then the solution was put in a 1000 mL closed bottle. 0.5 g of solution was used in a titration process to determine the quantities of formaldehyde in the solutions at the beginning. After the settling of the solution and allowing

formaldehyde release in the air for 24 hours, the outlet of a cartridge sampler was connected to a sampling pump with flexible tubing. The pump was turned on, and 800 mL of air was injected into the bottle through the cartridge sampler at a flow rate of 80 mL/min, and simultaneously, the same volume of gas for removed to a 2,4-dinitrophenylhydrazine (DNPH) cartridge for analysis by high-performance liquid chromatography (HPLC). The amount of formaldehyde in the remaining solution was analysed by titration.

2.3. Formaldehyde titration

The titration method for formaldehyde followed was that in reference [9]. Briefly, 0.5 g of formaldehyde solution was diluted with DI water into 100 mL. 20 mL of the solution was added into 25 mL of 0.05M I₂ and 10 mL of 1M NaOH. The solution was then put in a dark room for 15 minutes before 15 mL of 1M H₂SO₄ solution was added. Any excessive iodine was titrated by 0.1 M Na₂S₂O₃, resulting in a solution that was almost clear. After that, 1 mL of 1% w/w starch solution was added for use as an indicator in the solution. Then, 0.1M Na₂S₂O₃ was used for titration again, with the solution being added until the color changed from blue to clear.

A blank test was done using 20 mL of water for titration. For it, the calculation of the 0.1M Na₂S₂O₃ consumption is shown in equation (2). Each 1 mL of 0.1M Na₂S₂O₃ is can be reacted with 1.5 mg of formaldehyde while 1 mL of 0.05M I₂ can be reacted with 1.5 mg of formaldehyde.

$$[HCOH, ppm] = (V_{B1} - V_{Na_2S_2O_3}) \times 15 \times [Na_2S_2O_3] \times \frac{1000}{WS} \quad (2)$$

where $[HCOH]$ is the concentration of formaldehyde (ppm), V_{B1} is the volume of 0.1 M sodium thiosulphate solution (mL), $V_{Na_2S_2O_3}$ is the volume of 0.1 M sodium thiosulphate solution in the blank experiment (mL), $[Na_2S_2O_3]$ is the concentration of sodium thiosulphate solution (M), and WS is the weight of formaldehyde solution (g).

2.4. HPLC analysis of free formaldehyde

To the formaldehyde derivative in the DNPH cartridge sampler was added acetonitrile for the purpose of eluting each sample. Liquid chromatography was set according to the manufacturer's recommended conditions. 10 µL sample solutions were analyzed with an inertsil ODS-80A column (length 159 mm, internal diameter 4.6 mm) with 55% acetonitrile as mobile phase, and the concentrations were detected with photodiode array (PDA) detector (lamp type D2&W) at the wavelength of 360 nm. The flow speed used was 1.5 mL/min. After detection the peak area and peak height of formaldehyde were shown in the chromatogram results. The retention time of the sample derivative analyzed via HPLC was compared with the retention time of the standard formaldehyde, and the peak area of sample solution was interpreted from the standard curve of the calibration equation in order to calculate the concentration of the released formaldehyde.

3. Results and discussion

As mentioned previously, Taguchi's method was used to design the experiments, allowing the number of experiments to be reduced from 64 to 16 by orthogonal arrays (3 factors and 4 levels in each factor). Results and trends from both titration method and HPLC tend to agree, but since titration is less accurate and not accurate enough for the purposes of prediction, HPLC results are focussed on this section. Table 1 shows experimental conditions and corresponding concentrations of free formaldehyde released from HAE solution in water. Normalized concentration of free formaldehyde is calculated as the actual concentration of free formaldehyde multiplied by the ratio of 0.1 %w/v HAE to the actual concentration of HAE used. Taguchi's method can predict the mean value and SN ratio of the concentrations of free formaldehyde in all possible experiments based on statistical calculation. However, the predictions from Taguchi's method could not obtain the exact same value as the results from laboratory experiments due to normal variance in statistical analysis.

Table 2 is the response table for SN ratio of concentration of free formaldehyde using the concept of “smaller is better”. The delta was calculated from the difference between the maximum and the minimum SN ratio of each factor, with a high delta value indicating a high influence of the factor on released formaldehyde. Thus, the order in which parameters affect the released formaldehyde from the most to the least is as follows: concentration of HAE, temperature, pH.

Table 1. Concentrations of formaldehyde released from HAE solution diluted in DI water

Concentration of HAE (%w/v)	pH	Temperature (°C)	Concentration of formaldehyde (µg/ml)	Normalized concentration of formaldehyde	Predicted Taguchi Results (µg/ml)
0.1	None	4	0.183	0.183	0.046
0.1	13	28	0.304	0.304	0.137
0.1	11	40	0.325	0.325	0.503
0.1	12	90	1.008	1.008	1.146
0.2	None	28	0.395	0.198	0.452
0.2	13	4	0.275	0.138	0.530
0.2	11	90	2.397	1.199	1.841
0.2	12	40	0.354	0.177	0.608
0.8	None	40	0.391	0.049	0.154
0.8	13	90	1.066	0.133	1.176
0.8	11	4	0.403	0.050	0.611
0.8	12	28	0.388	0.049	0.322
1.6	None	90	0.767	0.048	1.095
1.6	13	40	0.429	0.027	0.242
1.6	11	28	0.437	0.027	0.621
1.6	12	4	0.631	0.039	0.319

Table 2. Response table for SN ratio for concentration of free formaldehyde

Level	Concentration of HAE (%w/v)	pH	Temperature (°C)
1	8.697	20.361	21.506
2	11.198	16.355	20.497
3	23.991	17.335	20.614
4	29.294	19.129	10.563
Delta	20.597	4.007	10.943

