Comparison of weight loss in natural rubber latex film (rubber dam) filled nanocrystal cellulose and synthetic dyes with soil burial methods

Hamidah Harahap*, Yoeselyn Wangi, Toni Chandra and Halimatuddahliana

Department of Chemical Engineering, Universitas Sumatera Utara, Almamater Street, Campus USU Medan 20155

*Email: hamidah.usu@gmail.com

Abstract. Biodegradation of natural rubber latex products filled with nanocrystal cellulose from peanut shell is carried out by soil burial methods with and without using fertilizer. Testing is done by calculating the loss of sample weight for 5 weeks with observation every 1 week. Samples were tested the morphology using Scanning Electron Microscope (SEM) and Fourier Transform Infra Red (FTIR). Natural rubber latex film samples showed that the loading of nanocrystal cellulose fillers from peanut shells was biodegradable faster in soil burial method with addition of fertilizer in soil compared to no addition of fertilizer.

1. Introduction
Rubber dam is a thin sheet of natural rubber latex that is used during dental treatment process. The principle of rubber dam is to isolate one or more teeth so that the dentist can focus the work on specific area. Rubber dam is usually made from natural rubber latex [1]. Natural rubber latex is a renewable natural resource that has excellent strength, flexibility and elasticity [2]. Natural rubber latex is a stable colloidal dispersion system consists of cis-1,4-polyisoprene as a main constituent with a high molecular mass in liquid [3].

According to Forrest [4], around 20 – 30% of solid latex wastes are disposed in landfill that caused environmental damage. To resolve this environmental damage, biodegradation can be applied in waste processing. Biodegradation is a natural process which microorganisms use complex organic material as a source of carbon and energy and biologically convert into simpler forms [5]. The difficulty of natural rubber latex waste to be degraded is due to curative materials such as sulphur, antioxidants and others. Sulphur cross linking prevents natural rubber latex products to decompose in environment [6].

Cellulose is one of the most potential organic filler because it is an abundant amount of natural polymer [7]. The advantages of cellulose are a renewable resource, high tensile strength properties and biodegradable [8]. Peanut shell is one of organic cellulose source. Peanut shell contains cellulose (35,7%), hemicellulose (18,7%), lignin (30,2%) and ash content (5,9%) [9].

Several studies on natural rubber latex products with organic fillers such as rice husk [10], peanut shell [11] and corn cob [12] where adding of organic filler will increase the physical and mechanical properties and the biodegradability.

With the increase concern about environmental damage that is caused by non-biodegradable materials, the development of biodegradable materials can be applied to overcome this concern. The purpose of this research is to study the effect of loading nanocrystal cellulose filler from peanut shell on
biodegradation properties by burying the test sample in the soil with and without fertilizer to observe changes and weight lost during the biodegradation process.

2. Methods

2.1. Preparation of nanocrystal cellulose (NCC)

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 1 L of 3.5% HNO₃ and NaNO₂. Delignification process with NaOH and Na₂SO₃. γ-cellulose separation process mixed with 17.5% NaOH. Bleaching 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

Nanocrystal cellulose, PVP and water were prepared by dispersion process in ball mill with 10% NCC, 1% PVP and water. Then fillers were mixed with natural rubber latex compound in prevulcanization process. The prevulcanization process was carried out at 70°C with formulation as shown in Table 1. Vulcanization process was carried at 120 °C for10 minutes.

Table 1. Formulation of natural rubber latex compounds.

| Compounds                              | Composition (gram) |
|----------------------------------------|--------------------|
| 60 % High Ammonia Latex                | 166.7              |
| 50 % Sulfur Dispersion                 | 1.2                |
| 50 % ZDEC Dispersion                   | 1.0                |
| 30 % ZnO Dispersion                    | 0.83               |
| 50 % Antioxidant                       | 4.0                |
| 10% KOH                                | 2.0                |
| 10 % Dispersion NCC, PVP and water     | 0; 2; 4; 6; 8      |
| Synthetic dyes                         | 0.6                |

2.3. Biodegradation of natural rubber latex film

Natural rubber latex products are cut into 4x4 cm specimens, weighed and buried in soil with and without fertilizer for 5 weeks with observations every 1 week. The sample is then removed from soil and washed with distillate water to remove impurities. The samples are dried in oven at 50°C until constant weight. The samples were then tested the morphology using Scanning Electron Microscope (SEM) and characterized by Fourier Transform Infra Red (FTIR). The weight loss percentage after biodegradation was determined by:

\[
\text{weight loss} = \frac{W_o - W(t)}{W_o} \times 100
\]

WhereWo is the initial mass and W(t) is the remaining mass at any given time, t.
3. Result and discussion

3.1. Weight loss

![Graph](image)

**Figure 1.** Weight loss of natural rubber latex film with synthetic dye for 5 weeks (a) without fertilizer and (b) with fertilizer.

