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The Effect of Nano Zinc Oxide on Characteristic Bionanocomposite

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Abstract. **Demand of plastic is increasing along with the increasing use of plastics invarious fields. Plastics are hard to decompose biologically, so that it will give negative impacts to environment. One of ways to decrease those negative impacts is by using eco-friendly materials. Bionanocomposite is one of eco-friendly materials for plastics; this composite can be made from natural polymer and nano particle. This research used nano zinc oxide as nano particle for bionanocomposite. Bionanocomposite can be used as packaging, semiconductor, and medical materials. This research aims to know the effects of various type of nano zinc oxide (nano zinc oxide from galvanic industry waste, commercial, and without nano zinc oxide), and concentration of poly vinyl alcohol (0.5%, 1%, and 1.5%) on the bionanocomposite characteristics. The produced bionanocomposites was analyzed based on its mechanical properties, morphology, and biodegradation. The result showed that nano zinc oxide have effects to tensile strength and elongation of bionanocomposite, it also produces homogenous structure. Bionanocomposite can be degraded for 4 weeks.**

Keyword: Bionanocomposite, nanoparticle, plastic, nano zinc oxide, eco- friendly materials

I. INTRODUCTION

The demand of plastic packaging is increasing because of the increasing demand on food or non-food packaging materials. The type of plastics consumed in Indonesia in year 2010 were polypropylene (34%), polyethylene (29%), polyethylene terephthalate (15%), polyvinyl carbonate (12%), polystyrene (5%), and others (5%) [1]. Plastics contributed significantly to the waste generation. In DKI Jakarta only, plastic waste production in 2010 reached 523.6 ton/day [2].

Awareness on green environment are increasing. It leads to the increasing demand of eco-friendly packaging materials, which are renewable and mostly come from natural polymers. The natural polymers are categorized into four groups, namely (1) agro-polymer produced from biomass. (2) polyester produced from fermentation of biomass, (3) polyester produced from synthesis from biomass monomer, and (4) polyester produced from synthesis of petroleum [3]. The application of natural polymer can be divided into three generations, namely the natural polymer content of 5%-20% (decomposable for 3-5 years), natural polymer content of 40% - 70% (decomposable for 2 – 3 years), and the total natural polymer which are completely compostable [4].

Polymer can be used also as composite. It is made from combination two or more materials, which have different of mechanic properties. The mixture will then produce new materials that will have new mechanic properties and characteristic different from original material [5]. If one of component (matrix, amplifier or additive) has a nanoparticle size, it will be called nanocomposite [6]. Nano zinc oxide is often used for nanocomposite, because of it photocatalitic characteristics [7], semiconductor [8], antimicrobial [9], sunscreen [10], antibacterial [11]. Research's used nanoparticle as nanocomposite film from mixture of nano argentums oxide and nano zinc oxide showed that it could decreased microbial content [12]. Combination of chitosan with nano zinc oxide could also increase antimicrobial activity [10].

The development of composite is not only from synthetic composites but also biopolymer composites, because the biopolymeris quantitatively available, renewable, biodegradable, light and strong. So, it leads to reduce the polymer consumption from

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petrochemicals that are pollutants of the environment [13]. Bionanocomposite is a packaging material consisted of biopolymer in nanoparticle size, so it has new functional material. The natural polymer is used as matrix and organic/anorganic materials as filler or amplifier or additive [6]. The characteristic of bionanocomposite shows the increased mechanical characteristics and thermal stability. It has some advantages, such as biocompatible, biodegradable, and unique functionality according to the inorganic materials added [14].

This research aimed to evaluate the effects of nano zinc oxide from waste industrial galvanized to the bionanocomposite characteristic.

II. METHOD

a. Materials and equipment's

Materials used in this research included nano zinc oxide (produce from synthesis of zinc acetate from waste zinc dross). Tapioca starch (Orang Tani brand), polyvinil alcohol (PVOH) from Bratachem, caragenan, glycerol from Bratachem, nano zinc oxide from Sigma Aldrich, aquadest, and chemicals for analysis. Equipment which used in this research include oven memmert, magnetic stirrer magsuda 5N, glassware, molding, stirrer. Sartorius analytic scale BSA 2245-CW, tensile strength and elongation analysis equipment.

b. Methods

Nano zinc oxide process. Ten gram zinc acetate (product from extraction of zinc dross with acetic acid) was filled in 100 ml methanol and mixed for 30 minutes. The solution of zinc acetate were applied by ultrasonification for 30 minutes, it was then added with natrium hidroxide 10% to adjust pH 10. It was applied again by ultrasonification for 30 minutes.The sedimentation process was conducted for 24 hour and then the liquid was filtrated. The sediment was dried at 100°C for 8 hours and was calcinated at 800°C for 3 hour. It was then grinded to puree.

