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Original Article

Effects of wood vinegar as an additive for natural rubber products

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Abstract

Wood vinegar, a product of wood burning in airless condition, is well known as an all- purpose natural chemical, since it can be used in agricultural, food, and pharmaceutical industries, even for home care products. Because of its acidity and anti microorganism growth property, it is of interest to use wood vinegar for rubber products by fully or partially replacing the usage of traditional acids in the production processes. This work is to study effects of crude coconut shell wood vinegar on natural rubber products. The experiment was conducted by introducing various concentrations of wood vinegar to block and sheet rubbers. Results showed that wood vinegar can improve initial plasticity, plasticity retention index and Mooney viscosity of rubber products. Moreover, it can also retard the growth of fungi in the products.

Keywords: wood vinegar; natural rubber; plasticity retention index; Mooney viscosity; anti fungi

1. Introduction

Thailand is one of the main natural rubber producing countries. Since 2008, fresh latex production in Thailand has reached approximately three million tons per year with an average yield of 5.64 tons of fresh latex per hectare. Fresh latex collected as liquid can be processed into primary rubber products such as concentrated latex, block rubber and ribbed smoked sheets, which can be subsequently processed into various final rubber products. Since natural rubber products are being exported to international markets, it is challenging for Thai manufacturers to seek appropriate methods to improve the quality of these products, especially through inexpensive local additive agents. In this case, wood vinegar, which is easily obtained locally, would be of interest to be used as an additive agent. Wood vinegar is a by-product of wood pyrolysis in the process of making charcoal. It is a dark brown liquid consisting of a number of chemicals such as organic acids, phenol, formaldehyde, alcohols, and others (Nakai *et al.*, 2007). Because of its constituents, it can be used in various applications depending on its purity and wood source. It can be used not only as a supplementary in pharmaceutical products, or in cosmetic and food industries, but also used in agriculture as fertilizers and pesticides. Moreover, it can be used in wood as anti fungi and anti termite attack substances (Kartal *et al.*, 2004).

As mentioned briefly above, primary rubber production includes block rubber process. In this process, cup lump natural rubber is one of the raw materials used in the industry. In practice, the block rubber process consists of washing, grinding, drying, and compacting. However, additional steps are required to improve the quality of raw materials such as a special pretreatment step in order to relax its stiffness by soaking raw cup lumps in an acid solution before washing. Another process is by adding some additives during washing and cutting stages. These special treatments

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can be easily modified and included into the traditional process. As for natural rubber sheet production, acid coagulant is one of the important chemicals to improve the rubber sheet quality. Some most widely used commercial acids are formic acid, acetic acid, and sulfuric acid (especially used in the Southern part of Thailand). One other alternative chemical is wood vinegar, which can be used to replace traditional chemicals. During the past few years, there have been various attempts to apply wood vinegar to rubber production processes; for example, as coagulating agent for natural rubber sheet production, in preservative-treated rubber wood, and as additives of rubber sheets (Ferreira *et al.*, 2005; Baimark and Niamsa, 2009). However, these works have concentrated mainly on using wood vinegar alone as a whole. But since wood vinegar is a mild acid, it insignificantly affects the quality of the products. Hence, this work has focused on the application of using it as an additive together with other traditional acids (formic acid and sulfuric acid). The purpose is to study the effects of using coconut shell wood vinegar at various mixtures on natural rubber products under the hypotheses of property improvement and anti fungi characteristics for both the sheet and block rubber products.

2. Materials and Methods

2.1 Materials

Crude coconut shell wood vinegar without purification that was supplied by a local manufacturer in Takam, Songkhla Province, Thailand, was used in this work. This vinegar is reddish brown in color with a pH and specific gravity of approx. 2.62 and 1.014, respectively. The boiling range based on ASTM-D86 test method was approximately 99-106°C. Principal compositions of the crude coconut shell wood vinegar as analyzed by GC (performed on a Hewlett Packard 5890 chromatograph system, a capillary column HP-INNOVAX (cross linked polyethylene glycol stationary phase; 30 m long 0.25 mm ID with 0.25 µm film thickness) at 250°C detector and injector temperatures) were methanol 0.41 g/L, phenol 2.10 g/L and acetic acid 10.77 g/L.

