Rubber Recovery from Centrifuged Natural Rubber Latex Residue Using Sulfuric Acid

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Abstract:

Waste latex sludge from centrifuged residue, which is null by-product of concentrated latex manufacturing, was digested to retrieve the rubber by using sulfuric acid. It was found that the acid concentration and digestion time affected on the amount and purity of retrieved rubber. Sulfuric acid at concentration more than 10% by weight with digestion time 48 hours completely digested waste latex sludge and gave rubber 10% by weight. The quality of retrieved rubber were examined for Mooney viscosity (MV), plasticity retention index (PRI), nitrogen content, and ash content. The average molecular weight of the retrieved rubber, from gel permeation chromatography (GPC), lower than that of normal natural rubber (NR) which is corresponded with the MV and initial plasticity (Po). The molecular structure from Fourier transform infrared spectroscopy (FT-IR) indicated that the retrieved rubber surface is wet composed with hydroxyl functional ended group. The residue solution was evaporated and crystallized. The structure of crystal was determined using power X-ray diffractometer.

Keywords: waste latex sludge; concentrated latex; rubber recovery; Boussingaultite;
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1. INTRODUCTION

The concentrated natural rubber latex (NRL) is always produced by using centrifugation of fresh field NRL. NRL is not only consisted of NR particles but also non-rubber parts such as magnesium (Mg). The NRL contains high Mg has an impact to the centrifugation process and the quality of concentrated latex. Therefore, it is necessary to remove the magnesium from NRL. The traditional method is adding of diammonium hydrogen phosphate (DAHP) to NRL and leave for more than 12 hours. The reaction of DAHP with Mg resulting in solid sludge formation and precipitation. The solid sludge characteristics have been investigated and reported their advantages for agronomic relevance since the year 2002 (Okieimen et al., 2002). Basic composition of this materials are rubber hydrocarbon, nitrogen, magnesium, and phosphorus for 12.5%, 3.3%, 12.2%, and 14.7% by wt. (dry weight), respectively (Boonsawang et al., 2008). Eventhough these material can be comparable used as commercial phosphatic fertilizers (Tekprasit, 2000) but the limitations, heavy metal content, and unsuitability to certain soils and crops must be concerned as well as the effect of rubber hydrocarbon which is not easily decomposed in soils.

Commonly, the waste sludge from waste water treatment plants was digested using acid (Pearson and Buswell, 1931) for difference purposes such as ammonia removal (Suschka and Poplawski, 2004) and phosphorus recovery (Stark, 2002). In this paper, the acid digestion of waste latex sludge from centrifugation was investigated for recovery the rubber and occurence of high purity ammonium magnesium sulfate.
2. Experimental

The sludge, collected from latex centrifuge machine, was kindly supplied by Chalong concentrated latex company limited and was used immediately. The sludge was grinded into small pieces as shown in figure 1. Grind sludge was weight for 300 gram before mixing with difference sulfuric acid concentrations (5%, 10%, 20%, 30%, and 40% by wt.) for 600 mL. The sulfuric acid was selected as it is very cheap and strong enough to remove non-rubber component with low recovery cost. Acid digestion reduced the volume of sludge and decomposed of inorganic substance results in floating retrieved rubber at room temperature. The volume of sludge was decreased with increasing the acid concentration due to decomposition of organic sludge which was converted into gases. The sulfuric acid for 5% by wt. was not strong enough to remove non-rubber component from the waste sludge. The sludge was still precipitated due to high density as illustrated in figure 2. The sludge digestion with high acid concentration resulted in low pH waste water and acid contaminated in retrieved rubber. The retrieved rubber with high acid contaminated has poor properties. In this experiment, the rubber recovery with 10% by wt. sulfuric acid digestion was selected.

Figure 1 Waste latex sludge before (a) and after grinding (b).
The retrieved rubber was separated, washed with water, sheeted, and dried in air oven at 70°C. The composition of the retrieved rubber was analyzed using Thermogravimetric Analyzer (TGA) (PerkinElmer, TGA7) comparing with that of waste sludge. The rubber structure and molecular weight were characterized using Fourier Transform Infrared Spectrometer (FT-IR) Model EQUINOX 55 (Bruker) and Gel permeation chromatography (GPC) (SHIMUDZU), respectively. Quality of the retrieved rubber was characterized and compared with standard NR which is classified in STR5L grade such as Mooney viscosity (MV), plasticity retention index (PRI), nitrogen and ash content. The Mooney viscosity was determined by Mooney viscometer (ALPHA Tech., MV2000) with large rotor at 100 °C. The Mooney viscosity was measured according to ISO 289. This standard specifies the test temperature, sample preheating time before the start of shearing (1 min) and shearing duration (4 min). The Mooney viscosity was reported in Mooney Unit (MU). At least three samples were used for experiment. The initial plasticity and plasticity retention index were measured according to ISO 2930. Die out six test-pieces from doubled sheet with the Wallace punch. The thickness of the test-pieces ranges between 3.4±0.2 mm. Random divided these into two sets of three, one sets for plasticity tests before aging and the other for test after aging for 30 min at 140 °C. After that, remove the test-pieces from the oven. Allow them to cool to room temperature for a minimum of 30 min and measured plasticity ($P_{30}$). The PRI estimated by the percentage ratio between $P_{30}$ and $P_0$ as given in equation 1. The nitrogen and ash content were measured according to ISO 1656 and ISO 247, respectively.

$$\text{PRI(\%)} = \frac{P_{30}}{P_0} \times 100$$

(1)
The residue waste water was characterized and was crystallized at room temperature. The crystal structure was characterized by using X-ray Diffractometer (X’Pert MPD, Philips, Netherlands).