Preparation of Bionanocomposite Film. Bio-nanocomposite film were prepared under various condition, namely polyvinyl alcohol concentrations (0.5%. 1.0% and 1.5%) and nano zinc oxide types (nano zinc oxide from waste, nano zinc oxide commercial, and no nano zinc oxide). The nano zinc oxide was dissolved with 200 ml distillate water; it was mixed for 1 hour. It was added with glycerol 1%, and was mixed for 15 minutes. The mixture was then added with carrageenan 1%, and mixed for 15 minutes. The mixture was preheated and added wit polyvinyl alcohol, it was then preheat until 70 °C wit addition of tapioca starch 5%. It was preheated again t 125°C until the gelatinization process occured. It wa poured in mold (30cmx20cm). It was dried in oven at 5 °C for 48 hour, chilled at 27 °C and the film was remove from mold, saved in desiccator.

In the further research step, the production o bionanocomposite film were realized with polyviny alcohol concentrations of 0.5%, 1.0%, and 1.5%, an nano zinc oxide concentrations of 0.05%, 0.10% an 0.15%.

Characterization of the Bionanocomposite Film Bionanocomposite film were analyzed its mechanica properties to know thickness, tensile strength and elongation, analysis of morphology to know nanoparticle of nano zinc oxide position and analysis biodegradation of bionanocomposite using burial method.

III. RESULT AND DISCUSSION

a. Formulation of bionanocomposite as eco-friendly material

The bionanocomposite formulation used som materials, such as tapioca starch; polyvinyl alcoho (PVOH), carrageenan, and glycerol and nano zinc oxide The materials have unique function in the preparatio process of bionanocomposite. The polymer filn formation can be done with were dry process or we process. The dry process use low water content using extruder. In the wet process the polymers were dispersed with solution and pourit in mold allowing i will dry [15].

There are there methods for bio-nanocomposite preparation, namely (1) in situ polymerization, the nanoparticles were mixed with monomer solution, and preheated or given radiation, (2) Solution casting, the polymer was dissolved with solvent or nanoparticle and was dispersed with solvent, and (3) melt processing, the nanoparticle was mixed with polymer in batch, and stirred and heated until polymer to be nanocomposite film [16]. This research used solution casting method. This method used water for media dispersion, because water is good media for nano zinc oxide, cheap, safe and eco-friendly.

b. Mechanical properties of bionanocomposite film

Analysis of bionanocomposite film mechanical properties aimed to know the homogeneous of bionanocomposite materials. The bionanocomposite mechanical properties included the thickness, the tensile strength and the elongation. Nano zinc oxide was added

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as additive of bionanocomposite, so it can effect the thickness, tensile strenght and elongation. Analysis the thickness of bionanocomposite film is shown at Fig. 1. The bionanocomposite film used nano zinc oxide from waste was thicker bio-nanocomposite film than the bionanocomposite film used commercial nano zinc oxide or without nano zinc oxide. The film's thickness was influenced by concentration of nano oxide and homogeneous of materials. this was due to molecul density decrease and free space at matrixes film increase so the film thickness increase.

The tensile strength of bionanocomposite film is shown in Fig. 2. The bionanocomposite film used nano zinc oxide from waste has the tensile strength higher than the bionanocomposite film used commercial nano zinc oxide or without nano zinc oxide. Analysis for the elongation of bionanocomposite film is shown in Fig. 3. The bionanocomposite film used nano zinc oxide from waste has the elongation higher than the bionanocomposite film used commercial nano zinc oxide or without nano zinc oxide. Analysis from mechanical properties above showed that the nano zinc oxide from waste has a potential to be used for preparation of bionanocomposite film.