Field latex was obtained from Toong Ngai Co-operative Ltd. in Songkhla Province. Its pH and specific gravity are approximately 6.65 and 0.975, respectively. Clean cup lumps were also gathered from a local industry in the province. Specific gravity of these cup lumps are approximately 0.975. Sulfuric acid used in the experiments is of commercial grade. All other chemicals used in the analyses were of AR grades obtained from Merck, Fluka, and Aldrich.

2.2 Methods

2.2.1 Wood vinegar testing on block rubber production

Cup lumps were pre-cleaned by immersing in water and then shredded to size about 5 mm before being immersed in crude coconut shell wood vinegar (7 liters of vinegar per a kilogram of cup lumps) at different concentrations (1, 3, 5, 7, and 10% by volume) for 24, 48, 72, and 120 hours. Thereafter these cup lumps were cleaned again using water then dried at 110°C for 4 hours. Each sample was tested according to ASTM for seven physical properties (Agriculture, 2001) viz. dirt content (ASTM D1278-91), ash content (ASTM D 1278-91), nitrogen content (ASTM D3533-90), volatile matter (ASTM D1278-91), initial plasticity (ASTM D2227-96), plasticity retention index (ASTM D3194-04), and Mooney viscosity (ASTM D1646-07). Fungal inhibition was also tested by cultivating *Penicillium sp.* from natural rubber (immerse 1 g. piece of rubber sample in 0.85 %wt. NaCl 5 ml and dilute) with in potato dextrose agar (PDA) for 72 hours (Suwanpinich and Suwanpinich, 1998). The anti fungi efficiency can be determined by the ratio of fungi growth area on the plate to the area of the plate.

2.2.2 Wood vinegar testing in sheet rubber production

The obtained field latex was filtrated before using in the experiment. The work introduced different concentrations of the crude coconut shell wood vinegar to a fixed amount of formic acid or sulfuric acid as coagulating agents to the field latex to form sheet rubber. The ratio of latex: water: acid: wood vinegar was 1500:1500: 450: "X" ml while "X" was varied from 25 to 250 ml. A 3-5 mm thickness of the sheet rubber was controlled. Each sheet was sun dried before testing for its physical properties according to Standard Block Rubber Test (2001) and fungal inhibition (Suwanpinich and Suwanpinich, 1998).

All property tests were run with three replicates and all were averaged for block rubber and sheet rubber productions. Excel 2003 was used for an analysis of variance (ANOVA), blocked by immersing time and wood vinegar concentration with the confidence limit used of 95% ($p \leq 0.05$) for block rubber production, while it was blocked by types of acid and wood vinegar concentration (pd"0.05) for sheet rubber production.

3. Results and Discussion

3.1 Effects of crude coconut shell wood vinegar on block rubber

Effects of crude coconut shell wood vinegar on dirt, ash, nitrogen, and volatile matter contents in block rubber are shown in Figure 1 a, b, c and d, respectively. After the first period, the limitation of mass transfer is significant because of equilibrium conditions. The figure shows that at the beginning, different wood vinegar concentrations give different values of each property due to a deviation of small pieces of cub lumbs of each sample. However, the repeated experiments (three times) show trend of changing from the reference point (initial time). Figure 1a shows that, dirt contents in block rubber decrease rapidly in the first 24 hours for every wood vinegar concentration since the polarity of

