Effect of Zinc Oxide Nanoparticles on the Thermal, Mechanical and Water Absorption Properties of Polylactic Acid/Chitosan Composites

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ABSTRACT : The aim of this work is to improve the mechanical, thermal and water absorption properties of PLCHZ nanocomposites. The formation of the composites are mixing polylactic acid with zinc oxide nanoparticles (ZnO) and chitosan as fillers. It produced through the precipitation method using a water bath under a temperature of 60 oC in the form of plastic film material. Five prepared samples are pure PLA, PLCH, PLCHZa, PLCHZb and PLCHZc. The incorporating eff ect of fillers on the properties of samples is investigated in terms of mechanical, thermal analysis TGA, and water absorbtion test. The result showed that mechanical and thermal properties increased with the addition of ZnO nanoparticles compared to pure PLA and PLCH (PLA with chitosan). Nevertheless, those properties increased up to 2 wt% of ZnO nanoparticles loading but decreased when the it content is increased up to 3 wt% and 4 wt%. PLCHZa with the smallest content of 2 wt% ZnO nanoparticles showed the highest value of 15 MPa in tensile strength and 330.6 oC in thermal resistant. In water absorbtion test, PLCHZc with 4 wt% has better absorb ability as well as the lowest percentage absorption rate than other samples. Basically, the nanopaticles with good crosslinking capability, thus advancing the overall quality. The result obtained in this work can be conclude that ZnO nanoparticles play an important role in the main properties of polymer composites.

KEYWORDS - *Polylactic Acid, Zinc Oxide Nanoparticles, Chitosan, Composites, Polymers.*

I. INTRODUCTION

Currently, around 50% of packaging products made of a polymer which is mostly generated from fossil fuels. Bio-based polymers can play an important role, unlike conventional plastics that can increase emissions of greenhouse gases (carbon dioxide) [1]. Besides, the production and use of biodegradable polymers can also help decrease the speed of fossil fuels consumption. Since the beginning the concept of chemical macromolecules was introduced, It has been a challenge for polymer scientists to figure out and invent new monomer-to-polymer systems that could form new polymer products accurately, controlling molecular weight and forming more promising material properties [2]. The resulting polymer products can be adapted to the ability of supramolecular induction in aqueous media or interfaces to produce micro or nanostructures with almost unlimited applications in the fields of pharmaceutical, medical and biotechnology.

Polylactic acid (PLA) is an abundant, commercially available, environmental friendly polymer due to its biodegradability and good sitfness properties. Another advantage of the PLA are transparent and safe to use for the medical field. PLA applied usually for beverage bottles, plastic bottles of chemicals, materials chairs, cutlery, plastic bags, car components, shelves, buckets, and others. The latest application of PLA the medical field are used as artificial leather, sewing thread operations, drug capsules and also for tissue engineering because the body can absorb it [3-5]. PLA can be formed through the esterification process lactic acid obtained by fermentation by bacteria using substrates starches or simple sugars [6]. In addition, the PLA has a lower mechanical and thermal properties compared to other polymers. Therefore, to overcome these weaknesses, PLA can be enhanced properties with the addition of filler material as chitosan, zinc oxide, clay and others in the form of nanocomposite [7].

Chitosan is a chemical compound derived from chitin biological material and organic compound that is abundant in nature after cellulose. Chitin is generally derived from the framework of the group of invertebrate animals Arthopodasp, sp Mollusk, Coelenteratasp, annelids sp, Nematodes

sp, and some of the group of fungi. As the main source is the shell of crustaceans sp, named shrimp, lobster, crab and other shell-bearing animals with chitin content of between 65-70 percent [8-9]. Because of the characters of chitosan are hydrophobic, high of stability and also has normal PH, the insertion of this inorganic particles to polymer such as PLA has proven to be efficient to improve main properties of polymer composites such as mechanical, thermal and water absorbtion properties [10-12].

ZnO (zinc oxide) formed as powder and insoluble in water such an inorganic compound which can be used as an additive for materials such as rubber, plastics, ceramics and others. It has a high capacity and thermal conductivity, and also high melting temperature [13-14]. ZnO nanoparticles can be formed in various ways such as process LeClaire, Direct Process, Wet Chemical Process, or a method of vapour-liquid-solid. ZnO nanostructures have some morphology, including nanowires, nanorod, tetrapods, and more [15-16]. Nanoparticles of zinc oxide is a well known inorganic environment-friendly and many researchs had use this because of multifunctional additives which can be regarded as a nanofiller for polymers that give properties such as antibacterial, increased mechanical, thermal and intensive ultraviolet absorption properties [17-19].

