Physical and mechanical properties of natural rubber latex film (Rubber Dam) products with filler nanocrystal cellulose from peanut shell (Arachis hypogea L.) and synthetic dyes

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Abstract. Rubber dam is considered as an ideal device for tooth isolation. Rubber dam is one of the example product from natural rubber latex. Peanut shell is one of the industrial waste containing 35.7% of cellulose. Nanocrystal cellulose from peanut shell can be an alternative waste utilization and have potential as filler in natural rubber latex films. Studies about effect of loading nanocrystal crystal as filler on natural rubber latex films with polyvinyl pyrrolidone (PVP) and using synthetic dyes have been carried out on crosslink density and mechanical properties such as tensile strength, elongation at break and tensile modulus. The process begins with pre-vulcanization of natural rubber latex at temperature 70°C with 0, 2, 4, 6, 8 gram of filler loading and followed by vulcanization at 120°C for 10 minutes. The results obtained with loading nanocrystal crystal filler using synthetic dyes for physical properties, crosslink density, will increase with the increase of filler loading. For mechanical properties, tensile strength and tensile modulus will increase with greater filler loading, while elongation at break will decrease. The best results are obtained for mechanical properties of natural rubber latex film products using synthetic dye on 6 gram nanocrystal cellulose of filler loading.

1. Introduction
Rubber dam is a thin sheet product that is used to facilitate dental care during dental surgery [1]. Most rubber dams are made of natural rubber latex as the main component [2]. Natural rubber latex (NRL) is raw material that has an important role in world industry. Natural rubber latex was obtained from Hevea brasiliensis tree in the form of colloidal dispersion with cis-1,4 isoprene compound. Natural rubber latex which contains 60% of dry rubber is widely used in household and medical needs [3].

In order to produces high quality natural rubber latex product, it is necessary to be produced into a latex compound. Natural rubber latex compound consists of curative and additive ingredients. Additives will not affect mechanical and physical properties such as the addition of dyes and fragrances. Curative materials affect the mechanical and physical properties of natural rubber latex films such as sulphur, ZnO, antioxidants, KOH, ZDEC and fillers. In this study cellulose was used as organic filler.

The use of organic fillers such as vegetable fiber in the polymer matrix is an alternative to increase biodegradability and reduce production cost [4]. Fillers with smaller sizes such as nanomaterials is better. Various multifunctional nanomaterials are used as fillers and antioxidant agents to enhance the mechanical and thermal of natural rubber latex product. Nano fillers have main role on improving mechanical properties of natural rubber latex [5]. Nanofillers can offer high stiffness and strength by inhibiting the propagation of cracks and delaying the breakdown of materials, along with an increase in the thermal stability of nanocomposites. To achieve the desired properties, the nanofillers must sufficiently disperse in the latex, as poor dispersion results in deteriorating of the performance properties [6].
Organic fillers is used from peanut shell. In many villages, peanut shells are only used for fuel, animal feed, traditional medicine or thrown away. Peanut shells contain cellulose (35.7%), lignin (30.2%), hemicelluloses (18.7%) and ash content (5.9%) [7].

2. Method

2.1. Preparation of nanocrystal cellulose

Peanut shell was extracted to get cellulose that consists of several stages. The first process is delignification of peanut shell to weaken the lignin bond. In pre-treatment, peanut shells were mixed with 3.5% HNO₃ and NaNO₂. Delignification process 2% NaOH and 2% Na₂SO₃. γ cellulose separation process with 17.5% NaOH and bleaching process with 1.75% NaOCl. After getting α-cellulose, for nanocrystal cellulose process, begins with hydrolysis using 45% sulfuric acid, then ultrasonicated and dialyzed in membrane.

2.2. Preparation of natural rubber latex film

10% filler was prepared to disperse the NCC into a dispersion system consisting of water and PVP. Table 1 provides the composition of NCC filler dispersion formulations.

| Ingredient     | Percentage (%) |
|----------------|----------------|
| NCC            | 10             |
| PVP            | 1              |
| Air            | 89             |

The pre-vulcanization process was carried out at 70 °C for 15 minutes with formulation in Table 2. And vulcanization process at 120 °C for 10 minutes.

| Ingredient                                      | Composition (gram) |
|------------------------------------------------|--------------------|
| 60 % High Ammonia Latex                        | 166.7              |
| 50 % Sulfur Dispersion                         | 1.2                |
| 50 % ZDEC Dispersion                           | 1                  |
| 30 % ZnO Dispersion                            | 0.83               |
| 50 % Antioxidant                               | 4                  |
| 10% KOH                                        | 2                  |
| 10 % Dispersion NCC and PVP                    | 0; 2; 4; 6; 8      |
| Synthetic dyes                                 | 0.6                |

2.3. Crosslink density

Calculation of Crosslink density based on ASTM D471 was calculated using the equation of Flory-Rehner [8]

\[
\left(2M_c^e\right)^{\frac{1}{2}} = \frac{\ln(1-V_r) - V_r \chi V_r^2}{2\phi_{NRL} V_0(V_r^{1/2})}
\]

\[
V_r = \frac{W_d/\rho_d}{W_d/\rho_d + W_{sol}/\rho_{sol}}
\]

2.4. Mechanical properties

Tensile strength testing on natural rubber latex film was cut according to ASTM D 412 standard. Tensile strength testing using INSTRON 5565 at speed of 500 mm/min with ambient temperature.
3. Result and discussions

3.1. Crosslink density on natural rubber latex film

Crosslink density is a value that indicates the amount of cross-linking in natural rubber latex film products using synthetic dyes. Figure 1. shows the higher of filler loading dispersion will increase the crosslink density, the highest value of crosslink density with 8 gram filler loading. This is related to Mc. Average molecular weight (Mc) is a parameter characteristics of crosslink polymers related to crosslink density. The value of Mc impact on physical and mechanical properties such as tensile strength and tensile modulus of polymers that support elastomer applications [9]. The crosslink density value increase with the addition of filler. Nuraya et al (2012) supported that increasing the loading fillers will increase the adhesion between fillers and natural rubber latex which results in reducing solvent entering natural rubber latex and affect lower swelling index values and increase crosslink density values [10].