Figure 1. shows the effect of loading nanocrystal cellulose from peanut shells on weight loss (%) for (a) without fertilizer and (b) with fertilizer on the biodegradation process. It could be observed that, the greater the filler content, the weight loss percentage will increase. The smallest percentage of weight loss is found at 0 gram filler loading with 3.77% and 5.68% respectively without and with fertilizer. Filler loading of 8 gram gives the highest percentage of weight loss with 12.22% and 16.00% respectively without and with fertilizer.

The addition of nanocrystal cellulose from peanut shell on natural rubber latex will increase the biodegradation rate. This is because cellulose in the film is consumed faster by the microorganisms than natural rubber latex leading to enhancement in porosity, void formation and damage the natural rubber latex matrix composition. As the result, the formation will be broken down into smaller particles and facilitates the biodegradation process [13]. Similar results were also obtained by Abraham et al [14] and Kadry and Abou [15] about the effect of loading nanocellulose fillers on biodegradation, which showed that increasing the amount of fillers will improve the biodegradation rate of the latex film.

Microbial activity in degrading is strongly influenced by nutrient content in soil such as nitrogen (N), phosphor (P) and potassium (K) [16]. Nutrient is an important factor in biodegradation process of a material. The addition of nutrients such as fertilizer will improve the biodegradation rate because increasing the carbon and nutrient content as a source of energy for microorganisms in the soil compared with no nutrient addition [17]. Vyas and Dave [16] described the effect of fertilizer on NPK content in soil that there is an increase in nitrogen, phosphor and potassium content in soil. Agarry and Oghenejoboh [18] investigated the biodegradation of naphthalene with and without fertilizer loading in soil. It was obtained that the best biodegradation rate with fertilizer loading in soil.
3.2. Morphology

![Image](a)

![Image](b)

**Figure 2.** SEM results on biodegradation natural rubber latex with 8 gram filler loading with magnification of 2000x (a) without fertilizer and (b) with fertilizer.

Figure 2 shows the results of Scanning Electron Microscope (SEM) of natural rubber latex surface that is buried with 8 gram of nanocrystallinene cellulose loading. Figure 2a and 2b show the SEM surface for soil burial without fertilizer and with fertilizer in sequence at magnification of 2000x.

Both images have significant differences where figure 2a shows an uneven surface like eroded. While figure 2b shows a surface that begins to rot, torn and voids. This difference is due to the addition of fertilizer that enhance the nutrients source in soil which will increase the population of microbial and accelerate the biodegradation process by microbes on natural rubber latex films.

Muniady et al [19] said that microbial attack took place on the sample surface, which was accompanied by massive loss of oligomer that leads to an eroded surface. This observation was evidenced through the increase in surface roughness and erosion, which was detectable in the natural rubber latex as the filler loading increased. In addition, there were cracks and voids on the surface caused by short oligomer through oxidative degradation. Microorganisms then metabolize oligomer and lead to the formation of void and eroded surfaces.

Hapuarachichi et al [20] described that the treatment of bacteria will give better results of biodegradation of natural rubber latex. It is indicated by shredded and eroded SEM images compared with no treatment that have smoother surface. The addition of filler content will increase the formation of cracks and micro cavities in SEM [21].

3.3. Fourier Transform Infra Red (FTIR)

![Graph](a)

![Graph](b)

![Graph](c)

**Figure 3.** FTIR spectrum natural rubber latex with 8 gram filler loading (a) without fertilizer, (b) with fertilizer and (c) before soil burial.
Figure 3 show FTIR spectrum natural rubber latex with 8 gram filler loading on transmittance for a,b and c, respectively without fertilizer, with fertilizer and before soil burial. FTIR characteristic is tool to determine whether new functional groups are formed or disappearing groups and to identify biodegradability of a material.