A composite material is a mixture of two or more phases, which are different to produce specific properties and characteristics that cannot be achieved by the single material [20-21]. Currently, focus of research is how to improve an existing product on the market to be even more reliable than the original product. Polymers are on the fast track of product innovation. Composites have strength, roughness, toughness, heat resistance or a combination of desired properties better when compared to the properties of a single element [22-24].

The purpose of this study is to produce and investigate nanocomposites PLCHZ (Polylactic acid/Chitosan by adding some concentration of ZnO nanoparticles) in several variation (PLCHZa, PLCHZb, and PLCHZc). Nanocomposites polymers are formed by dispersing ZnO nanoparticles into the PLA polymer matrix mixed with chitosan [25]. ZnO nanoparticles as supporting material synthesis are using the method of direct precipitation through direct mixing sol-gel forming solution with the advantage is a simpler

and lower cost. As the result, nanocomposites showed an increase in mechanical, thermal stability, and water absorbtion properties without increasing specific gravity and loss of optical properties [26-27]. Several methods of characterization were performed using Thermogravimetric Analysis (TGA), Mechanical test (tensile, modulus and elongation at break), and water absorbtion test.

II. MATERIALS AND METHODS
2.1 MATERIALS

All the chemicals used for the formation of ZnO nanoparticles and composites as are analytical reagents (99.9% pure), Polylactic Acid (PLA) grade (3001D) derived from Nature Work LLC, USA with a melting point of 190 °C and 1.24 g/cm of specific gravity, zinc acetate dehydrate (CAS. 5970-45-6) supplied from Merck, NaOH pellet (sodium hydroxide) (CAS. 1310-73-2) was obtained from Merck, Ethanol (CAS. 64-17-5) supplied by Sigma-Aldrich, and chloroform (CAS. 67-66-3) is used as a solvent, and chitosan C3646 commercial from Sigma-Aldrich as an additional ingredient for fillers and reinforcing.

2.2 METHODS
2.2.1 Preparation of ZnO Nanoparticles

A total of 0.25 M solution of zinc acetate dihydrate ($Zn(CH_3CO_2) \cdot 2H_2O$) was prepared with deionized water by dissolving it. Then 0.8 M of NaOH was added a few drops into solution of zinc acetate dihydrate with continue stirring at temperature of 25 °C for about 2 hours [28].The solution was continuously stirred until a white precipitate is formed cause the reaction of NaOH and zinc acetate dihydrate. Once formed, the precipitate is done then filtered and washed with ethanol and water to remove residual sodium hydroxide. The precipitate then dried for about 24 hours at 50 °C in the oven, then grinded with PSA tools (nanoParticaSZ-100V2 Series) to form ZnO nanoparticles.

2.2.2 Preparation of Composites (PLA, PLCH, PLCHZa, PLCHZb and PLCHZc)

Samples was formed as a composite test sample are divided into five types. Those are PLA, PLCH (Polylactic acid/chitosan), and PLCHZa, PLCHZb, PLCHZc (PLCH and ZnO nanoparticles with different concentrations). Formation of pure PLA is carried out through mixing PLA pellet of 20

grams with 15 wt% solution of chloroform to form a viscous liquid with the mixing process in a water bath at 60 °C [29]. Subsequently a solution are casted evenly on Petri dish a thickness of about 0.1 mm and dried for 24 in order to evaporate the chloroform as solvent.

It was followed by the formation of PLCH wherein 20 grams of PLA film mixed with 5 wt% chitosan by the same method as before using chloroform solvent until all the ingredients are fully soluble, then printed with the same thickness on a baking sheet [30]. Likewise, the variatedPLCHZa, PLCHZb, PLCHZc samples (2 wt%, 3 wt% and 4 wt% of ZnO nanoparticles, respectively) are carried out through the same method as the previous step in the same solvent (choloform), same filler (chitosan) and ZnO as the support material based on each the samples concentration. The solution was stirred at 60 °C until the handler to dissolve completely. Then the sample allowed to stand for 24 hours to throw away the solvent and peeled from the mould to doing test in the form of mechanical, thermal resistant, and water absorbtion test.