![Crosslink Density vs Filler Loading](image1.png)

**Figure 1.** Effect of nanocrystal cellulose filler loading on the crosslink density of natural rubber latex films using synthetic dyes.

3.2. Tensile strength on natural rubber latex films

Tensile strength is the maximum force that used to decide the sample per initial cross-sectional area.

![Tensile Strength vs Filler Loading](image2.png)

**Figure 2.** Effect of nanocrystal cellulose filler loading on the tensile strength of natural rubber latex films using synthetic dyes.

Figure 2. shows that the increasing of filler loading will increase the tensile strength value. The highest value of tensile strength is obtained from 6 gram filler loading. The increase in tensile strength and tensile modulus values are observed from the amount of nanocrystal cellulose (NCC) added, which related to the limitation of polymer chain movement around the NCC [11]. However, at the loading filler.
of 8 gram the value tensile strength decrease, this is supported by Harahap et al (2018) when crosslink density passes in certain point the tensile strength will decrease [12].

3.3. Elongation at break on natural rubber latex films
Elongation at break was measured when sample that is tested on tensile strength break related to tensile modulus.

![Figure 3](image-url) Effect of nanocrystal cellulose filler loading on elongation at break of natural rubber latex films using synthetic dyes.

Figure 3. shows the effect of nanocrystal crystal loading on elongation at break, as filler loading increases, the elongation at break value will decrease due to the addition of fillers will increase chemical interactions each phase that cause the chain difficult to move and become more rigid. This decrease is closely related to crosslink density which causing mobility and rubber molecular chain more resistant. Mobility resistance or movement of the rubber molecular chain will cause the rubber vulcanisate to break [13].

3.4. Tensile modulus $M_{100}$ and $M_{300}$ on natural rubber latex films
$M_{100}$ and $M_{300}$ show the elasticity of natural rubber latex when being pulled.

![Figure 4](image-url) Effect of nanocrystal cellulose filler loading $M_{100}$ of natural rubber latex films using synthetic dyes.
Figure 5. Effect of nanocrystal cellulose filler loading $M_{300}$ of natural rubber latex films using synthetic dyes.

Figure 4. and Figure 5. Shows the highest value of $M_{100}$ and $M_{300}$ obtain filler loading of 6 gram, which mean filler loading at 8 gram will decrease value tensile modulus. This increase in modulus tensile value is influenced by the strong interaction between the matrix and the filler which increases the number of crosslinking polymer chains and reduces flexibility of natural rubber latex, so the elongation at break value decreases but increase the tensile modulus which results natural rubber latex more harder and stiff. Decreased modulus tensile value is due to agglomeration of filler at higher loading [14].

4. Conclusions
From the results, the amount of filler loading on film natural rubber latex (rubber dam) increase the crosslink density, tensile strength, and tensile modulus but decreasing the elongation at break. Especially in 6 gram filler dispersion which has the highest mechanical properties than others filler loading.

References
[1] Khathoon, S.M Shabana and James D R 2015 Journal of Pharmaceutical Sciences and Research 7 1007 - 1010.
[2] NOHSC. 2011. Material Safety Data Sheet ivoclar Vivadent Optrad Dam/ Optra Dam Plus.
[3] Jayathilaka I, Thilini U A and S M Egodage. 2018 Powdered Corn Grain and Cornflour on Properties of Natural Rubber Latex Vulcanizates: Effect of Filler Loading Moratuwa Engineering Research Conf. (Katubedda: University of Moratuwa) pp 235 -240
[4] Zini E, Baiardo M, Armelao L and Scandola M 2004. Macromolecular Bioscience, 4 286 - 295
[5] Ghosh O S, S Gayathri, P Sudhakara, S K Misra and J Jayaramudu 2017 Rubber Nano Blends Preparation, Characterization and Applications (Springer links) pp 15-65
[6] TE Motaung, A S Luyt and S Thomas 2011 Polymer Composites 32 1289–1296
[7] Raju GU, Kumarappa S and Gaitonde V N 2012 Material Environmental Science 3 907 – 916
[8] Fuquan Z, L Lusheng, W Yongzhou, W Yueqiong,, H Hongsai, L Puwang, P Zhang and Z Rizhong 2016 Journal of Rare Earths 34 221 – 226.
[9] Ding Z Y, Aklonis, J J and Salovey R Journal Polymer Science 29 1035 -1038.
[10] Nuraya A S S, A Baharin, A R Azura, M H Mas R H, I Mazlan, M Adnan and A A Noorziah. 2012 Journal of Rubber Research 15 124 – 140.
[11] Zhang C, T Zhail, Ronald S, Craig C, Yi D and Lih-Sheng T 2014 Journal of Biobased Materials and Bioenergy 8 317 – 324
[12] Harahap H, Yuni L L, Taslim, Iriany, Halimatuddhalina N and Hamda E A Proc of the Int. Conf. Material and Metallurgical Engineering and Technology 945 020060-1 - 020060
[13] Yuniati, Irwin Syahri Cebro., Nurlaili. 2013 Proceeding Seminar Nasional Tahunan Teknik Mesin XII (Bandar Lampung: BKS TM Indonesia)
[14] Kader M M A, S M Abdel-wehab, M A Helal and H H Hassan 2012 Housing and Building National Research center 8 69–74