Photodegradation Effect of Structure of Linear Low Density Polyethylene – Starch – Clay Nanocomposite Film

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Abstract. Degradable plastic is a topic that continues to be discussed, especially for disposable applications. Blending starch with commercial plastics such as Linear Low Density Polyethylene was the alternative that continues to be developed. The degradation mechanism of biopolymer may occur as microorganisms and also through the mechanism of exposure to sunlight or Ultra Violet light. In this work, degradation test on Linier Low Density Polyethylene-starch-clay nanocomposite film was conducted with a Xenon Arc. Nanocomposite samples were prepared from masterbatch clay and 10% wt and 20% wt of starch. Pure Linear Low Density Polyethylene was used as a control parameter. On day 7th, 20% wt starch sample was already brittle and 10%wt starch was brittle on day 14th. In the 3th day of Xenon Arc aging, starch granulates already disappeared on the surface of sample and the degraded starch leave a hole on the surface of Linear Low Density Polyethylene matrix. The hole dimension became larger with time increasing of Xenon Arc aging. Thermo Gravimetric Analysis result showed decreasing onset temperature degradation for the starch. The oxidation and degradation of starch was occurred during the aging. Meanwhile onset temperature degradation of Linear Low Density Polyethylene in the nanocomposite sample was increased might be this occurred due to the formation of crosslink on Linear Low Density Polyethylene before degraded. Image of 10% wt and 20% wt starch observed using Atomic Force Microscope also showed that the degradation occurs on starch. It was proved by the image after 14 days aging become the same as the image of Linear Low Density Polyethylene used as a control that showed the lamella of Linier Low Density Polyethylene.

1. Introduction
The disposable plastic packaging was the largest contributor to waste production. To reduce the problem of plastic waste, a lot of research done on plastic degradable either use of natural resources or the use of additives such as pro-oxidant [1-5]. Starch was one of the natural resource that was developed in packaging material. However, the addition of starch could reduce mechanical, barrier properties and transparency [1, 3]. Reinforce nanoclay was used to enhance mechanical and barrier properties of starch plastic.

Blending starch with commercial plastic will improve degradability [1,4]. Degradation in polymer material can be stimulated by different factor, such as light, moisture, heat and microorganism. Photodegradation generates material to undergo degradation mechanism with atmospheric oxygen in the presence of light [6-8]. Photodegradation can be done with direct sunlight exposure method.
(outdoor) or using accelerated weathering chamber (indoor), used to exposed material at accelerated atmospheric condition [6,8]. For outdoor exposure test, needed long time period to complete the experiment, compare to indoor method that faster, easier and expected close to real condition or similar to outdoor exposure.

For further analysis of photodegradation is necessary to evaluate the result. Several analysis were performed after photodegradation such as, color changes, mechanical, chemical and thermal properties [6,8]. The objective of this research was to characterized morphological structure of degradable LLDPE starch clay nanocomposites after photodegradation.

2. Experimental

2.1. Material
Clay used was organo layer silicate (OLS) cloisite 20A from Southern Clay that had been treated with glycerol monostearate (GMS). Glycerol monostearate was provided by anonymous local company. Ethanol was used as a solvent to dissolve GMS. Polyethylene graft maleic anhydride (PEgMA) from Sigma Aldrich and cassava starch from commercial market was used as a compatibilizer and biodegradable material. LLDPE Asrene UF 1810, PT. Chandra Asri for blown film application was used as polymer matrix

2.2. Methods and Characterization
PEgMA, OLS treated with GMS and cassava starch was masterbatching with Rheomix Haake refer to our previous work [9]. Masterbatch and LLDPE were dry mixed before feeding to twin screw extruder, ZK 25 E-Collin to produce compound at 40 – 170°C and 20 rpm. Then, the compound was dried in an oven vacuum for 24 hours at 50°C. Sample film was prepared by Blown Film Rheomix Haake. Degradation process of sample film was conducted using Xenon Arc Ci 3000 at the condition: radiant 0.55 ± 0.01 W/m² @ 340 nm, a single cycle run for 4.8 hours with 1 hour dark and 3.8 lights. The condition of 1 hour dark were at temperatures of 38°C; RH: 95% and 3.8 hours light were at temperatures of 89°C and RH of 50% for 14 days (fig.1). Thermal gravimetric analysis (TG 209 Tarsus, Netzch) was performed at 50 – 600°C under nitrogen gas atmosphere.

Samples surface after treated in Xenon Arc were characterized with SEM (JSM-6510LA, Jeol) with a magnification of 500 times. The samples were coated with thin layer of platinum. The surface morphological of thin layer sample was also examined using Atomic Force Microscope (AFM-5500, Agilent). Samples were placed between two silicon wafers, heated at 120°C and then pressed to form a thin layer prior to AFM preparation test. The AFM observation by mean topographic and phase images analysis were taken simultaneously, perform in non-contact mode and scan size 5x5μ. Fourier Transform Infra Red (FTIR) spectroscopy (Bruker, Tensor 27) were conducted to observe the degradation that occurs. Samples measured with free standing film method.
3. Result and Discussion

Figure 1.a showed film samples before aging with xenon Arc and figure 1.b showed most film samples were already degraded. Observation result after photodegradation in elongation at break of 10% wt and 20% wt Starch-LLDPE-Clay Nanocomposite decreased significantly [10].