Analysis of the thickness of bionanocomposite film use various concentrations of nano zinc oxide and various concentrations of polyvinyl alcohol is shown in Fig. 4. It was shown that the thickness of bionanocomposite film was 0.35 mm – 0.47 mm. The bionanocomposite film has the highest thickness at a nano zinc oxide concentration of 0.15% and a polyvinyl alcohol concentration of 1.0%. The tensile strength of bionanocomposite film is showed in Fig. 5. The tensile strength bionanocomposite film were 0.23MPa–9.57MPa. The bionanocomposite film has the highest tensile strength at a nano zinc oxide concentration of 1.0% with a polyvinyl alcohol concentration of 0.05%. The tensile strength explains about homogeneity of materials mixture in the bionanocomposite film.

The latest research explained that the higher addition of magnesium hydroxide, the lower tensile strength of bionanocomposite film produce [10]. Thermoplastic starch (TPS) decreased the tensile strength of bionanocomposite film, while compatibilizer increased the tensile strength of bionanocomposite film [17].

The elongation of film bionanocomposite film used concentration of nano zinc oxide with concentration of polyvinyl alcohol is shown in Fig. 6. The film elongations of 9.95%-37.85% were observed then at a polyvinyl alcohol concentration of 1.0% with nano zinc oxide concentration of 0.1%. The elongation of bionanocomposite film shows that it has good flexibility for material packaging. Bio-nanocomposite was used for medical, agricultural, packaging, sunscreen, pharmacy [18]. The filler with nanoparticle starch increased the tensile strength and decreased the elongation of bionanocomposite film [19]. The bionanocomposite film have sago starch as matrix and nano zinc oxide as filler increased the tensile strength and decreased the bionanocomposite film elongation [20]. Glycerol in bionanocomposite can decrease the tensile strength and the elongation [21].

Analysis for mechanical properties of bionanocomposite film had the best thickness of 0.37%, the tensile strength of 6.99 MPa and the elongation of 37.85%, observed at a nano zinc oxideconcentration of 0.10% and a polyvinyl alcohol concentration of 1.0%. This showed that this film has good thickness, strength and elasticity, so it is suitable for material packaging.

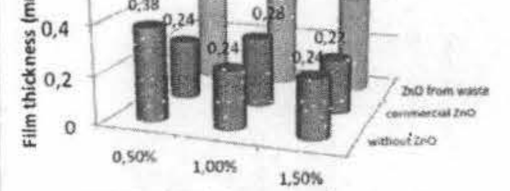

Figure 1. Analysis of the film thickness of bionanocomposite based on nano ZnO types

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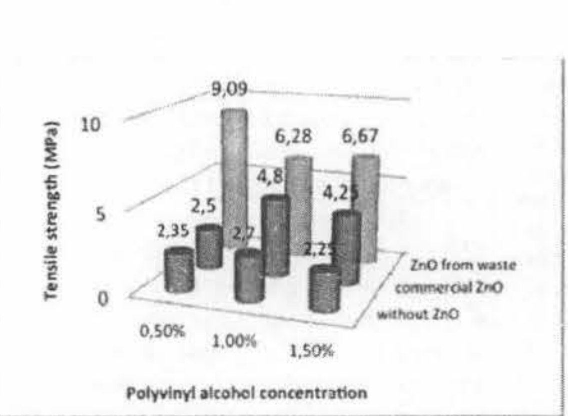

Figure 2. Analysis of the tensile strength of bionanocomposite based on nano ZnO types

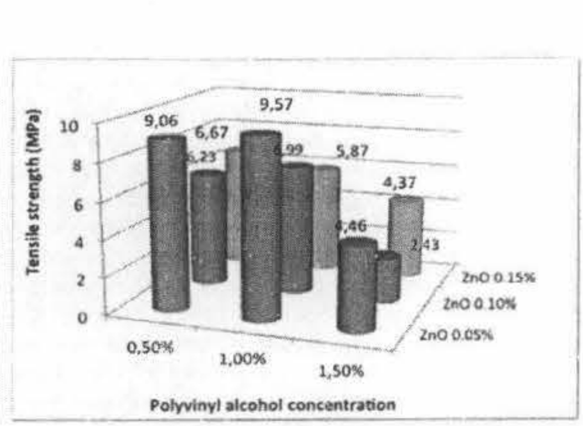

Figure 5. Analysis of the tensile strength of bionanocomposite based on nano ZnO concentration