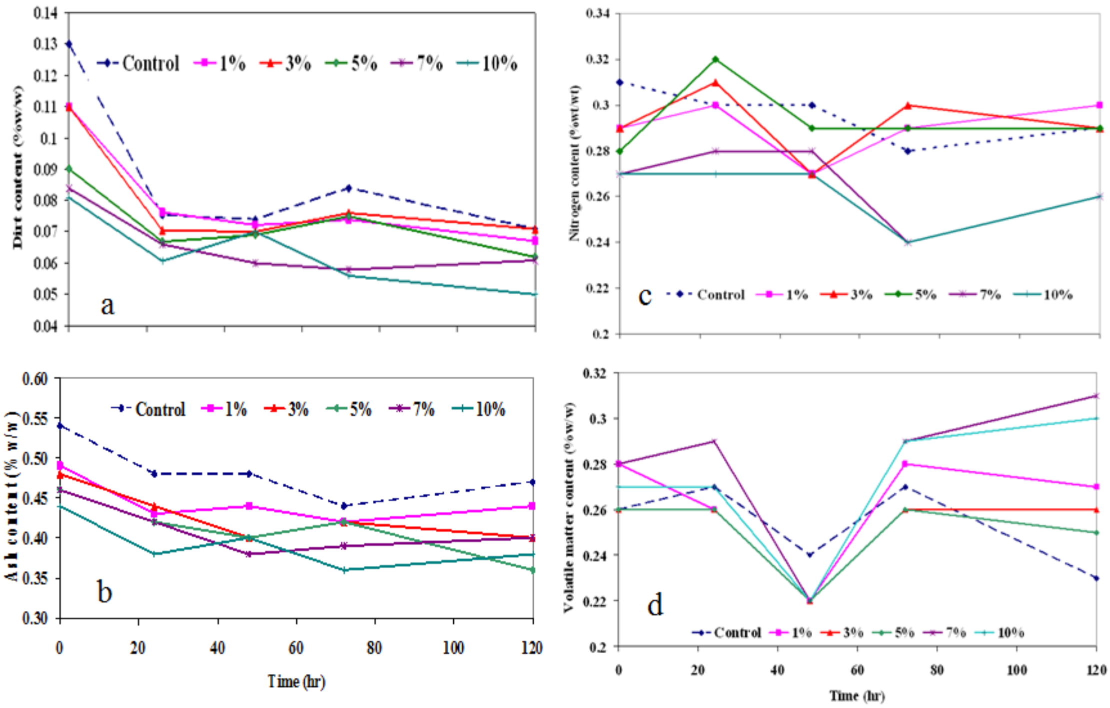

Figure 1. Effect of crude wood vinegar concentration (%v/v) and immersing time on contents of block rubber: a-dirt content, b-ash content, c-nitrogen content and d- volatile matter.

water and wood vinegar can dissolve dirt from the rubber. It is fair to say that the optimal time for all concentrations (including the control experiment) is about the first 24 hours. Beyond 24 hours, the dirt contents are fluctuated about the optimal value because mass transfer of dirt is in its equilibrium since these experiments were done under batch processes. Figure 1b shows that each concentration can reduce ash content in the first 24 hours and the ash contents fluctuate after that as the same reason for dirt content. Figure 1c indicates that using wood vinegar increases the nitrogen content in the first 24 hours. This is because wood vinegar contains some organic compounds with N atoms, for example, pyridine (Ratanapisit *et al.*, 2009), while water can dissolve the nitrogen from the beginning. However, after 24 hours, each wood vinegar concentration can also reduce the nitrogen content and reach minimum values at 48 hours (1%, 3% wood vinegar) and 72 hours (7%, 10% wood vinegar), respectively, and then fluctuate due to the nitrogen equilibrium. And increasing the immersing time from 24 to 48 hours decreases the volatile matter content in the block rubber at any concentration of wood vinegar (95% confidence) as shown in Figure 1d because the wood vinegar solution can dissolve volatile matters. But, the volatile matters also swing after an immersing time longer than 48 hours since it has reached equilibrium.

Initial plasticity is the ability of rubber to deform and Mooney viscosity represents the stress of the rubber. As the same reason for the initial values of the properties in previous part, Figure 2, 3, and 4 show that the initial values of initial plasticity, Mooney viscosity, and plasticity retention index of each wood vinegar concentration are different. Nevertheless, increasing concentration of wood vinegar and immersing time increases both initial plasticity and Mooney viscosity (95% confidence) as depicted in Figure 2 and 3, respectively. It was found that formaldehyde in the wood vinegar (Ratanapisit *et al.*, 2009) reacts with amine groups in the rubber to produce formic acid (http://www.tutorvista.com, 2011) and breaks the crosslink, thus the rubber can simply transform. Another property is the plasticity retention index which is a measure of natural rubber oxidation resistance at a specific temperature (Barlow, 1993). From Figure 4, it can be seen that increasing either the immersing time or the wood vinegar concentration increases the amount of phenol - an anti-oxidant - in the rubber, resulting in the significant increase of the plasticity retention index (95% confidence).

In addition to these properties, the block rubber under each condition was sampled for anti fungi examinations. The results are shown in Figure 5. Increasing wood vinegar concentration can reduce the amount of fungi in block rubber. The fungi growth area reduces from approximately 75% (control) to 0.19% (7%v/v) because of phenolic compounds and acetic acid in the wood vinegar (Kartal *et al.*, 2004).

