Physical decoloration in the concentration process of natural rubber

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Abstract

Natural rubber (NR) latex contains many components, especially non-rubber components, which can affect the color of products made from it. There is a growing demand in NR products which are lightly colored or color filled. One way to reduce the yellow color of NR is to remove non-rubber components, for example, lipids and proteins, from NR. This study focused on several NR latex decoloration techniques, including controlling centrifugation speed and time as well as percentage of total solid content (% TSC) of field latex. It was found that the best condition to reduce yellow color was centrifugation of the field latex containing less than 35% TSC at 12,000 rpm for 30 min. In addition, decoloration of NR latex was very effective by washing the centrifuged latex at least twice. Other factors, such as storage time and drying conditions, promoted coloration of NR due to the oxidation of the non-rubbers.

KEYWORDS

color index, decoloration, latex, lipids, natural rubber, non-rubber, proteins

1 | INTRODUCTION

Natural rubber (NR), from *Hevea brasiliensis* trees, both solid and in concentrated latex form, is an important agricultural product of Thailand. NR is a key raw material of many industrial and consumer products, such as vehicle tires, automobile parts, dock fenders, gloves, condoms, and others. Owing to the fact that NR is inherently yellowish in color, lightly-colored and colored filled products require pale rubber or light or extra-light graded rubber as feedstock, which are produced by bleaching during the production process. In case of concentrated NR latex, there is, however, no particular grade for producing light-colored latex products.

The yellow color of NR is due not only to the presence of non-rubbers but also depend on clonal and seasonal variations, soil types, and tapping frequency. The distinctive yellow color in NR has been attributed to the presence of carotenoids.[1] Extraction and analysis of carotenoids from RRIM600 and PB235 clones revealed the presence of four major carotenoids, namely lutein, zeaxanthin, α-carotene and β-carotene.[2] Polyphenol was
reported to be the most important component that causes discoloration of raw NR\textsuperscript{[3,4]} and vulcanized NR because polyphenol can react with substances such as proteins via non-enzymatic reaction.\textsuperscript{[3]} In addition, polyphenol compounds, including gallic acid, naphtoic acid and quercetin, could be detected in latex C-serum and rubber-processing effluent.\textsuperscript{[5]} The different extracted solvents were used to extract total phenolic content (TPC) in three grades of NR.\textsuperscript{[6]} It was found that the mixture of cyclohexane: methanol (4:1, vol/vol) could extract the highest content of TPC. Sakdapipanich et al.\textsuperscript{[7]} reported that colorants extracted from various NR latex fractions, for example, fresh latex, bottom fraction, cream fraction, and Frey-Wyssling (FW) particles, contained similar constituents for example, carotenoids, tocotrienol esters, fatty alcohol esters, tocotrienols, unsaturated fatty acids, fatty alcohols, diglycerides, and monoglycerides. Madsaith and Cheewasedtham\textsuperscript{[8]} reported that the non-rubber coloring components impacting the color of NR are polyphenol, followed by proteins and carotenoids, respectively. Oxygen-dependent oxidation of polyphenols catalyzed by polyphenol oxidases (PPO) generates ortho-quinones. These quinones react with amino acids and proteins present in latex resulting in colorant formation.\textsuperscript{[9]} PPO, which plays a role in plant defense mechanism on the tapping wound of rubber tree, was reported to be present in both lutoid and FW particles with higher activity in the former.\textsuperscript{[4]} The PPO activities could be detected in the C-serum, the effluent\textsuperscript{[10]} and the cell suspension.\textsuperscript{[11]} Discoloration occurs after PPO is released from the ruptured particles. Proteins and amino acids in NR latex can react with carbonyl compounds, such as reducing sugars, aldehydes and ketones, in the presence of heat to produce coloring substances via the Millard reaction. Anionic detergents were found to be more effective activators of PPO, when compared with other ionic and nonionic detergents.\textsuperscript{[4]} In addition, discoloration possibly involves the oxidation of lipids, especially unsaturated fatty acids.

