Deciphering the discoloration in the manufacturing of natural rubber

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Abstract

Many naturally occurring color components, especially non-rubber components, are present in natural rubber (NR) latex, limiting some NR applications, particularly for light-colored NR products in high demand. Non-rubber components, like lipids and proteins, can be removed from NR to reduce its yellow color. This study looked at the factors that influence the yellow index (YI) in NR and NR latex discoloration techniques. Proteins were a crucial factor directly determining the YI of NR. Thus, increasing the number of centrifugation washings, speed, and time was used to remove proteins to minimize the YI of NR. Percentage of total solid content (% TSC) of field NR latex, the blend ratio between cream rubber and skim latex, or bottom fraction from fresh-field NR latex collected from centrifugation process, were also important factors. The addition of sodium metabisulphites as a polyphenol oxidase (PPO)-reducing agent reduced the YI significantly. The oxidative breakdown of endogenous non-rubber components at high temperatures was also confirmed to serve the increase in YI value due to air-drying conditions of NR.

1. Introduction

Natural rubber (NR) is a major agricultural product of Thailand, produced from Hevea brasiliensis trees in both solid and concentrated latex form. Vehicle tires, automobile parts, dock fenders, gloves, condoms, and other consumer products use NR as a key raw material. Because NR is naturally yellowish, light-colored and colored-filled goods require light or extra-light graded rubber as a feedstock manufactured during the manufacturing process. In the case of concentrated NR latex, there is no specific grade for making light-colored latex products.

The yellow color of NR is influenced by clonal and seasonal changes, soil types, tapping frequency, and non-rubber components. The presence of carotenoids is thought to be responsible for the unique yellow hue of NR [1]. Carotenoids from RRIM600 and PB235 clones were extracted and analyzed, revealing the presence of four important carotenoids: lutein, zeaxanthin, carotene, and carotene [2]. Because polyphenol can react with compounds such as proteins via a non-enzymatic reaction, it has been identified as the most important component that causes discoloration of raw NR [3,4] and vulcanized NR [3]. Colorants extracted from various NR latex fractions, including fresh latex, bottom fraction, cream fraction, and Frey-Wyssling (FW) particles, contained similar constituents, such as carotenoids, tocotrienol esters, fatty alcohol esters, tocotrienols, unsaturated fatty acids, fatty alcohols, diglycerides, and monoglycerides, according to Sakdapipanich and colleagues [5]. Non-rubber coloring components such as polyphenol, proteins, and carotenoids, according to Madsa-ih and Cheewasedtham [6], impact the color of NR. Orthoquinones are produced by the oxygen-dependent oxidation of polyphenols catalyzed by polyphenol oxidases (PPO). Colorants are formed when these quinones react with amino acids and proteins found in latex [7]. PPO is a phytohormone that aids in plant defense on a tapping wound of the rubber tree has been found in both lutoid and FW particles, with the former
having higher activity [4]. PPO is released from the ruptured particles, causing discoloration. When proteins and amino acids in NR latex combine with carbonyl molecules, including reducing sugars, aldehydes, and ketones in the presence of heat, they generate colorful substances known as the Millard reaction.

Many studies have been conducted to discolor NR latex by suppressing enzyme activity, removing the substrates involved through chemical treatment, or using both combinations [8]. It has been reported that stimulating the Hevea tree with an optimal dosage of ethephon suppresses enzymatic browning in NR [9]. To overcome coloring compounds inherent in NR, purifications by deproteinization [10] and transesterification [11] are procedures for eliminating proteins and lipids from NR latex/solution, respectively. Despite the fact that sodium metabisulphite (SMS) acts as an enzymatic browning inhibitor, it does not affect the color of NR [12]. As a result, this current work uses a colorimeter to determine a yellow index to figure out the main component that affects the yellowness of NR (YI). When scaled up, systematic research of the factor and the procedure to lower the YI will be conducted to implement a feasible way to manufacture light-colored NR and latex for industrial choice.

2. Experimental

Materials: Thai Rubber Latex Group Public Co., Ltd. provided fresh field latex (FL) from a plantation in Chonburi, Thailand, from Hevea rubber tree clone RRIM 600. FL-latex was treated with 0.6 percent w/v ammonia and 0.5% w/v potassium laurate, then filtered using a muslin cloth to eliminate contaminants and coagulum. The FL-latex was cast on a clean, dust-free petri dish and dried at room temperature to make fresh NR (FNR) film. Bangkok Synthetics Co. Ltd., Thailand, provided cis-1,4 polyisoprene or synthetic isoprene rubber (IR).

