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Short Communication

Rubber recovery from centrifuged natural rubber latex residue using sulfuric acid

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Abstract

Waste latex sludge from centrifuged residue, which is a 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 have an effect on the amount and purity of the retrieved rubber. Sulfuric acid at concentrations of more than 10% by weight with a digestion time of 48 hours completely digested waste latex sludge and gave rubber 10% by weight. The quality of the retrieved rubber was examined for Mooney viscosity (MV), plasticity retention index, nitrogen content, and ash content. The average molecular weight of the retrieved rubber, using gel permeation chromatography, was lower than that of normal natural rubber (NR) which corresponds with the MV and initial plasticity (P_o). 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 crystals was determined using power X-ray diffractometer.

Keywords: waste latex sludge, concentrated latex, rubber recovery, Boussingaultite

1. Introduction

Concentrated natural rubber latex (NRL) is usually produced by using centrifugation of fresh field NRL. NRL is not only consisted of natural rubber (NR) particles but also non-rubber parts such as magnesium (Mg). The NRL can show high Mg contents, which have 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 diammonium hydrogen phosphate (DAHP) to NRL and leaving it for more than 12 hours. The reaction of DAHP with Mg results in solid sludge formation and precipitation. The solid sludge characteristics have been investigated and their advantages for agronomic relevance have been reported since 2002 (Okieimen *et al.*, 2002). Basic composition of this materials are rubber hydrocarbon, nitrogen, magnesium, and phosphorus with 12.5%, 3.3%, 12.2%, and 14.7% by wt. (dry weight), respectively (Boonsawang *et al.*, 2008). Even though these materials can be also used as commercial phosphatic fertilizers (Tekprasit, 2000), it has limitations, due to heavy metal content, as well as the unsuitability to certain soils and crops must be concerned. Additionally, rubber hydrocarbon is not easily decomposed in soils. Commonly, the waste sludge from waste water treatment plants was digested using acid (Pearson and Buswell, 1931) for different 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 the recovery of the rubber and the occurrence of high purity ammonium magnesium sulfate.

2. Experimental

The sludge, collected form a latex centrifuge machine, was kindly supplied by Chalong Concentrated Latex Com-

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pany Limited and was used immediately after. The sludge was grinded into small pieces as shown in Figure 1. Grind sludge was weighted for 300 grams before mixing with different 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 components 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 contamination has poor properties. In this experiment, the rubber recovery with 10% by wt. sulfuric acid digestion was selected.

The retrieved rubber was separated, washed with water, sheeted, and dried in an air oven at 70ºC. 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 100ºC. 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 the experiment. The initial plasticity and plasticity retention index were measured according to ISO 2930. Six test-pieces were died out from doubled sheets with the Wallace punch. The average thickness of the test-pieces was 3.4±0.2 mm. They were randomly divided into two sets of three, one set for plasticity tests before aging and the other for testing after aging for 30 min at 140ºC. After that, the test-pieces were removed from the oven. Then they were allowed to cool down to room temperature for a minimum of 30 min and after that plasticity (P_{30}) was measured. The PRI was 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.

$$PRI(\%) = \frac{P_{30}}{P_0} \times 100 \qquad (1)$$

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 of moisture, rubber hydrocarbon and inorganic substance with 35%, 20%, and 45% by wt., respectively. Acid digestion released most of the bound water in the sludge and the retrieved rubber composed of more than 95% by wt. of rubber. Most of the inorganic substances were decomposed and dissolved in the solution of sulfuric acid.

Figure 1. Waste latex sludge before (a) and after grinding (b).

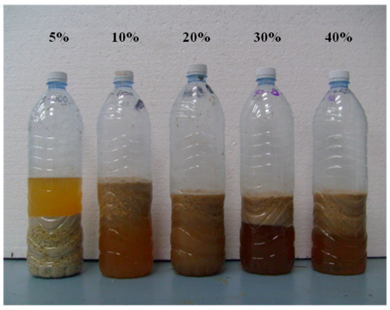

Figure 2. Effect of the sulfuric acid concentration on the sludge digestion.