NR latex discoloration can be prevented by inhibiting either enzymatic activity, or eliminating the substrates concerned by chemical treatment or the combination of both.\textsuperscript{[12]} The prevention of enzymatic browning in NR by stimulation Hevea tree with optimum concentration of ethephon has been reported.\textsuperscript{[13]} The ethephon increased the content of thiol of the latex which acted as antioxidant by reacting with phenolic compound to form colorless products. A decrease of PPO activity in latexes at the first tapping after stimulation has been reported.\textsuperscript{[14]} Thiol compound is one component in a bleaching mixture used in a production of pale crepe rubber. It was found that the mixture containing thiothiolic could provide higher bleaching efficiency than that consisting of alkylthiol.\textsuperscript{[15]} Besides using thiol compound as bleaching agent, it was found that soaking of coagulated NR in hot water could reduce the color as well as the total phenolic content in NR.\textsuperscript{[16]} Purifications by deproteinization\textsuperscript{[17]} and trans-esterification\textsuperscript{[18]} are methods for removing proteins and lipids from NR latex/solution, respectively, that will reduce coloring substances present in NR. Vulcanized NR prepared from highly purified rubber by saponification was light-yellow in color.\textsuperscript{[19,20]} Despite sodium metabisulphite (SMS) acting as an enzymatic browning inhibitor, it did not significantly affect the color of NR.\textsuperscript{[20]} However, the removal of proteins and lipids by these chemical methods is too complicated and not practical in the manufacturing process of concentrated NR latex (CNRL). In this work, we describe a physical treatment method to produce decolorized NR latex and rubber. The findings are significant and provide a possible method for the production of light-colored NR latex and latex for adoption by the industry when scaled up.

2 | EXPERIMENTAL SECTION

2.1 | Materials

Fresh field latex (FL-latex) from Hevea rubber tree clone RRIM 600 was provided by Thai Rubber Latex Group Public Co., Ltd. from a plantation at Chonburi, Thailand. 0.6% wt/vol ammonia and 0.5% wt/vol potassium laurate were added to FL-latex, then filtered with a muslin cloth to remove impurities and coagulum. Fresh NR (FNR) film was prepared by casting the FL-latex on a clean and dust-free petri dish and dried at room temperature (RT). Cis-1,4 polyisoprene or synthetic isoprene rubber (IR) was provided by Bangkok Synthetics Co. Ltd., Thailand.

2.2 | Preparation of purified NR

FL-latex was purified by various treatments to remove proteins and lipids presenting in the NR matrix. Deproteinized NR (DPNR) latex was prepared by incubating 30% DRC of FL-latex with 0.04% wt/vol proteolytic enzyme (Kao KP-3939) in the presence of 1% wt/vol sodium dodecyl sulphate (SDS) at 37°C for 16 h,\textsuperscript{[17]} followed by washing twice by centrifugation at 12,000 rpm for 30 min. DPNR film was cast on a clean petri dish and dried at RT.

Transesterified NR (TENR) was obtained by treating a 0.5% wt/vol FNR solution in toluene with freshly
prepared sodium methoxide for 3 h with stirring at RT.\textsuperscript{[18]} TENR after deproteinization (DP-TENR) was prepared by the same procedure as TENR, except using DPNR as starting material instead. The TENR and DP-TENR were further purified by precipitation of the treated rubber solution into methanol. The samples were dried under vacuum until a constant weight was obtained.

2.3 Preparation of concentrated NR

CNRL was prepared by centrifugation of FL-latex at 25°C for 30 min. The factors in the actual process of centrifugation at the factory which may affect the color of NR were also carried out, that is, percentage total solid content (% TSC) of FL-latex before centrifugation, centrifugation time, centrifugation speed and the number of washing cycle. The % TSC of FL-latex was varied from 25 to 35 before centrifugation at 12,000 rpm for 30 min for this study. The effect of centrifugation time set at 12,000 rpm was between 20 and 60 min while the centrifugation speed was varied between 6000 and 18,000 rpm at a fixed time of 30 min. In case of the number of washing, the FL-latex was centrifuged at 12,000 rpm to prepare 35% TSC latex with 0.5% wt/vol potassium laurate (aq) from the recovered cream fraction and then washed by centrifugation once, twice and thrice. All the resulting CNRL were adjusted to 60% wt/wt TSC with 0.5% wt/vol potassium laurate (aq). The CNRL film was prepared from 4 g of the diluted CNRL (50% wt/wt TSC) by casting on a clean petri dish (60 mm diameter) and dried at RT for overnight and further dried under vacuum until a constant weight was obtained.