Sample preparation: Proteins were extracted from FL by incubating 30% DRC of FL with 0.04 % w/v proteolytic enzyme (Kao KP-3939) in the presence of 1 % w/v sodium dodecyl sulphate (SDS) for 16 h at 37°C [10], followed by washing twice with 12,000 rpm centrifugation for 30 min. Deproteinized NRL or DPNRL refers to the latex that has been obtained. The DPNRL was cast in a clean petri dish as a film and dried at room temperature. A reaction of a 0.5% w/v FNR solution in toluene with freshly produced sodium methoxide for 3 h at 37°C yielded transesterified NR (TENR) [11]. The same technique was used to make TENR following deproteinization (DP-TENR); however, DPNR was used as the starting material instead of TENR. FL-latex was centrifuged for 30 minutes at 25°C to produce concentrated NR latex (CNRL). The percentage total solid content (% TSC) of FL before centrifugation, centrifugation time/speed/number of washing cycles, and other aspects in the actual centrifugation process at the manufacturing that may affect the color of NR were also explored. The TSC of FL was changed from 15 to 40% before centrifugation at 12,000 rpm for 30 min. All of the CNRL that resulted were modified to 60% w/w TSC and 0.5% w/v potassium laurate (aq). The CNRL film was made from 4 mL of diluted CNRL (50 % w/w TSC) by casting it on a clean petri dish (60 mm diameter) and drying it at room temperature overnight, then drying it under vacuum until reaching a steady weight.

Characterization

Determination of color: According to ASTM E313 @ 10°, the yellow index (YI) of the rubber films was measured using a Hunter Lab (ColorQuest®XE) CIE colorimeter with an Illuminant D65 light source.

Determination of nitrogen content: A LECO FP 528 Nitrogen Analyzer was used to determine the nitrogen concentration of NR. The nitrogen content was determined by duplicate analysis with a standard deviation of 0.0015%, comparable to the EDTA standard.

Determination of ester content: Fourier-transform infrared (FT-IR) spectroscopy was used to analyze the ester content of each dry rubber sample by measuring the variety of mixture of methyl stearate as a standard and synthetic cis-1,4 polyisoprene, as described in our earlier work [11].
3. Results and discussion

Compared with the control FNR and synthetic IR rubber, Figure 1 illustrates the appearance and change in YI and N/ester contents of various types of NR, i.e., DPNR, TENR, and TE-DPNR, after removing the non-rubber components (NRC). The YI of DPNR, TENR, and TE-DPNR all dropped from 24 for FNR to 10, 8, and 3 for DPNR, TENR, and TE-DPNR, respectively. The colors in Figure 1 correlate to the actual color of the rubber samples. FNR and DPNR were yellowish and pale yellow, respectively, whereas TENR was virtually colorless and TE-DPNR and IR were transparent. The N content, ester content, YI value, and color of TE-DPNR and IR were surprisingly equivalent. According to these findings, proteins seem to be the most important component dictating the yellowness of NR.

In practice, centrifugation yields concentrated NRL from TSC of 30 to 60. As a result, numerous parameters were investigated thoroughly to decide the proper condition, including altering the percent TSC of FL, centrifugation time and speed, and the number of washings (as shown in Figure 2). The best speed is 12,000 rpm for 30 min, and the percent TSC should be less than 30%.

To investigate the component derived from the composition of FL after centrifugation, a mixture of cream rubber and skim latex and the bottom fraction were prepared. Figure 3 illustrates the change in ester and nitrogen contents as a function of YI values for various amounts of skim latex and bottom fraction mixed with the cream rubber. It is noticeable that as the nitrogen content of the skim latex and bottom fraction increased, the YI increased proportionally. The findings of (a) may be compared to the screw adjustment in the centrifugation at the factory, which will separate approximately 20-25%, as the so-called skim latex, which would produce the best CNRL quality. The N contented, and YI values increased dramatically as the BF content was increased in experiment (b), while the ester content remained constant. These findings suggest that removing as much BF before centrifugation will reduce the YI of the CNRL obtained.

Figure 4 shows how the YI of several NRs changed before and after sodium metabisulfite (SMS) was added. The incorporation of SMS as a PPO-reducer could improve the YI of rubber by approximately 10%. By comparison with the control NR dried at 50°C for 48 h and FNR, Figure 5 shows the change in YI and characteristics of NR after drying at various conditions. The darkening was seen in the samples 150h-NR and 150h-NR, which were dried at higher temperatures. Because of the oxidative degradation of the non-rubber components, this finding suggests that a high-temperature drying process could boost the high YI of NR.
4. Conclusions

The niche CNRL and light-colored NR were established in this investigation by fine-tuning the centrifugation processes and removing non-rubber components, including proteins, and the drying process. The approaches are manageable and achievable for manufacturing consent with the smallest alteration to becoming a machine. A light color CNRL can meet the demand, and the higher processing charge can be ignored.

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