3.2 Effect of crude coconut shell wood vinegar on sheet rubber

As shown in Figure 6, without the introduction of wood vinegar the use of formic acid yields higher initial plas-

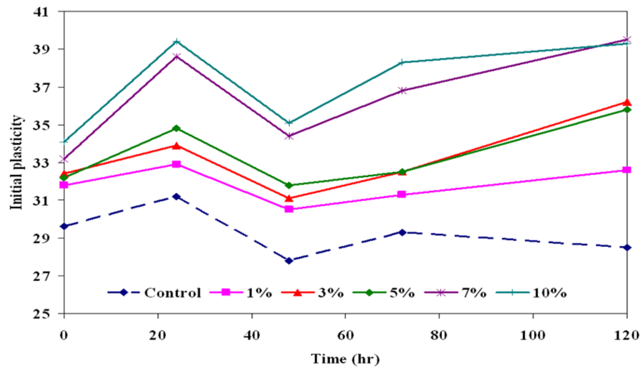

Figure 2. Effect of crude wood vinegar concentration (%v/v) and immersing time on initial plasticity of block rubber.

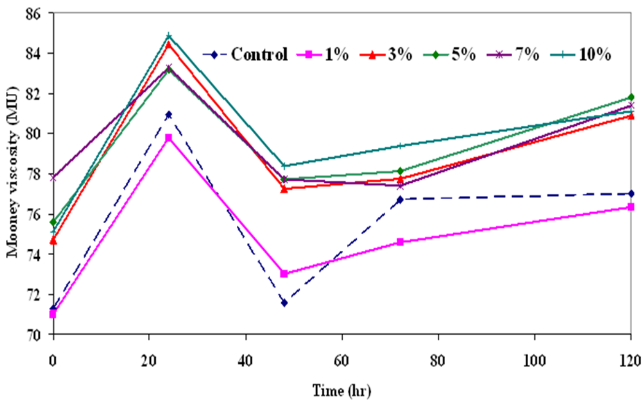

Figure 3. Effect of crude wood vinegar concentration (%v/v) and immersing time on Mooney viscosity of block rubber.

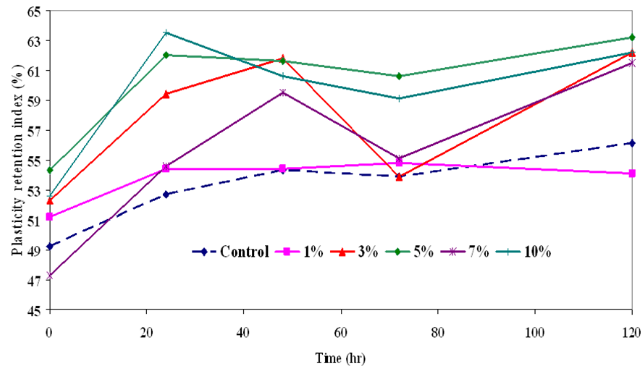

Figure 4. Effect of crude wood vinegar concentration (%v/v) and immersing time on plasticity retention index of block rubber.

ticity to the sheet rubber than that employing sulfuric acid since the latter has a stronger acidity than the former. Comparing the acidity among three acid (formic acid > acetic acid > sulfuric acid), an increasing amount of wood vinegar into the formic acid reduces the initial plasticity (95% confidence), while adding wood vinegar into sulfuric acid tends to increase the initial plasticity as the amount increases. Therefore the acidity effects on the initial plasticity.

The effect of wood vinegar on plasticity retention index and Mooney viscosity for sheet rubber is shown in Figure 7and 8, respectively. For the case of formic acid, increasing the amount of wood vinegar does not significantly improve the PRI and the Mooney viscosity. The % PRI and the Mooney viscosity from this study are close to the ones from Baimark and Niamsa (2009). And for the sulfuric acid case, it remarkably improves both properties (95% confidence) when adding the wood vinegar greater than 150 ml. Because the rubber can be contaminated with bacteria during collecting process and this bacteria effects the oxidation of the rubber (Santos *et al.*, 2005). Therefore, adding wood vinegar increases the phenolic group to the rubber that improves the properties.

3.2.1 Anti fungi characteristics

The effect of crude coconut shell wood vinegar on fungal growth is shown in Table 1. Results show that wood vinegar can prevent fungi growth on sheet rubber as well as for block rubber due to phenolic compound and acetic acid. However, introduction of wood vinegar into sulfuric acid is more effective than that into formic acid because of more acidity in the former.