2.3 Characterization
2.3.1 Mechanical Test

Tensile properties included strength, modulus and elongation at break solving pure PLA films and composite films mix is determined by using Shimadzu Universal Testing Machine Model E43. It uses set capacity of 10 kN, based on ASTM D638. his is carried out under tension mode at a single strain rate of 10 mm/min at room temperature and the result is taken as the average of four tests.

2.3.2 Thermo Gravimetric Analysis (TGA)

The thermal stability of the samples is determined by means of thermogravimetric analyzer, using a Perkin Elmer thermogravimetric analysis at a heating rate of 10 °C/min under nitrogen atmosphere, from 50 °C to 700 °C. Approximately 2 mg of each sample is analyzed and consequently the weight loss of samples is determined.

2.3.3 Water Absorption Test

Water absorption is carried out by preparing a 6 mm ball-shaped sample according to ASTM D570. Furthermore, the samples were dried at 60 ° C for 1 hour, then allowed to cool in a desiccator. The sample was weighed immediately after being rotated and immersed in deionized water in room temperature for about 24 hours. After completing it, the sample is transferred in a dry state and weighed. After that, do the same treatment again. Samples were prepared to go back into the air and weighed again for ten days. Water absorption is expressed as the increase in weight percent and is calculated according to the formula shown in bellow:

Water absorbtion (%) = $(W2-W1)/W1 \times 100\%$ (1)

III.RESULT AND DISCUSSION
3.1 MECHANICAL PROPERTIES

Tensile strength, tensile modulus and elongation at break of the PLA, PLCH and PLCHZa, PLCHZb, and PLCHZc composites have been investigated through coaxial force by Universal Testing Machine tools. The variation in the tensile strength, tensile modulus and elongation at break are functions of the optimum dispersion and good inter-component interaction between the PLA, chitosan and ZnO nanoparticle.

Fig. 1 (a) describes the values of tensile strength of each samples. Based on these graphs, it can be seen that the addition of chitosan and ZnO nanoparticle showed improvement better mechanical properties of the polymer when compared to pure polymer without mixing (PLA). Pure PLA has a tensile strength of 13 MPa and declined after added chitosan. However, the addition of ZnO nanoparticles has further increased tensile strength as reported in previous studies [30]. PLCHZa with 2 wt% of ZnO nanoparticles is the most significant variation value tensile strength of 15 MPa compared with PLCHZb and PLCHZc with a tensile strength of only 11.5 and 12 MPa, respectively. The same thing was also found in other studies using ZnO concentrations of 2 wt% producing the best mechanical value [31-32]. This pattern of results tells us that the strong nature of the attraction decreases modulus because the amount of ZnO that is not ideal in mixed. This state of decrease in tensile strength is due to the formation of intramolecular hydrogen bonds due to the portion of one of the excess materials, so there is a split in the mixed matrix. A similar explanation occurs in the modulus results.
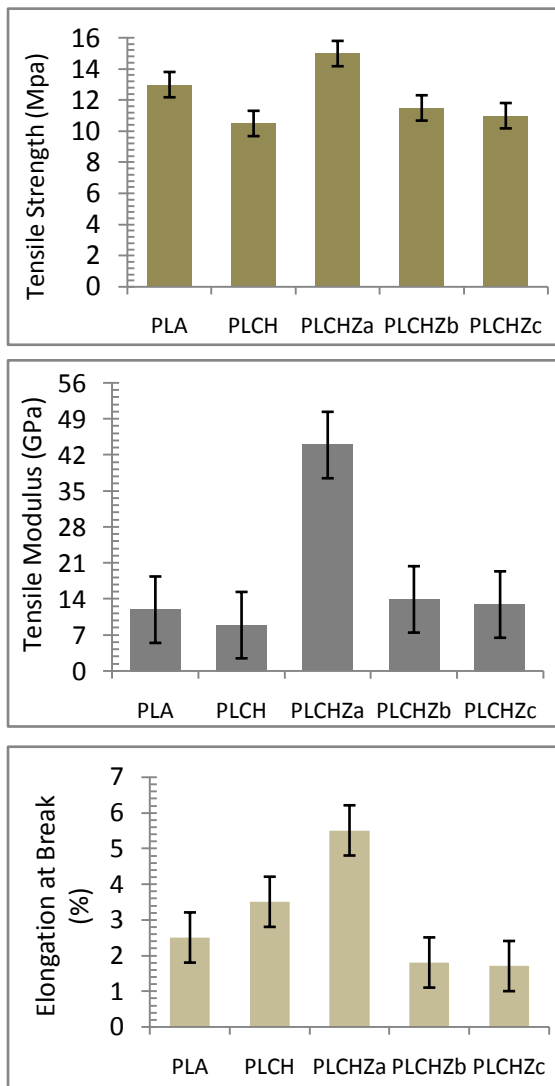
Fig. 1. (a) Tensile Strength of various composites, (b) Tensile Modulus of various composites, (c) Elongation At Break of Various Composites