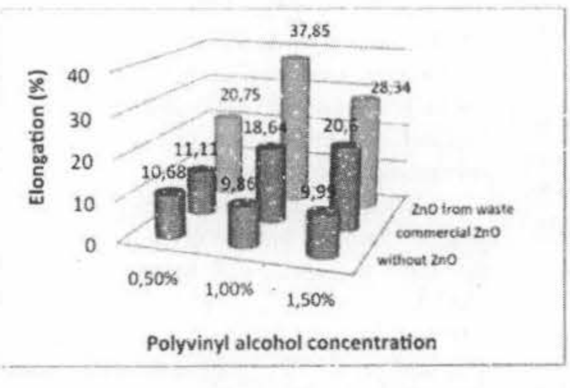

Figure 3. Analysis of the elongation of bionanocomposite based on nano ZnO types

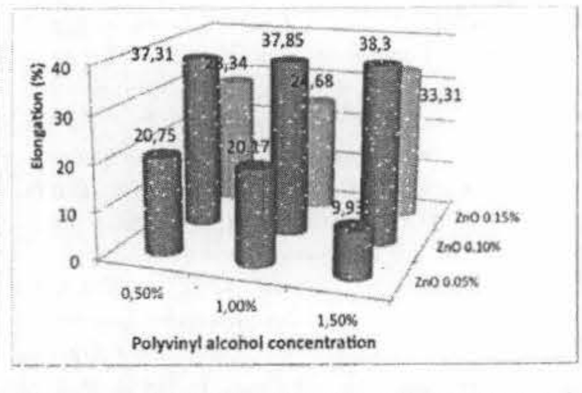

Figure 6. Analysis of the elongation of bionanocomposit based on nano ZnO concentration

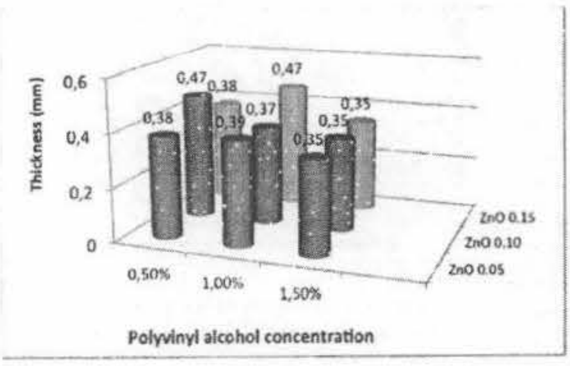

Figure 4. Analysis of the film thickness of bionanocomposite based on nano ZnO concentration

c. *The morphology of nano zinc oxide*

Characterization of the bionanocomposite fil morphology aimed to know the nanoparticle zinc oxi position in the bionanocomposite film. This was analyz by using Scanning Electron Microscope (SEM) [16]. Tl morphology of nano particle zinc oxi bionanocomposite is shown in Fig 7. The composite particle are isotropic, and the articles were interfa bond with the matrix. This composite have advantages small particle size [22].

The figure depicts that the nano zinc oxi concentration of 0.10% is more spread on tl bionanocomposite surface. In hot water, glycerol ar tapioca starch mode adhesion bond, so the nano zi oxide can be bound in the matrix [18

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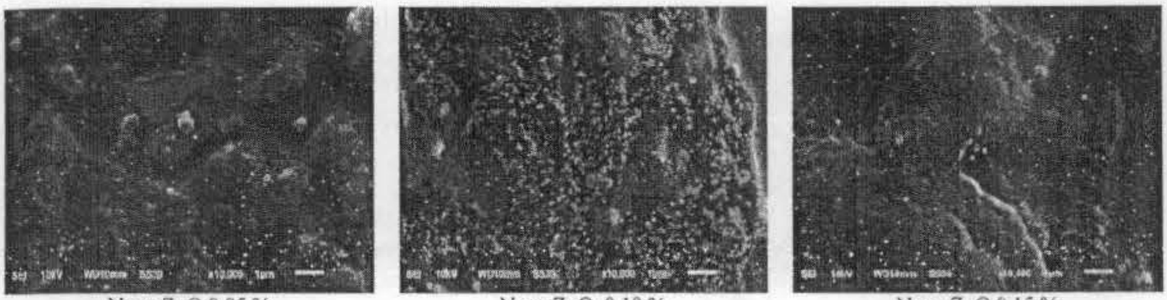