The released formaldehyde is shown to depend on HAE concentration, pH, and temperature, and the SN ratios of the concentration of free formaldehyde released from HAE solution are shown in Figure 1 for each of these three factors. The concept of smaller is better shows here that the high value in the graph indicates a lesser amount of free formaldehyde. It was found that the concentrations of free formaldehyde increased with increasing the concentration of HAE. Also, higher concentration of HAE tends to result in decreased normalized free formaldehyde concentration. Temperature increase has an influence on the increase of formaldehyde released, with the highest release at 90°C (because

this temperature is close to the boiling point of formaldehyde solution, 98°C). The graph of SN ratio of concentration of free formaldehyde versus pH is bell-shaped with a maximum of formaldehyde released at a pH of 11 and with decreasing normalized concentration of free formaldehyde with further increasing pH value. On the other end of the spectrum, the pH at the original condition, for which no KOH was used, was, when diluted with DI water, approximately 10, from which KOH affects the amount of formaldehyde released. A higher pH resulted in the ratio of concentration of free formaldehyde decreasing.

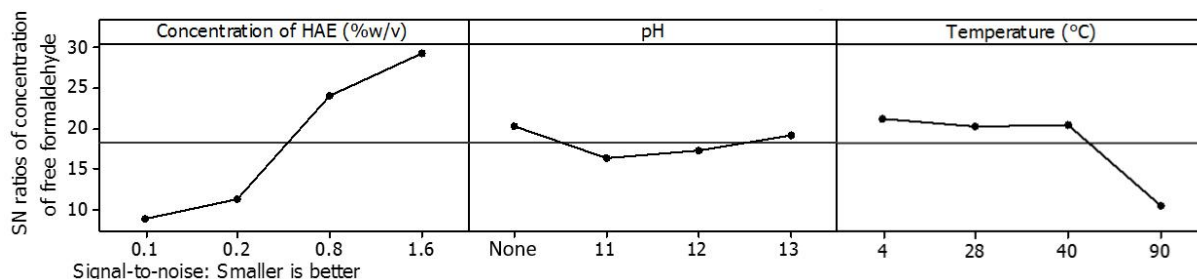


Figure 1. Effect of parameters on SN ratios of concentration of formaldehyde

For comparison purposes, the 16 experiment designed for DI water using Taguchi's method are set beside 4 further experiments with NR latex. HAE was dissolved in the latex at a fixed temperature at 28°C, and the results were compared to those obtained for identical conditions with DI water. However, of these four experiments, two—0.1 and 0.2 %w/v HAE—are not shown due to complications from reactions between HAE and proteins in latex. NR latex can be kept for more than 1 month only when it is preserved by more than 0.4 %w/v HAE [10]. Experimental conditions and results are shown in Table 3. The concentrations of free formaldehyde from NR latex at 0.8 and 1.6 %w/v HAE were close to those released from DI water solutions. The normalized concentration of free formaldehyde in NR latex decreased with increasing concentration of HAE. The pH at the original condition when diluted with NR latex was 7.83, and as for DI water, at higher values of pH, the SN ratio of concentration of free formaldehyde decreases and then rises again for yet higher pH. Table 4 shows the predicted Taguchi results for HAE solution in water at different temperatures.

Table 3. Concentrations of formaldehyde released from HAE solution diluted in NR latex

Concentration of HAE (%w/v)	pH	Temperature (°C)	Concentration of Formaldehyde in NR Latex (µg/ml)	Normalized concentration of formaldehyde in NR Latex	Normalized concentration of formaldehyde in DI water
0.8	12	28	0.441	0.055	0.049
1.6	11	28	0.505	0.032	0.027

Table 4. Suitable conditions from prediction by Taguchi's method

Concentration of HAE (%w/v)	pH	Temperature (°C)	Predicted Taguchi Results (µg/ml)
1.6	13	4	0.238
1.6	13	28	0.246
1.6	13	40	0.240
1.6	13	90	1.175

The results from the prediction by Taguchi's method can be used to specify suitable experimental conditions, those for obtaining the lowest concentration of free formaldehyde being 1.6 %w/v HAE, temperature in the range of 4 to 40°C, and the original pH. Using the original pH, however, is problematic, since EDTA requires a pH of more than 10 (in order to coordinate metal ions such that they form circular structures, i.e., chelate circles) [11] and since this original pH is itself 7.83 (i.e., more than 10). Referring to the SN ratios obtained, it then follows that the best choice, in the range pH >10, is a pH of 13. At this value, one obtains a high SN ratio and complications with EDTA.

4. Conclusion

This study focused on the quantity of free formaldehyde released from HAE in DI water and natural rubber latex solutions. The concentration of HAE, temperature, and pH has significant effects on the released formaldehyde and also on the quality of latex after preservation. The released formaldehyde increased with increasing concentration of HAE. Temperature increases resulted in increased amount of formaldehyde released, with the highest amount being released at 90°C. KOH affected the released formaldehyde. Higher pH led to the decreasing normalized concentration of free formaldehyde. The concentrations of free formaldehyde from NR latex were close to those released from DI water. The experimental conditions which cause the release of the least amount of formaldehyde were as follows: 1.6 %w/v HAE, temperatures in the range of 4 to 40 °C, and the original pH (less than 10). Nevertheless, the pH value in NR latex should be more than 10 due to the use of EDTA in the system, leading to a pH value of 13 giving the best results in the suitable pH range. Based on the findings in this work, HAE could be used to replace the typical ammonia system and maintain the quality of latex for long-term storage. Agricultural applications also remain open, since HAE results in reduced impact on environmental toxicity relative to the existing ammonia systems.

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