Based on modulus as shows in Fig. 1 (b), the pattern of results is similar to tensile strength which the PLCH tensile modulus decreased compared to PLA from 12 GPa to 9 GPa. It is due to both of chitosan and PLA formed intermolecular hydrogen bond, leading to a composite tensile modulus of PLCH dropped being in formed a phase separation between the two main component [33-34]. PLCHZa is still the most excellent compositions at 44 MPa modulus value is almost 2 times higher than pure PLA, and higher than other samples PLCHZb and PLCHZc with value of 14 GPa and 13 GPa, respectively.

Fig. 1 (c) showed elongation at break intensity of the samples. PLA, PLCH and

PLCHZais increased in elongation at break with the addition of chitosan and also ZnO nanoparticles. Those are almost constant in the composite PLCH of 2.5% increased and up again in the presence of ZnO nanoparticles in PLCHZa, as reported by [35]. PLCHZa with 2 wt% ZnO nanoparticles is the greatest variation breaking extension value of 5.5%. However, this is not consistent on other samples, which decrease in instensity caused of presence of ZnO nanoparticle in PLCHZb and PLCHZc composites with value of 1,8 % and 1,7 %, respectively.

In previous research, uniform dispersion between polymer matrix and filler material which is highly compatible will produce a good interaction which in turn leads to increased mechanical properties and thermal stability of the composite [36]. Improving composite mechanical properties supported by the main controller tensile strength that is the effectiveness of reinforcement properties to facilitate the effective stress transfer at the interface of matrix and filler. In this experiment, ZnO nanoparticles act as an amplifier nanoscale leading to the strain transfer between matrix and filler. However, the composite tensile strength decreases when the amount of ZnO nanoparticle increased to 3 wt% and 4 wt%. Similarly to the results of modulus and elongation at break of the weakest in the same sample, caused of the chitosan and PLA contains ring structures. Intermolecular hydrogen bonds was formed by NH3, OH, and C=O, which mainly inhibit the movement of molecular chains. When ZnO nanoparticle incorporated, the hydrogen bonds between molecules weaken and new hydrogen bonds formed between PLA, chitosan and ZnO nanoparticle, making the rotation and movement of the chain molecules more easily, so that its mechanical properties of the composite becomes brittle once doping with excess ZnO nanoparticle.

3.2 Thermogravimetric Analysis (TGA)

Improvement in thermal stability of composites occurred significantly marked by the onset temperature, maximum degradation temperature and percentage of decomposition of various composites, as displayed in Table 1. Temperature degradation test material in this study ranged in the value of 360-380 $^{\circ}$C.

Table 1. Data of various composite TGA

Sample	Onset Temp (^{o}C)	Max Deg Temp (^{o}C)	% Decomposition
PLA	290.5	367.2	90.0
PLCH	297.7	370.5	78.0
PLCHZa	330.6	389.7	89.8
PLCHZb	321.9	385.6	83.0
PLCHZc	298.4	379.9	80.9

The onset temperature of pure PLA started at 290.5 °C with the percentage of decomposition of 90.0%. In one hand, the thermal stability of PLCH composite shown improvement compared to pure PLA as the onset temperature started at 297.7 °C with the percentage of decomposition of 78%. The presence of ZnO nanoparticles produces more remarkable effects than in pure PLA or PLCH with increases onset temperature of 330.6 oC in PLCHZa.

