Effect of cellulose nanocrystals from corn cob with dispersion agent polyvinyl pyrrolidone in natural rubber latex film after aging treatment

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Abstract. This study about the resistance of natural rubber latex films using nanocrystals cellulose filler from corn cob waste by aging treatment. Corn cob used as organic filler composed of cellulose, hemicellulose, and lignin. Each component has a potential for reuse, such as cellulose. Cellulose from corn cob has potential application as a filler prepared by hydrolysis process using a strong acid. The producing of natural rubber latex films through coagulant dowsing process. This research started with the pre-vulcanization process of natural rubber latex at 70 °C and followed by process of vulcanization at 110 °C for 20 minutes. Natural rubber latex films that have been produced continued with the aging treatment at 70 °C for 168 hours. The mechanical properties of natural rubber latex films after aging treatment are the tensile strength, elongation at break, M_{100} and M_{300} have performed.

1. Introduction
Natural rubber latex (NRL) obtained from Hevea Brasiliensis, and it consists of rubber particle (cis-1,4 polyisoprene) and nonrubber in water. Natural rubber latex products have disadvantages such as other polymers susceptible to oxidation or degradation due to heat (high temperatures) and low mechanical properties in thin films [1]. To improve the quality of NRL products, they are commonly incorporated with inorganic and organic fillers. However, the addition of fillers has its limitation since some of them are polar while the rubber matrix is nonpolar. Therefore, it is necessary to modify the filler. Several studies reported that modification of fillers succeeds in enhancing the quality of filled rubber [2-4].

Polyvinyl pyrrolidone (PVP) is an amorphous thermoplastic that has been used for various purposes, such as an additive in ultrafiltration membranes, as a stabilizer in suspension polymerization, as a thickener in the cosmetic or food industries, as a coating aid in the photographic industry, and more recently as a sizing material for fiber reinforced composites. [5].

So many factors can significantly affect the durability of a polymeric material, such as temperature, irradiation, moisture, chemicals [6]. The objectives of testing the quality of a product with thermal aging treatment are to see and estimate the rate of change that will take place from the rubber product after being treated with high-temperature effects over a period [7]. Therefore, it will test the mechanical properties of natural rubber latex film using cellulose nanocrystals (CNC)s as a filler and polyvinyl pyrrolidone (PVP) as a dispersion agent after aging treatment.
2. Materials and Methods

2.1. Materials
Raw materials (Corn Cob Waste) were obtained from corn ice trader around Jl. Dr. Mansyur, University of Sumatera Utara (USU), Medan, North Sumatera, Indonesia. Aquadest (H$_2$O), nitric acid (HNO$_3$), sulfuric acid (H$_2$SO$_4$), hydrogen peroxide (H$_2$O$_2$) brand MERCK, sodium hydroxide (NaOH), sodium hypochlorite (NaOCl), sodium nitric (NaNO$_2$), sodium sulfite (Na$_2$SO$_3$) brand Duran.

2.2 Isolation of α-Cellulose from Corn Cob
75 grams of corn cob fiber was inserted into beaker glass, then added by mixture 1 L of 3.5% HNO$_3$ and 10 mg NaNO$_2$, after that it was heated on a hot plate at 90 °C for 2 hours. Then it was filtered, and the fibers are washed until the filtrate is neutral. Next, it was digested with 750 ml of a solution containing 2% NaOH and 2% Na$_2$SO$_3$ at 50 °C for 1 hour. Then it was filtered, and the fibers are washed until the filtrate is neutral. Bleaching was conducted with 250 ml of 1.75% NaOCl solution at boiling temperature for 30 minutes. Then it was filtered, and the fibers are washed until the filtrate is neutral. After that, α-cellulose purification of the sample with 500 ml of 17.5% NaOH solution was obtained at 80 °C for 30 minutes. Then it was filtered, and the fibers are washed until the filtrate is neutral. Bleaching was taken with 10% H$_2$O$_2$ at 60 °C in the oven for 1 hour. Then it was filtered, and the fibers are washed until the filtrate is neutral.

2.3 Isolation of Cellulose Nanocrystals from α-Cellulose
1 grams of α-cellulose dissolved in 25 ml of 45% H$_2$SO$_4$ at 45 °C for 45 min. Then cooled and added with 25 ml aquadest, then left it for one night until the suspension is formed. The suspension was centrifuged at 10000 rpm for 25 min until pH was neutral. Then it was ultrasonicated for 10 minutes, put into the dialysis membrane and soaked in 100 ml aquabidest, left it for four days while stirring. Then the aquadest was evaporated at 70 °C to obtain cellulose nanocrystals.