Nano ZnO 0,05 %   Nano ZnO 0,10 %   Nano ZnO 0,15 %

Fig.7. Morphology of nano partikel zinc oxide bionanocomposite

Fig 7 also shows that the bionanocomposite film are homogenous mixture of polyvinyl alcohol, tapioca starch and carrageenan, so surface area is good and flat, and the nanoparticle zinc oxide was attached on the matrix.

d. Biodegradibility of bionanocomposite

Analysis for the bionanocomposite film biodegradability aimed to know the degradability of polymer in the bionanocomposite film. The biodegradation process was observed in several ways, in which oxidation and radiation were applied. The plastic waste containing content dissolve polymer could be processed by the activated sludge and composting methods. The activated sludge method degraded the polymer waste for 2 weeks, while the composting method degraded the polymer waste in several weeks [23].

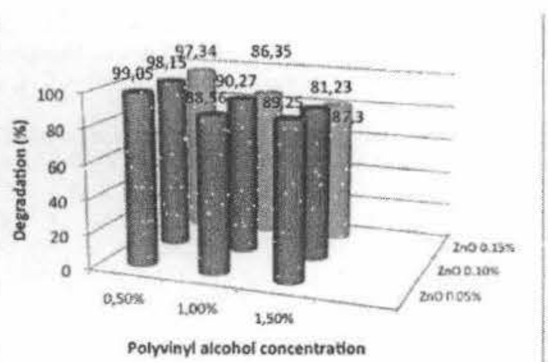

Figure 8. Film degradation of bionanocomposite for 4 weeks

The soil burial method can degrade the natural polymer [17]. The increase of starch concentration and period of soil burial increased the weight loss, because many starch was degrade by microbial in composting soil [24]. This research used soil burial test. The result of soil burial test during 4 weeks was shown at Fig. 8. The highest degradation level of bionanocomposite film of 99.05% was observed at polyvinyl alcohol concentration of 0.5% with nano zinc oxide concentration of 0.05%.

IV. CONCLUSION

Bionanocomposite can be made by formulation of tapioca starch, carrageenan, glycerol, polyvinyl alcohol and nano zinc oxide. Nano zinc oxide from waste of industrial galvanized can be used for bionanocomposite film process as additive. The bionanocomposite film prepared from nano zinc oxide from waste of industrial galvanized was characterized by higher thickness, tensile strength and elongation than the bionanocomposite films without nano zinc oxide addition, or with the commercial nano zinc oxide. The best thickness, tensile strength and elongation of bionanocomposite film were observed at nano zinc oxide concentration of 0.10%. Good structure of the bionanocomposite film was found at a nano zinc oxide concentration of 0.10%. Approximately 81.23%-99.05% of the bionanocomposite film could be degraded with soil burial method for 4 weeks. The bionanocomposite film content nano zinc oxide from waste industrial galvanized could be used for ecofriendly packaging material 0.10% and polyvinyl alcohol concentration of 1.0%.

REFERENCES

[1] Budiyono, "Kondisi, perkembangan dan prospek industri kemasan," in *Workshop BBKK, Kementrian perindustrian* Jakarta, 2012.

[2] Dinas Kebersihan DKI Jakarta, "Laporan Tahunan 2010 " Pemerintah Daerah Prop. DKI Jakarta2011.

[3] W. Gacitua, A. Ballerini, and J. Zhang, "Polymer nanocomposites: synthetic and natural fillers a review," *Maderas. Ciencia y tecnologia,* vol. 7, pp. 159-178, 2005.

[4] G. L. Robertson, *Food packaging: principles and practice*: CRC press, 2012.

[5] S. Agustina, "Pemanfaatan limbah kelapa sawit sebagai komposit untuk meubel," *Proceeding teknik kimia universitas parahyangan,* 2010.

[6] J. H. Koo, *Polymer nanocomposites*: McGraw-Hill Professional Pub., 2006.

[7] G. Patrinoiu, J. M. Calderón-Moreno, D. C. Culita, R. Birjega, R. Ene, and O. Carp, "Eco-friendly synthetic route for layered zinc compound and its conversion to ZnO with photocatalytical properties," *Solid State Sciences,* vol. 23, pp. 58-64, 2013.