Before soil burial, there is absorption at 3299,14 cm\(^{-1}\) which are OH stretching. There are peaks in the region of 1743,47 cm\(^{-1}\) and 1663,15 cm\(^{-1}\) which corresponds to C=O stretching and C=C stretching, respectively. Peaks at region of 2964,61 cm\(^{-1}\) is a C-H stretching group followed by C-O stretching at 1127,98 cm\(^{-1}\).

After soil burial with and without fertilizer, the intensity of the bonds were decreased. OH stretching group decrease with absorption at range 3250 – 3420 cm\(^{-1}\) respectively with and without fertilizer. Peaks at region of 1738,08 cm\(^{-1}\) and 1663,20 cm\(^{-1}\) which is C=O and C=C groups also have weakened intensity [21]. Peaks at 2858,02 cm\(^{-1}\) is C-H group which attributed with C-O group at 1128,30 cm\(^{-1}\) also decreased due to microbial attack in the soil during biodegradation process. Similar results is obtained by Manaila et al [22]. The intensity decrease is more significant than without fertilizer. The weakened intensity shows that natural rubber latex with 8 gram filler loading has been degraded during soil burial [20].

4. Conclusion
Filler loading of nanocrystal cellulose from peanut shell can increase the biodegradability of natural rubber latex products in soil. 8 gram of filler loading provides the best biodegradation rate compared to other variations that can be proved with the weight loss percentage for both with and without fertilizer. Biodegradation process in soil with addition of fertilizer has better results than without fertilizer. This is supported by the Scanning Electron Microscope (SEM) test and Fourier Transform Infra Red (FTIR).

References
[1] Svec T A, John M P, David L dan Trenholm N 1996 *Journal of Endodontics* 22 253-256
[2] Blackley D C 1997 *Polymer latices science and technology* (London: Chapman & Hall)
[3] R Roslim, M Y Amir H and P T Augurio 2012 *Journal of Engineering Science* 8 15-27
[4] Forrest M J 2014 *Recycling and Re-use of Waste Rubber* (UK: Smithers Rapra)
[5] Das M P and Kumar S 2014 *International Journal of ChemTech Research* 6 300
[6] Misman M A and A R Azura *Advanced Materials Research* 844 486-489
[7] Chen D, Lawton D, Thomson M R And Liu Q 2012 *Carbohydrate Polymers* 90 709-
[8] Zaaba N F, Hanafi I and Mariatti J 2014 *BioResources*, 9 2128-2142
[9] Punnadiyil R K, Sreejith M P and E Purushothaman 2016 *Journal of Chemical and Pharmaceutical Sciences* pp12-16
[10] Ramasamy S, H Ismail and Y Munusamy 2015 *Journal of Vinyl & Additive Technology* 21 128-133
[11] Sareena C, M P Sreejith, M T Ramesan and E Purushothaman 2014 *Journal of Reinforced Plastics and Composites* 33 412-429
[12] Harahap H, Y A Lubis, Taslim, Iriany, H Nasution and H E Agustini 2018 *Int. Conf. on Materials and Metallurgical Engineering and Technology* 1945 020060
[13] Bras J, M L Hassan, C Bruzesse, E A Hassan, N A El-Wakil and A Dufresne 2010 *Industrial Crops and Products* 32 627-633
[14] Abraham E, P A Elbi, B Deepa, P Jyotishkumar, L A Pothen, S S Narine and S Thomas 2012 *Polymer Degradation and Stability* 97 2378-2387
[15] Kadry G and A E F A El-Hakim 2015 *Research Journal of Pharmacetical Biological and Chemical Science* 6 659-666
[16] Vyas T K and B P Dave 2010 *Indian Journal of Marine Sciences* 39 143-150
[17] Satti S M, A A Shah, T L Marsh and R Auras 2018 *Journal of Polymers and the Environment* 26 3848-3857
[18] Agarry S E and K M Oghenejoboh 2015 *International Journal of Environmental Bioremediation & Biodegradation* 3 48-53
[19] Muniandy K, H Ismail and N Othman 2012 *BioResources* 7 957-971
[20] Hapuarachchi S N S, S R Kariyapper, M B D M D Gunawaranda, S Edodage and TU Ariyadasa 2016 *Biodegradation of natural rubber latex by a novel bacterial species isolated from soil* (Katubedda: University of Moratuwa) pp 293-296
[21] Taib M N A M, W A Yehye and N M Julkapli *Fibers and Polymers* 20 165-176
[22] Manaila E, M D Stelescu and G Craciun *Int. Journal of Molecular Sciences* 19 2862