2.4 Filler
Table 1 shows the Percentage of cellulose nanocrystals (CNC)s with polyvinyl pyrrolidone.

| Material                  | Percentage (%) |
|---------------------------|----------------|
| Cellulose Nanocrystals    | 10             |
| Polyvinyl Pyrrolidone     | 1              |
| Water                     | 89             |

2.5 Natural Rubber Latex Compound
Table 2 shows the formulation of NRL compound for the pre-vulcanization process at 70 °C.

| Compounds                 | Amount (gram) |
|---------------------------|---------------|
| 60 % High Ammonia Latex   | 166.7         |
| 50 % Sulfur Dispersion    | 3             |
| 50 % ZDEC Dispersion      | 3             |
| 30 % ZnO Dispersion       | 0.83          |
| 50 % Antioxidant          | 2             |
| 10 % KOH                  | 3             |
| 10 % Filler Dispersion    | System        |
|                           | 0; 2; 4; 6; 8  |
2.6 Mechanical Properties of Natural Rubber Latex Film
Natural rubber latex film was cut into dumbbell-shaped specimens according to ASTM D 412. The mechanical properties test were performed with Universal Testing Machine Instron 5565 at room temperature.

3. Results and Discussions
The obtained cellulose nanocrystals were spherical shaped with an average particle size of 9-29 nm and the crystallinity is 70.05% from previous research.

3.1. Mechanical Properties of Natural Rubber Latex Film

Figure 1 shows the tensile strength of the natural rubber latex film filled cellulose nanocrystals with polyvinyl pyrrolidone. The tensile strength of the natural rubber latex film before aging is decreased after adding the CNCs and PVP but increased along filler loading. And after aging treatment obtained that the tensile strength increased along with the addition of the filler loading indicate that cellulose nanocrystals have an excellent ability as a filler in natural rubber latex film. This is due to the small size of the cellulose nanocrystals particles that can improve the interaction of film interface. The good interaction of CNCs causes the filler is more easily dispersed in the natural rubber latex evenly throughout the surface, thereby it can reduce the aging effect due to the heat-sensitive rubber, with the addition of a cellulose nanocrystals filler leading to a reduced portion of the degradable rubber [8].

With an addition of PVP, the results showed that has higher tensile strength compared with the products which only added cellulose nanocrystals to the film. Higher tensile strength after aging treatment means that PVP has an ability to increase the strength of a product because with an addition of PVP it can increase the stress on natural rubber latex film [10].
Figure 2 shows the elongation at break of natural rubber latex film filled cellulose nanocrystals as a filler and PVP as a dispersion agent. At a load of filler 2, 4 and 6 grams the elongation at breaks of natural rubber latex films before and after aging relatively same, even an addition of (CNC)s it can generate an extension value. At a load of filler 8 grams, the elongation at break of natural rubber latex film was higher after and before aging treatment. Along with an addition of (CNC)s and PVP, it will produce a high shear stress. High elongation values caused by increased of filler loading improve the film ability on holding the decrease of the film quality due to aging process [11,1]. The chemical degradation of natural rubber through oxidation with thermal-oxidation has superior properties in the product that increases tensile strength and breaking elongation [9]. Overall, the elongation at break values was not significantly different between before and after the aging treatment.

**Figure 3a.** Effect of Aging Treatment in Natural Rubber Latex Film Filled Cellulose Nanocrystals From Corn Cob and Polyvinyl Pyrrolidone to $M_{100}$

**Figure 3b.** Effect of Aging Treatment in Natural Rubber Latex Film Filled Cellulose Nanocrystals From Corn Cob and Polyvinyl Pyrrolidone to $M_{300}$
Figure 3a shows the tensile modulus at 100% elongation ($M_{100}$) is the number of forces that given when the sample has 100% elongation and Figure 3b shows the tensile modulus at 300% elongation ($M_{300}$) represents the amount of force that given when the sample has 300% elongation. Modulus shows the stiffness relativity of the material. The small value shows the elastic nature of the material while the large value shows the stiff properties of the material. During aging, the tensile modulus increases as the main-chain scission take place and effect of cross-linking predominates [12]. This led to the increasing value of the $M_{100}$ and $M_{300}$.

4. Conclusion
Cellulose nanocrystals have a good role as a filler in natural rubber latex film products before and after aging treatment with adding PVP which also produced the products that have high mechanical properties. As proved by the high value of tensile strength, elongation at break and tensile modulus of NRL films produced.

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