[8] Nuryetti, H. Hermansyah, and M. Nasikin, "Bionanokomposit: Peluang Polimer Alami Sebagai Material Baru Semikonduktor," *Jurnal Riset Industri Online,* vol. 6, 2012.

[9] C. L. Wilson, *Intelligent and active packaging for fruits and vegetables*: CRC Press, 2007.

[10] Y. Cao, H.-J. Wang, C. Cao, Y.-Y. Sun, L. Yang, and Y.-N. Zhang, "Synthesis and anti-ultraviolet properties of monodisperse BSA-conjugated zinc oxide nanoparticles," *Materials Letters,* vol. 65, pp. 340-342, 2011.

[11] T. Gordon, B. Perlstein, O. Houbara, I. Felner, E. Banin, and S. Margel, "Synthesis and characterization of zinc/iron oxide composite nanoparticles and their antibacterial properties," *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* vol. 374, pp. 1-8, 2011.

[12] A. Emamifar, M. Kadivar, M. Shahedi, and S. Soleimanian-Zad, "Effect of nanocomposite packaging containing Ag and ZnO on inactivation of Lactobacillus plantarum in orange juice," *Food Control,* vol. 22, pp. 408-413, 2011.

[13] C. Baillie, *Green Composites: Polymer Composites and the Environment*: Taylor & Francis, 2005.

[14] S. H. Othman, "Bio-nanocomposite Materials for Food Packaging Applications: Types of Biopolymer and Nano-sized Filler," *Agriculture and Agricultural Science Procedia,* vol. 2, pp. 296-303, 2014.

[15] M. Chalid, "Kondisi dan perkembangan teknologi edible film serta prospeknya," in *workshop litbang BBKK, Kementrian Perindustrian,* Jakarta, 2012.

[16] V. Ojijo and S. S. Ray, "Processing strategies in bionanocomposites," *Progress in Polymer Science,* vol. 38, pp. 1543-1589, 2013.

[17] Waryat, M. Romli, A. Suryani, I. Yuliasih, and S. Johan, "Karakteristik Morfologi, Termal, Fisik-Mekanik, dan Barrier Plastik Biodegradabel Berbahan Baku Komposit Pati Termoplastik-LLDPE/HDPE," *Jurnal Agritech Fakultas Teknologi Pertanian UGM,* vol. 33, 2013.

[18] X. Ma, P. R. Chang, J. Yang, and J. Yu, "Preparation and properties of glycerol plasticized-pea starch/zinc oxide-starch bionanocomposites," *Carbohydrate Polymers,* vol. 75, pp. 472-478, 2009.

[19] M. Valodkar and S. Thakore, "Organically modified nanosized starch derivatives as excellent reinforcing agents for bionanocomposites," *Carbohydrate Polymers,* vol. 86, pp. 1244-1251, 2011.

[20] A. M. Nafchi, R. Nassiri, S. Sheibani, F. Ariffin, and A. Karim, "Preparation and characterization of bionanocomposite films filled with nanorod-rich zinc oxide," *Carbohydrate polymers,* vol. 96, pp. 233-239, 2013.

[21] A. Souza, R. Benze, E. Ferrão, C. Ditchfield, A. Coelho, and C. Tadini, "Cassava starch biodegradable films: Influence of glycerol and clay nanoparticles content on tensile and barrier properties and glass transition temperature," *LWT-Food Science and Technology,* vol. 46, pp. 110-117, 2012.

[22] E. S. Iriani, "Pengembangan produk biodegradable foam berbahan baku campuran tapioka dan ampok," 2013.

[23] M. Abdullah, Y. Virgus, N. Nirmin, and K. Khairurrijal, "Review: Sintesis Nanomaterial," *Jurnal Nanosains & Nanoteknologi,* vol. 1, pp. 33-57, 2009.

[24] G. Swift, "Requirements for biodegradable water-soluble polymers," *Polymer Degradation and Stability,* vol. 59, pp. 19-24, 1/3/ 1998.

[25] S. Susilawati, I. Mustafa, and D. Maulina, "Biodegradable Plastics From A Mixture Of Low Density Polyethylene (LDPE) And Cassava Starch With The Addition Of Acrylic Acid," *Jurnal Natural,* vol. 11, 2011.