The addition of fillers such as chitosan and ZnO nanoparticles into the PLA matrix gives the effect of increasing the thermal stability of the polymer composite, this behaviour was partially already reported in a previous work [37]. It may be attributed to the formation of bond promoted by the polymer and filler fused stronger, besides acting as efficient protection towards the cracked, provides an effective thermal shielding which make them difficult to separated and degradation become better [38].

Despite the fact that the addition of the fillers bring significant increase in thermal stability, an interesting feature is represented by PLCHZb and PLCHZc with onset temperature of 321,9oC and 298.4 oC, respectively. The percentage of decomposition observed of 83% and 80%, respectively. PLCHZb with

the presence of 3 wt% ZnO nanoparticles losses about 0,03% of thermal stability compared to PLCHZa, whereas by loading 4 wt% this loss is shifted to 0,1% for PLCHZc.

It is important to underline the decreased reached after addition of more over 2 wt% of ZnO nanoparticles. The both of composites was not still retains at temperature founded in previous sample tested. Thermal behaviour was reduced due to the excess of fillers which made composites becomes brittle and affects to the thermal stability weaker. It is attributed to a barrier effect of the fillers towards polymer decomposition that not produced ablation, thus decreasing both onset temperature and percentage of decomposition. In general, the better dispersion of the filler in the polymer matrix and the enhancement of the interface between them to form a composite then composites helped provide a high thermal stability.

3.3 Thermogravimetric Analysis (TGA)

Water absorption properties of these materials are based on the amount of water is reduced in a trial that has been established over ten days. The pattern of water absorption of the test material is presented in Fig. 2.
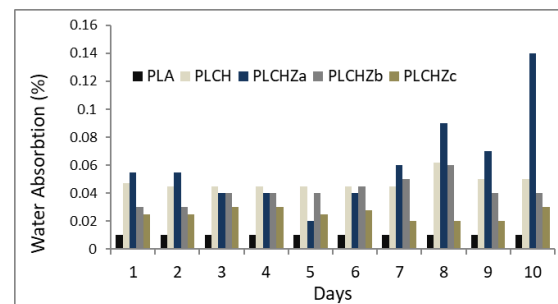

Fig. 2. Water Absorption Behaviour of Pure PLA, PLCH, and PLCHZ series Composites (for various ZnO nanoparticles loading)

It was observed that the water absorption rise and fall inconsistently throughout the test as different amount of water is absorbed by the composites tested. It can be observed from Fig.2 pure PLA did not show signs of moisture absorption during the 10 days period, it was confimed that the PLA has hydrophobic properties which sufficiently water resistant showed in value remained constant.

However, the different results shown in other sample after blending with chitosan, the water absorption of PLCH composite showed an increased, ranging from 0.045% to 0.062%, this is due to chitosan highly moisture-sensitive. Similar test results are also reported in other studies that found that PLA composite absorption value reached 0.06% within two days [40].

The incorporation of ZnO nanoparticles into the PLCHZa, PLCHZb and PLCHZc showed the water absorption of different percentages during the test period. PLCHZc showed the the most of water absorption ranging from 0.06% to 0.14%. This implied that the incorporation of 4

wt% ZnO nanoparticle enhanced the composite with better water barrier property compared with PLCHZa and PLCHZb which lower in water absorption properties of 0.035% to 0.06% and 0.02% to 0.03%, respectively.

Therefore, it can be concluded that PLA/CS/ZnO NPs composites possessed good water barrier properties and the property is more pronounced with higher ZnO nanoparticles loading, this is also reported in other studies [41-42]. It can be tailored to the needs and specific applications that will be used.

IV. CONCLUSION

Influenced of ZnO nanoparticles and chitosan on improving the mechanical properties, thermal and water absorption of varoius composites have been investigated. The results showed that chitosan and ZnO plays an important role in increasing the properties of polymer composites. The mechanical and thermal properties increased with the addition of collaboration of chitosan and ZnO particles than pure PLA and PLCH only. This is indicate by samples of PLCHZa as the highest values on tensile strength and tensile modulus of 15 MPa and 44 GPa, respectively. In line with the best thermal resistance of the sample is also shown on the PLCHZa with increasing the thermal degradation temperature of 330.6 oC. While other composite samples PLCHZb and PLCHZc experienced a decrease in mechanical and thermal value due to the influence of excess ZnO components. Meanwhile, the water absorption test found that PLCHZc has better absorption ability than other samples with the lowest percentage absorption rate of 0.06% to 0.14% during the test day.