3. Results and Discussion

The compositions of waste latex sludge and retrieved rubber from TGA is illustrated in figure 3. The waste latex sludge composed with moisture, rubber hydrocarbon and inorganic substance for 35%, 20%, and 45% by wt., respectively. Acid digestion released most of bound water in the sludge and gave retrieved rubber composed with rubber for more than 95% by wt. Most of inorganic substance were decomposed and dissolved in the solution of sulfuric acid.

![Figure 3 TGA thermogram of solid sludge before and after digestion with sulfuric acid.](image)

The FT-IR spectra of the retrieved rubber compared with standard NR (STR5L) is shown in figure 4. The major characteristic peaks of standard NR are at 2962 cm\(^{-1}\) (CH\(_3\) asymmetric stretching), 2855 cm\(^{-1}\) (CH\(_2\) asymmetric stretching), 1650 cm\(^{-1}\) (C=C
stretching), 889 cm\(^{-1}\) (CH\(_3\) wagging), and 837 cm\(^{-1}\) (=C-H wagging). For the retrieved rubber, the occurrence of peak at 713 cm\(^{-1}\) (O-H out-of-plane bend) and the broader peak at 3340 cm\(^{-1}\) (hydroxyl group, H-bonded OH stretch) indicating the higher number of water molecules surrounding the membrane and functional ended group of the retrieved rubber might be hydroxyl and carbonyl (Santos, et al., 2005).

The GPC result of the retrieved rubber as shown in figure 5 was found that the average molecular weight by number (M\(_n\)) and the average molecular weight by weight (M\(_w\)) of the retrieve rubber are 90,000 and 313,000 g/mol, respectively. The molecular weight, represented rubber molecule chain length, of the recovered rubber from sludge is very low compared with the standard NR (M\(_n\) = 442,400 g/mol, M\(_w\) = 1,745,500 g/mol).

\begin{figure}
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\includegraphics[width=\textwidth]{figure5.png}
\caption{GPC chromatogram of the retrieve rubber.}
\end{figure}

\begin{table}
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\begin{tabular}{|c|c|}
\hline
Rubber & Properties of retrieved rubber from solid sludge \\
\hline
Mooney viscosity & 7000 \\
Initial plasticity & 100 \\
\hline
\end{tabular}
\caption{Table 1 Properties of retrieved rubber from solid sludge}
\end{table}

The rubber properties of retrieved rubber compared with standard NR (STR5L) is illustrated in table 1. The Mooney viscosity and initial plasticity of the retrieved rubber are
lower than that of standard NR due to the low molecular weight of retrieved rubber but the PRI of retrieved rubber is higher than that of standard NR indicated that the retrieved rubber is not easily oxidation degraded because of some natural anti-oxidant contamination. The results of this study hold promise as an apparent feasible solution to the problem of waste disposal in the NR latex concentrated factories with cost effectiveness and gains the valued NR from waste sludge which is cheap throw away material.

The waste water from sludge digestion with 10% by wt. sulfuric acid is dark brown color with pH = 5.8 and was analyzed for BOD and COD. The results was found that the BOD and COD were 2,200 and 27,200 mg/L, respectively. The residue digestive was concentrated by evaporation at 100°C and allowed the crystals formation at room temperature.

Figure 6 Crystals from residue solution.

The occurrence crystals are white to clear color and the gloss is vitreous as shown in figure 6. The powder X-ray diffraction pattern of the crystals as shown in figure 7 were in good agreement with Boussingaultite mineral (RRUFF ID- R070597.9) (Margulis et. al., 1962) and the refine unit cell parameters are $a=9.327(3)$ Å, $b=12.600(4)$ Å, $c=6.210(1)$ Å, $b=107.091(6)^\circ$, and $V=697.6(8)$ Å³ (Shimobayashi et. al., 2011).
4. Conclusions

The rubber removal from waste sludge using sulfuric acid is feasible solution to solve the problem of waste disposal in the NR latex concentrated factories in any developing country like Thailand. It is not only to retrieve high value NR but also the magnesium ammonium sulfate, which is essential nutrient in crop production, from null throw away materials.

5. Acknowledgement

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References


Table 1 Properties of retrieved rubber from solid sludge

<table>
<thead>
<tr>
<th>Properties</th>
<th>Rubber</th>
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<tbody>
<tr>
<td></td>
<td>STR 5L</td>
</tr>
<tr>
<td>Mooney Viscosity [ML1+4, 100°C]</td>
<td>60</td>
</tr>
<tr>
<td>Initial Plasticity (Po)</td>
<td>40</td>
</tr>
<tr>
<td>Plasticity Retention Index (PRI)</td>
<td>77</td>
</tr>
<tr>
<td>Nitrogen content (%)</td>
<td>0.3</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>0.1</td>
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</tbody>
</table>
Figure 1 Waste latex sludge before (a) and after grinding (b).

Figure 2 Effect of the sulfuric acid concentration on the sludge digestion.
Figure 3 TGA thermogram of solid sludge before and after digestion with sulfuric acid
Figure 4 FT-IR spectra of retrieved rubber and standard NR (STR5L)

Figure 5 GPC chromatogram of the retrieve rubber
Figure 6 Crystals from residue solution

Figure 7 Powder X-ray diffraction patterns of the retrieved crystals.