The Effect of Drying Temperature on Natural Rubber Latex (NRL) Films with Modification of Nanocrystal Cellulose (NCC) Filler

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Abstract. The process of vulcanization in the formation of NRL products is influenced by temperature at which the drying temperature has important role in the process of crosslinking that can affect the mechanical properties of NRL films produced. This study discusses about the effect of drying temperature on the mechanical properties of NRL films with modification of corn cob NCC filler obtained from the hydrolysis process with sulfuric acid. NCC filler is made of dispersion system involving polyvinylpyrrolidone (PVP) as a dispersion agent. The resulting product was prepared by mixing NRL compound with modified NCC filler with a polyvinylpyrrolidone dispersion agent by coagulant dipping method. The coagulant utilized in the process of formation of NRL films used 10% calcium nitrate and NRL films which formed with variation of drying temperature 100°C, 110°C, and 120°C for 20 minutes. In this study mechanical properties such as tensile strength, elongation at break, and M_{100} dan M_{300} of NRL films has been analyzed. The results showed that mechanical properties such as elongation at break increase with the higher of drying temperature, it was different with tensile strength, M_{100} and M_{300}. In addition, in this study crosslink density and morphological of NRL films were also analyzed.

1. Introduction

In general, NRL have low physical and mechanical properties. To make NRL product with good physical and mechanical properties, curative materials are. In addition to curative materials, filler should also be added. In this study cellulose was used as organic filler.

The addition of cellulose fillers in NRL compounds is expected to improve the performance of better materials with respect to mechanical properties. Many types of cellulose have been used as fillers in polymer materials. These cellulose particles can be distinguished from one another by size, morphology, crystallinity and crystal structure [1].

Besides curative materials and fillers, NRL films are affected by the drying temperature. Drying temperature plays a role in the process of crosslinking which can affect the mechanical properties of the films [2].

For some polymer and rubber products, the temperature influences the properties of the product as some previous studies indicate. High drying temperature causes uncontrolled side reactions which
leads to decreasing product quality [3]. On the other hand, low drying temperature produces better quality and product appearance than high drying temperatures [4].

The present study uses various drying temperature to determine the best temperature in production of NRL films with NCC from corncobs with and without the addition of PVP.

2. Procedure

2.1. NCC Preparation

Cellulose was extracted from corncob waste through several stages. The first process was delignification of corncobs that have been blended smoothly. In the delignification process, 75 grams of corncob were mixed with 1 L of 3.5% HNO3 and 10 mg NaNO2 at 90°C for 2 hours. The bleaching process was then performed using 250 ml of 1.75% NaOCl solution at 70°C for 30 minutes. Subsequent purification of α-cellulose from the sample with 500 ml of 17.5% NaOH solution at 80°C for 30 minutes was performed.

After α-cellulose was obtained, then the process of nanocrystal cellulose isolation began. This process uses acid hydrolysis method with 45% sulfuric acid. Then it was followed by centrifugation, ultrasonification and separation with dialysis membrane.

2.2. The Production of NRL Films

10% dispersion solution was prepared which is a corncob nanocrystal cellulose and PVP.

| Ingredient | Percentage (%) |
|------------|----------------|
| NCC        | 10             |
| PVP        | 0              |
| Water      | 90             |

Table 1. Dispersion System of NCC and PVP

The pre-vulcanization process was carried out at 70 °C for 10 minutes with formulation in Table 2. And then vulcanization process with various drying temperature of 100°C, 110°C, and 120°C for 20 minutes followed.

| Ingredient | Composition (gram) |
|------------|--------------------|
| 60 % High Ammonia Lateks | 166.7 |
| 50 % Sulphur | 3 |
| 50 % ZDEC | 3 |
| 30 % ZnO | 0.83 |
| 50 % Antioxidant | 2 |
| 10 % KOH | 3 |
| 10 % Dispersion of NCC and PVP | 4 |

Table 2. Formulation for NRL Compounds Ingredients

2.3. Determination of Crosslink Density

Crosslink Density of NRL films in accordance to ASTM D471 is determined using the following equation by Flory-Rehner [5]:

\[
(2M_c^{-1}) = \left[ -\ln(1-V_c) - V_c - \frac{2}{V_c} \right] = \frac{2\rho_{NRL}V_0(V_c^{1/3})}{V_c^{1/3}}
\]
2.4. Mechanical Testing and Morphology
The NRL films were cut to specimen for tensile strength with ASTM D 412 standard. The tensile strength was performed using an INSTRON 5565 engine at speed of 500 mm/min with room temperature. Then, morphological test was analyzed using Scanning Electron Microscope (SEM) JEOLJSM 6360-LA.

3. Result and discussion

3.1. Crosslink Density of NRL Films
The crosslink bond increase will occur if the cure rate of NRL also increase. The NRL cure rate is affected by the drying temperature.

In addition, the influence of PVP is also important. However, high drying temperature didn’t make PVP work optimally, thus disrupting the formation of crosslink and decreasing the value of crosslink density that occurs will affect the mechanical properties of NRL films.

![Figure 1. Effect of Drying Temperature on Crosslink Density on NRL Films with 4 Gram NCC Filler from CornCob with and Without Addition of PVP](image)

Figure 1 shows that increasing drying temperature causes decrease in crosslink density value of NRL films without and with the addition of PVP. High drying temperature will cause the drying process runs faster than films formation, thereby reducing the occurrence of crosslink reaction. This is supported by Milani, et al. (2013), drying temperature that is too high can also produce unstable crosslink [6].