2.4 Characterizations

2.4.1 Determination of color

The yellow color of the rubber films was analyzed using a Hunter Lab (ColorQuest\textsuperscript{®}XE) CIE colorimeter with an Illuminant D65 light source, according to ASTM E313 at 10°. The yellowness index (YI) was calculated using Equation (1).

$$YI_{E313} = \frac{100(C_x X - C_y Z)}{Y}.$$  \hspace{1cm} (1)

where $X$, $Y$, and $Z$ are the CIE Tristimulus values and coefficients $C_x$ and $C_y$ (for D65 illuminant and 10° standard observer are 1.3013 and 1.1498, respectively.

2.4.2 Determination of non-rubber components

**Determination of nitrogen content**

The nitrogen content in NR was analyzed by a LECO, FP 528 Nitrogen Analyzer. Approximately 0.25 g of the rubber sample, accurately weighed in an aluminum pan, was used for the analysis. The nitrogen content was calculated from duplicate analysis, SD $\leq$0.0015%, as comparable to EDTA standard. Calculation of nitrogen content was performed by built-in-software. The precision range of measurement is 80 ppm. The nitrogen content of purified synthetic cis-1,4-polyisoprene (JSR IR-2200) was found to be 0.008%, also out of the limit of detection.

**Determination of ester content**

The ester content of each dry rubber sample was analyzed quantitatively a series of mixtures of methyl stearate as a standard and synthetic cis-1,4 polyisoprene using Fourier transform infrared (FTIR) spectroscopy. Each rubber mixture was dissolved in chloroform (1% wt/vol), cast onto a KBr disk, and scanned at a resolution of 4 cm$^{-1}$ for 128 scans. A calibration curve was constructed from a plot of the intensity ratios of absorptions of C=O and C=C at 1739 and 1664 cm$^{-1}$, respectively, from FTIR spectra of the rubber mixtures against the concentrations of methyl stearate in the ranges of 2–40 mmol/kg rubber. The content of the fatty acid ester groups per weight of rubber was obtained by substituting the intensity ratio of absorptions of carbonyl groups (C=O) at 1739 cm$^{-1}$ and unsaturated carbon (C=C) at 1664 cm$^{-1}$ ($A_{1739}/A_{1664}$) into the equation of the calibration curve (Equation (2)).

$$y = 0.0093x + 0.0046.$$ \hspace{1cm} (2)

where

$y = A_{1739}/A_{1664}$.

$x = $ Quantity of ester groups (mmol/kg-rubber).

3 Results and Discussion

3.1 Purified NR

Proteins and lipids which have been shown to affect Hevea NR were removed from NR by enzymatic deproteinization method, transesterification method and the combination methods of deproteinization and transesterification, respectively. The color change (represented by YI), N content and ester content of NR samples, that is, FNR, DPNR, TENR, TE-DPNR, and IR are shown in...
Figure 1. It was found that the N and ester contents of DPNR and TENR were much lower than those of FNR, suggesting the removal of proteins and lipids by the respective treatments. TE-DPNR showed the lowest amount of both N content and ester content as expected.

The YI, which is calculated using Equation (1), is a number describing the color changes in a material specimen from clear or white to yellow viewed under daylight lighting condition. The YI of dry rubber films decreased from 24 for FNR to 10, 8, and 3 for DPNR, TENR, and TE-DPNR, respectively. The colors of the rubber samples given in Figure 1 correspond to their actual color. In terms of color, FNR and DPNR were yellowish and pale yellow, respectively, while TENR was nearly colorless and both TE-DPNR and IR were colorless. It is interesting that both TE-DPNR and IR showed very similar N content, ester content, YI value and color. The results suggest that both proteins and lipids significantly affect the yellowness of NR. Although the removal of proteins and lipids from NR by these chemical methods is possible and a likely cause of the yellowness of the rubber, it is impractical for the manufacturing process of CNRL. Hence the physical treatment method is investigated in the latex and rubber production process.