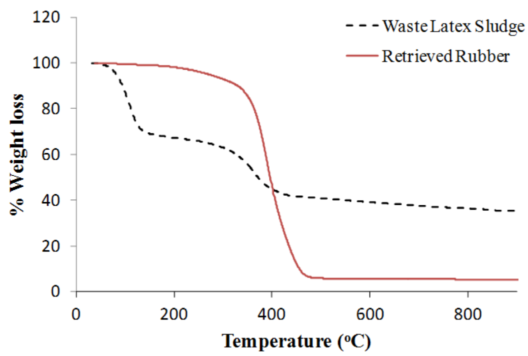

Figure 3. TGA thermogram of solid sludge before and after digestion with sulfuric acid.

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 a peak at 713 cm^{-1} (O-H out-of-plane bend) and a broader peak at 3340 cm^{-1} (hydroxyl group, H-bonded OH stretch) indicating a higher number of water molecules surrounding the membrane and the 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 found that the average molecular weight by number (M_n) and the average molecular weight by weight (M_w) of the retrieved rubber are 90,000 and 313,000 g/mol, respectively. The molecular weight, representing the 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).

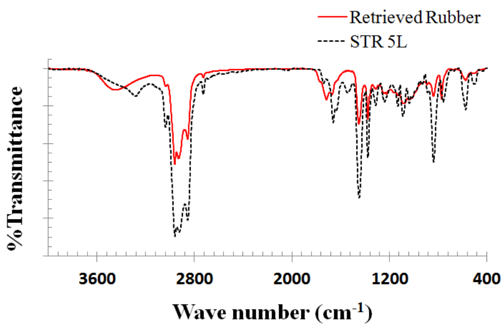

Figure 4. FT-IR spectra of retrieved rubber and standard NR (STR5L).

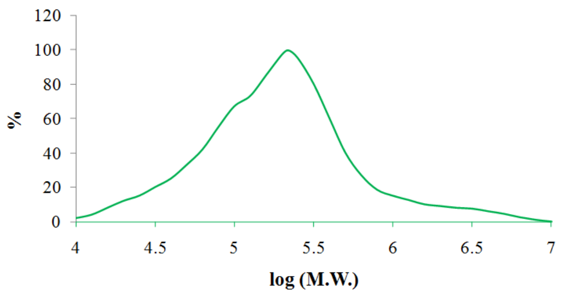

Figure 5. GPC chromatogram of the retrieve rubber.

The rubber properties of the 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 contamination with natural anti-oxidants. The results of this study hold promise as an apparent feasible solution to the problem of waste disposal in the NR latex concentrating factories with cost effectiveness and also gains valued NR from waste sludge, which is usually a cheap throw away material.

Table 1. Properties of retrieved rubber from solid sludge

Properties	Rubber	
	STR 5L	Retrieved rubber
Mooney Viscosity [ML1+4, 100°C]	60	49
Initial Plasticity (Po)	40	33
Plasticity Retention Index (PRI)	77	93
Nitrogen content (%)	0.3	0.9
Ash content (%)	0.1	3.5

The waste water from sludge digestion with 10% by wt. sulfuric acid is dark brown in color with a pH = 5.8; it was analyzed for BOD and COD. The results 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 crystal formation at room temperature.

The occurred crystals are white to clear in 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)°, and V=697.6(8) $Å^3$ (Shimobayashi *et al.*, 2011).

Figure 6. Crystals from residue solution.

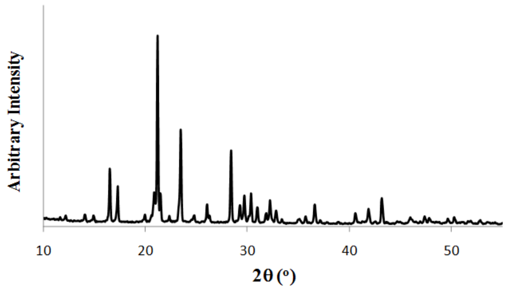

Figure 7. Powder X-ray diffraction patterns of the retrieved crystals.

4. Conclusions

The rubber removal from waste sludge using sulfuric acid is a feasible solution to solve the problem of waste disposal in the NR latex concentrating factories in any developing country like Thailand. The process is not only retrieving high value NR but also magnesium ammonium sulfate, which is an essential nutrient in crop production; both retrieved form a throw away material.

Acknowledgement

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