Figure 2 and 3 showed morphological surface of 10% wt and 20% wt Starch-LLDPE-Clay Nanocomposite before and after Xenon Arc photodegradation, characterized with SEM. Its showed that before aging, the starch granulates were observed at the sample surface. In the 3rd day of Xenon Arc aging, starch granulates already disappeared on the surface of sample and the degraded starch leave a hole on the surface of LLDPE matrix. The hole dimension became slightly larger with time increasing of Xenon Arc aging. In 20% wt starch, the hole dimension of degraded starch had larger than the 10% wt starch. LLDPE control sample without starch and clay showed no changes after photodegradation with Xenon Arc (fig.4).

Figure 2. Morphological structure of 10% wt Starch-LLDPE-Clay Nanocomposite by SEM, before and after Xenon Arc photodegradation: (a) before, (b) after 3 days, (c) after 7 days and (d) after 14 days.
Figure 3. Morphological structure of 20%wt Starch-LLDPE-Clay Nanocomposite by SEM, before and after Xenon Arc photodegradation: (a) before aging, (b) after 3 days, (c) after 7 days and (d) after 14 days.

Figure 4. Morphological structure of LLDPE control by SEM, before and after Xenon Arc photodegradation: (a) before and (b)after 14 days.

AFM images showed fine spherical particle on surface structure of 10% wt and 20% wt Starch-LLDPE-Clay Nanocomposite before aging. This particle was blocklet of starch, similar to the result of reported by Park et al., 2009 that was 50-200 nm blocklets of starch [11,12]. Fig. 5.b1 showed the blocklet dimension of 10%wt starch about 200 nm meanwhile the blocklet dimension of 20% wt starch was about 100 nm. LLDPE before aging showed lamella structure with thickness of lamella was about 60 – 80 nm (fig.5.a1). Topography of lamella structure characterized with AFM was refer to
Chen et al., 2011 and Golebiewski et al. 2008 [13,14]. There was no significant changes in lamella structure of LLDPE before and after 14 day aging with Xenon Arc. Morphological structure surface of 10% wt and 20% wt Starch-LLDPE-Clay Nanocomposite after 14 days aging showed the similar structure of LLDPE control, but the diameter of lamella more smaller (table 1). This shows that the starch has been degraded by no longer visible on the surface of the sample as well as changes in LLDPE lamella size. The degradation, further observed by FTIR spectroscopy measurements.

**Table 1.** Morphology of 10% wt, 20% wt Starch-LLDPE-Clay Nanocomposite film and LLDPE control, before and after 14 days Xenon Arc.

| Sample          | Aging          | Blocklet/lamella diameter (nm) | Possible structure      |
|-----------------|----------------|--------------------------------|-------------------------|
| 10% wt starch   | Before Aging   | ±200                           | Starch blocklet at surface |
|                 | Aging 14 days  | 40 - 80                        | Lamella LLDPE           |
| 20% wt starch   | Before Aging   | ±100                           | Starch blocklet at surface |
|                 | Aging 14 days  | 40 - 60                        | Lamella LLDPE           |
| LLDPE control   | Before Aging   | 60 - 80                        | Lamella LLDPE           |
|                 | Aging 14 days  | 60 - 80                        | Lamella LLDPE           |

![Image](a.1) ![Image](a.2) ![Image](b.1) ![Image](b.2)
Figure 5. Morphological structure by AFM (topography), before and after Xenon Arc photodegradation: (a) LLDPE control, (b) 10% wt Starch-LLDPE-Clay Nanocomposite and (c) 20% wt Starch-LLDPE-Clay Nanocomposite; (1) before aging and (2) after 14 days.

Figure 6 showed FTIR spectroscopy result for nanocomposite 10% wt and 20% wt starch proved that degradation was occurred by increasing the intensity in the wave number at 1722 cm\(^{-1}\), corresponding to carbonyl bond [4]. The longer the degradation, the intensity of carbonyl bond was higher. The oxidation rate of LLDPE due to photodegradation was proportional to amorphous region and the degree of crystallinity will increase. Crystallinity bands arising can be observed (fig. 6) in the splitting of the CH\(_2\) rocking band into a pair of bands at 732 cm\(^{-1}\) and 719 cm\(^{-1}\).

Figure 6. FTIR spectrum of 10 and 20 %wt starch, before and after 14 days Xenon Arc.

Thermo Gravimetric Analysis result (table 1) showed decreasing onset degradation temperature for the starch in nanocomposite. The oxidation and degradation of starch was occurred during the aging. Meanwhile onset temperature of LLDPE in nanocomposite sample was increased, this occurred due to the high energy radiation that lead the formation of chain scission or crosslink on LLDPE before degraded. Image of 10%wt and 20%wt starch observed using Atomic Force Microscope also showed that the degradation occurs on starch. It was proved by the image after 14 days aging become the same as the image of LLDPE used as a control that showed the lamella of LLDPE.
Table 2. Onset Degradation Temperature of 10% wt and 20% wt Starch in Nanocomposite film, before and after 14 days Xenon Arc.

| Sample          | Onset Degradation Temperature (°C) |
|-----------------|-------------------------------------|
|                 | Before Aging | Aging 14 days |
| 10 % wt starch  | Starch       | 282.6         | 266.6         |
| 20 % wt starch  | Starch       | 279.3         | 259.0         |
|                 | LLDPE        | 447.2         | 450.2         |
|                 | LLDPE        | 440.9         | 445.4         |

4. Conclusion
Degradation at 10% wt and 20% wt Starch in nanocomposite film sample were occur initially at starch. There were no changes in lamella of control LLDPE without starch, after 14 days photodegradation with Xenon Arc. SEM analysis showed a hole in surface nanocomposite film sample causes by starch granulate degradation. FTIR and TGA result also proved that degradation occurred at starch and LLDPE in nanocomposite film sample.

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