3.2 Concentrated NR

Industrially, the centrifugation method is used to concentrate field latex from approximately 30% TSC to about 60% TSC. Here, CNRL is prepared using a batch centrifuge, instead of the continuous centrifuge, and controlled by varying the %TSC of FL-latex, centrifugation time and speed and the number of washing. First, the preparation of CNRL was carried out by centrifugation FL-latex at various rotational speeds from 6000 to 18,000 rpm at 25°C for 30 min to separate into two major fractions of cream and serum.

The appearance of the latex after centrifugation, the volume of CNRL (60% TSC) obtained, the color characteristics and the YI of the rubber films prepared from the latex are shown in Table 1. In the \( L^*a^*b^* \) color system, the \( L^* \) defines lightness from black at 0 to white at 100. The positive and negative \( a^* \) indicates redness and greenness, respectively, and the positive and negative \( b^* \) describes yellowness and blueness, respectively. However, many industries widely use the YI to determine color difference, especially quantifying the material degradation. It was observed that the cream fraction could be separated clearly by centrifugation with a rotational speed of 10,000 rpm or higher. In addition, the rotational speed affected the obtained yield (volume) of CNRL, \( b^* \) value and YI, that was, increase in rotational speed led to increase in the yield of CNRL and decrease in \( b^* \) value and YI, but not in the case of \( L^* \) and \( a^* \) values that changed insignificantly. The results suggest that the higher speed of centrifugation can separate cream fraction from serum fraction effectively and simultaneously remove the non-rubbers and the water-soluble species. Nevertheless, the change in \( b^* \) value and YI was insignificant at the rotational speed over 12,000 rpm. In addition, at higher rotational speed of 14,000 and 16,000 rpm, the cream fraction was tightly packed and could not be re-dispersed completely due to coagulum formation. The optimum rotational speed of centrifugation that could separate cream fraction with high yield and high performance thus was 12,000 rpm.

It is known that TSC (%) and DRC (%) of FL-latex from *Hevea* depend on clones, age of tree, tapping systems and regional climate, and so forth. The FL-latex before subjecting to centrifugation is generally reported to contain about 25–35 %DRC. In order to study the effect of TSC (%) of FL-latex on the color of CNRL film, the CNRL were processed by centrifugation of FL-latex containing 25–35 %TSC at 12,000 rpm at 25°C for 30 min. Table 2 shows that the YI of CNRL film increased from 6.61 to 7.54 and 9.35 when %TSC was increased from 25% to 30% and 35%. This result suggested that removal of non-rubbers is more effective at low % TSC of FL-latex. Hence, it is recommended to use FL-latex containing 25% to 30% DRC to prepare CNRL for manufacturing light-colored NR latex products.

The results in Table 3 show that original FNR has the highest YI value at 16.46, compared to those from CNRL films prepared at various centrifugation durations. The YI of the CNRL films decreased to about 12 when
the centrifugation time was increased to 20 min and continue to decrease to 10 when the centrifugation time was 30 min or more. However, longer centrifugation period also resulted in partial coagulation and a decrease in yield of CNRL. Thus, the most suitable centrifugation conditions to obtain high yield and high quality (light color) CNRL is 12,000 rpm at 25°C for 30 min.

Substances causing coloration of CNRL were removable by washing the latex at least three times with 0.5% wt/vol potassium laurate. The N content, ester content and YI of the CNRL samples before and after washing are shown in Figure 2. The N content of the CNRL obtained after the first and the second washing decreased from 0.82 to 0.24 and 0.17% (wt/wt), respectively, and dramatically to 0.02% (wt/wt) after the third washing. The washing treatment also reduced the ester content and the YI of the CNRL samples. The ester content of the latex decreased from 25 to 18 and 15 mmol/kg for the first and the second washing, respectively, after that, no significant change was observed. The YI was reduced from 23 to 14, 5 and 4 after the CNRL was washed once, twice and thrice, respectively. The results show that more than 95% of proteins can be removed after washing for three times, whereas (based on ester content), up to about 60% of lipid content can be removed. The color of CNRL was greatly decreased after washing at least two times. The decline of YI parallels a corresponding reduction in the N content and ester content of the latex after washing for several times. This suggested that the washing treatment could remove almost all proteins and significant amount of lipids, which cause the discoloration of the CNRL film.