NRL films with addition of PVP have a higher value than without addition of PVP. This happens because PVP has worked in dispersing filler into the latex compound. PVP has contribution in increasing the number of crosslink formed on NRL films. This is because PVP contains an amine which can increase the pH of natural rubber compound so that it will increase the cure rate [7].

3.2. Tensile Strength
The value of tensile strength was related to the value of crosslink density. The tensile strength will reach the maximum value at the largest crosslink density value. This is because the crosslink bond will withstand most of the force applied to the NRL films [8].
Figure 2. Effect of Drying Temperature on Tensile Strength on NRL Films with 4 Gram NCC Filler from CornCob with and Without Addition of PVP

Figure 2 shows that the higher drying temperature, the lower tensile strength value of the NRL films will decrease. This is because the high drying temperature will interfere with the formation of crosslink and will result in an unstable crosslink bond so that the required force to break the NRL films is smaller. More crosslink bond then leads to more force required to break the NRL films so that the value of tensile strength is higher too. The results of this study indicates that high drying temperature resulted in lower tensile strength value. As seen on the figure of 110 and 120°C drying temperature have value lower than the drying temperature of 100°C. The result are supported by the result of Harahap, et al. (2013) which observed the effect of the drying temperature on tensile strength of the NRL films. The results show the drying temperature at 100°C will produce the relatively higher tensile strength than the drying temperature at 120°C [9].

From Figure 2, the addition of PVP to the NRL produce causes higher tensile strength than without the addition of PVP. This is because PVP disperses the NCC filler and will prevent the agglomeration of NRL films. This is supported by the result of Mondal, et al. (2013) which says that the addition of PVP increases tensile strength value in nanocomposite films [10]. This can also be explained by SEM analysis of NRL films. It supports the value of tensile strength. The decrease of tensile strength with increasing drying temperature can be explained in Figure 3.

Figure 3. SEM Analysis of NRL Films With Filler and Without PVP At Drying Temperature (a) 100°C, (b) 110°C, and (c) 120°C

Figure 3 (a) shows that the corncob's NCC fillers are well dispersed in NRL because the NRL and filler particles were more evenly distributed on the surface of the films. This is because NCC has fairly
good stability at 100°C drying temperature even without PVP. Therefore, high tensile strength was obtained drying temperature at 100°C.

Figure 3 (b) and (c) show the NCC filler particles from corncob were not well dispersed and tend to agglomerate in NRL films. This happens because high drying temperature will cause the movement of NCC filler particles faster so that easy to experience collisions and agglomeration occurs. Agglomeration in NRL is what causes the value of tensile strength becomes lower. It was proven by the value of tensile strength at 110°C and 120°C drying temperature getting lower.

3.3. Elongation At Break

The magnitude of the length of sample being tested is kept until it has been break off and has a relation inversely proportional with modulus.

![Figure 4](image-url)

**Figure 4.** Effect of Drying Temperature on Elongation At Break on NRL Films with 4 Gram NCC Filler from CornCob with and Without Addition of PVP

Figure 4 shows that elongation at break value in NRL films with 120°C drying temperature give higher result than NRL films with 100°C and 110°C drying temperature. In general, the reaction will occur more quickly when the temperature is raised. If the reaction rate is higher, then the distribution of the compound will increase as well. This is supported by Harahap, et al (2013), which observed that at higher drying temperature an increased distribution of curative compounds within NRL results in NRL films having elastic properties [9].

The effect of addition of PVP gives higher result when compared to NRL films without the addition of PVP. This is because PVP acts as plasticizer that increase elasticity to the NRL films [11].

3.4. M100 and M300

M100 and M300 show the elasticity of the NRL films.

![Figure 5](image-url)

**Figure 5.** Effect of Drying Temperature on M100 on NRL Films with 4 Gram NCC Filler from CornCob with and Without Addition of PVP
Figures 5 and 6 show M100 and M300 give the higher value for 100°C drying temperature. This related to the crosslink density value of the NRL films, where at 100°C crosslink density of the films also show the higher value. Increasing the crosslink bond on the films, causing the film to be formed will be stiffer but has the higher tensile strength. The crosslink makes the NRL films harder and stronger [12].

Figures 5 and 6 also show that the M100 and M300 values were in maximum at addition of 1% PVP. PVP was used as a binder with the advantage of producing better comparability [13].

3.5. Characterization of Fourier Transform Infra-Red (FTIR)

FTIR of NRL films with NCC fillers with and without PVP dispersion agent can be seen in figure 7.

![Graph showing the effect of drying temperature on M300](image)

**Figure 6.** Effect of Drying Temperature on M300 on NRL Films with 4 Gram NCC Filler from CornCob with and Without Addition of PVP

There are several apex peaks that are key in analyzing the functional group changes of the NRL films. The absorption peak at the wave number 1658.78 cm⁻¹ indicates the presence of the C = O group in which this group represents the existence of amide group. This amide group was carried by PVP where it acts as an excellent dispersion agent [14].
Large bands at wave numbers 3483.44 and 3282.84 cm\(^{-1}\) indicate the presence of -OH groups. At the absorption peak with wave number 2819.93 cm\(^{-1}\) indicates the presence of C-H and C-O carbonyl groups at wave numbers 1739.79 cm\(^{-1}\) which was also typical cellulose group. This indicates that cellulose can react with curative that can produce complexes that can form strong chemical interactions with each other [15].

4. Conclusions
The NCC filler is an organic filler that has good reinforcing properties and PVP is able to modify the NCC filler so as to improve the mechanical properties of the NRL films. On the other hand, increased drying temperature decreases the value of tensile strength and tensile modulus, but increases the value of elongation at break of the NRL films.

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