4. Conclusions

Crude coconut shell wood vinegar used in this study can improve various properties in both block and sheet rubbers. Due to its acidity, when applying to block rubber it can reduce dirt, ash and nitrogen contents. It can also improve the initial plasticity, plasticity index, and Mooney viscosity for both block and sheet rubbers, because phenolic compound in wood vinegar works as an antioxidant. Additionally, it can retard fungal growth for the rubber since it contains acetic acid and phenolic compound and thus it can be used as also an anti-fungi chemical.

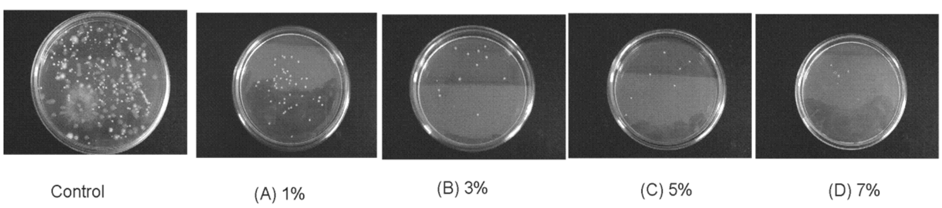

Figure 5. Effect of crude wood vinegar concentration (%v/v) on anti fungi property of block rubber.

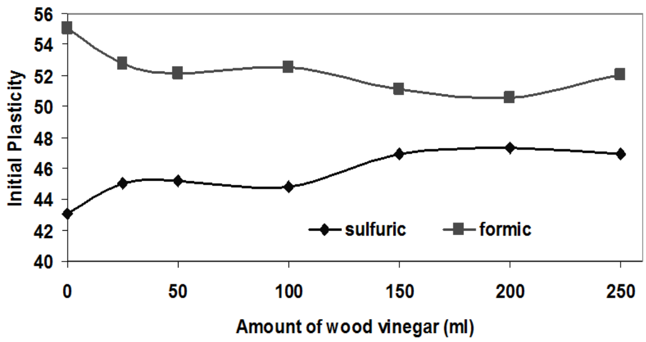

Figure 6. Effect of wood vinegar on initial plasticity of sheet rubber.

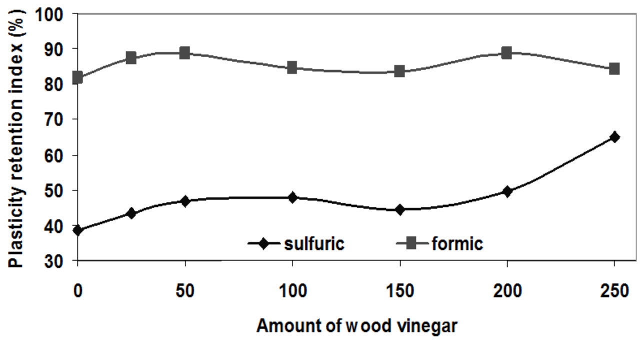

Figure 7. Effect of wood vinegar on plasticity retention index of sheet rubber.

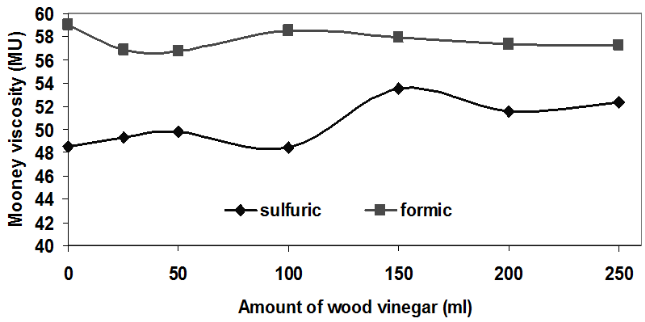

Figure 8. Effect of wood vinegar on Mooney viscosity of sheet rubber.

Table 1. Percentage of fungi growth area at different amounts of wood vinegar added with different acids for sheet rubber.

Amount of wood vinegar (ml)	% Area of fungi growth	
	Formic acid	Sulfuric acid
0 (control)	98.07	65.52
25	97.8	15.79
100	89.58	13.92
250	89.13	12.12

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