It is clear from above results that by controlling the centrifugation parameters and optimizing the removal of proteins and lipids, the CNRL can be produced at a high yield and high quality.
rate of the non-rubber components that cause coloration of the CNRL coupled with incorporating an effective washing protocol in the process it is possible to produce a very light color CNRL and NR. By using batch centrifugation to obtain CNRL with high yield and high color quality, here the optimum condition identified for centrifugation is that of using FL-latex at 35% TSC centrifuged at 12,000 rpm at 25°C for 30 min followed by a washing protocol.

Another issue to be addressed deals with the known fact that physical properties of NR change with time as a result of storage hardening. The impact of storage on the color change of CNRL films was studied. CNRL films cast from latex prepared at various centrifugation speeds were kept in the dark at ambient temperature for 1 month. The YI of the CNRL films before and after storage for 1 month were shown in Table 4. The YI of all CNRL samples increased around 2–4 units, which could be distinguished by human eyes. The color change of the samples is likely to arise from the oxidation of non-rubbers, that is, proteins and lipids.

The effect of accelerated aging test on NR film was also investigated. Vulcanization is an integral part of the manufacturing process of a NR/latex product. Vulcanizing the rubber at >100°C in the presence of residual non-rubbers will cause changes to the color of the rubber. For this work FL-latex (30% DRC) was centrifuged at 12,000 rpm for 30 min at RT. The cream phase was re-dispersed with distilled water (to 60% DRC) and cast into thin films on petri dish and then dried at 50°C for 48 h, represented as a control NR. Other four samples were further subjected to aging at 100 and 150°C for 1 and 3 h, represented as 100°C-NR, 150°C-NR, 100h-NR, and 150h-NR, respectively. Another film from FL-latex or FNR was used for comparison as a non-centrifuged latex. Each film was then subjected to color analysis and the results are shown in Figure 3. It is clear that the yellowness of NR improved remarkably by centrifugation with YI dropping from 28.15 to 9.23 for the FNR and control NR or centrifuged NR. This difference in YI is discernable by the appearance of the film: A decrease in the yellowness and more transparent of the film cast from the CNR latex compared that of the FNR. After aging at 100°C for 1 and 3 h, the YI increased a bit from 9.23 to 10.28 and 13.65, respectively. While aging at 150°C for 1 and 3 h, the YI increased remarkably from 9.23 to 64.53 and 90.05, respectively. The color of both rubber samples after aging at higher temperature turned to dark-brown in color. These results suggest that heating at high temperature during vulcanization is affecting the color of rubber product.

### 4 CONCLUSIONS

The removal of non-rubber components, in particular proteins and lipids in NR by chemical methods, can help to reduce the YI of NR to a level comparable to that of synthetic polyisoprene. However, a more practical and simpler physical process is proposed in which process parameters such as % TSC of FL-latex, centrifugation speed and duration for centrifugation of latex were optimized to produce the lightest colored CNRL. Using a batch centrifuge, the optimum conditions for centrifugation of FL-latex are identified at % TSC less than 35% at 12,000 rpm for 30 min. Washing of the latex at least two times during the centrifugation process will ensure the

| Speed (rpm) | YI 0 month | YI 1 month | Δ YI |
|------------|------------|------------|------|
| 6000       | 21.31      | 25.06      | 3.75 |
| 8000       | 17.35      | 20.40      | 3.05 |
| 10,000     | 17.35      | 20.30      | 2.95 |
| 12,000     | 15.51      | 17.54      | 2.03 |
| 14,000     | 15.17      | 18.26      | 3.09 |
| 18,000     | 16.72      | Nd         | —    |

Abbreviation: CNRL, concentrated NR latex; FNR, fresh NR; Nd, not determined; NR, natural rubber; YI, yellowness index.
lightest colored CNRL is obtained. The yellow color of the rubber films increased only slightly upon aging for a month. In addition, drying rubber at high temperature and/or for extended period could accelerate the coloration of NR. Our findings demonstrate that niche CNRL and light-colored NR can be produced by fine tuning the centrifugation conditions. The process is simple and feasible for adoption by the industry with the least modification to existing facilities. A light color CNRL can meet demand for niche NR applications where this additional higher treatment cost is justified.

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CONFLICT OF INTEREST
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

DATA AVAILABILITY STATEMENT
Data available on request due to privacy/ethical restrictions.

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