V. Conflicts of interest

There are no conflicts to declare.

VI. Acknowledgements

REFERENCES

[1]   M. Abbasian, B. Massoumi, R. Mohammad-rezaei, H. Samadian, and M. Jaymand, "Scaffolding polymeric biomaterials: Are naturally occurring biological macromolecules more appropriate for tissue engineering". Int. J. Biol. Macromol, 134, 2019, 673–694.

[2]   Shamsun Alam, MdForhad Mina, Mohammed Jellur Rahman, Md Abdul Gafur, KaziHanium Maria, TetsuMieno, AKMMoshiul Alam, MdDalourHossen Beg, "Effects of micrometre-sized graphite flake to reinforce the performances of poly(lactic acid) thermoplastic biocomposites". Polymers and Polymer Composites, 27, 2018, 20-23.

[3]   O. Valerio, M. Misra, and A. K. Mohanty, "Statistical design of sustainable thermoplastic blends of poly (glycerol succinate-co-maleate) (PGSMA), poly (lactic acid) (PLA) and poly (butylene succinate) (PBS)". Polym. Test, 65, 2018, 420–428.

[4]   K. Piekarska, E. Piorkowska, and J. Bojda, "The influence of matrix crystallinity, filler grain size and modification on properties of PLA/calcium carbonate composites". Polym. Tes, 62, 2017, 203–209.

[5]   S. M. Bhasney, K. Mondal, A. Kumar, and V. Katiyar, "Effect of microcrystalline cellulose [MCC] fibres on the morphological and crystalline behaviour of high density polyethylene [HDPE]/polylactic acid [PLA] blends". Compos. Sci. Techno, 19, 2020, 1–23.

[6]   JamiluddinJaafar, JanuarParlaunganSiregar, MohdBijarimi Mat Piah, TezaraCionita, Sharmiza Adnan, TeukuRihayat. "Influence of Selected Treatment on Tensile Properties of Short Pineapple Leaf Fiber Reinforced Tapioca Resin Biopolymer Composites". Journal of Polymers and the Environment, 26, 2018, 4271–4281.

[7]   AzadehKhosravia, AbdolhosseinFereidoona, Mohammad Mehdi KhorasanibGhasemNaderic Mohammad Reza Ganjali de PayamZarrintajf Mohammad Reza SaebgTomyJ.Gutiérrezh, "Soft and hard sections from cellulose-reinforced poly(lactic acid)-based food packaging films: A critical review" Food Packaging and Shelf Life, 23, 2020, 1-17.

[8]   L. Midya, A. Shankar, C. Banerjee, A. Baran, and S. Pal, "Novel nanocomposite derived from ZnO/CdSQDs embedded crosslinked chitosan: An efficient photocatalyst and effective antibacterial agent". J. Hazard. Mater, 369, 2019, 398–407.

[9]   TeukuRihayat, M. Saari, M. HilmiMahmood, Wan MdZin Wan Yunus, Suraya Abdul Rashid, K.Z.H.M. Dahlan, S. M. Sapuan, "Mechanical Characterisation of Polyurethane/Clay Nanocomposites". Polymers and Polymer Composites, 15, 2007, 647-652.

[10]   E. Bahremandi, S. Karbasi, H. Salehi, and M. Rafienia. "Potential of an electrospun composite scaffold of poly (3-hydroxybutyrate) - chitosan/alumina nanowires in bone tissue engineering applications". Mater. Sci. Eng. , 99, 2019, 1075–1091.

[11]   V. Hooda, "Talanta Increasing the efficiency of immobilization and chitin determination using copper oxide nanoparticles". Talanta, 168, 2017, 246–256.

[12]   P. Taylor, D. Kurniawan, B. S. Kim, H. Y. Lee, J. Y. Lim, D. Kurniawan, B. S. Kim, H. Y. Lee, and J. Y. Lim, " Effect of Silane Treatment on Mechanical Properties of Basalt Fiber / Polylactic Acid Ecofriendly Composites Effect of Silane Treatment on Mechanical Properties of Basalt Fiber / Polylactic Acid Ecofriendly Composites". Polymer-Plastics Technology and Engineering, 1, 2015, 37–41.

[13]   TeukuRihayat, Suryani, "Synthesis and properties of biobasedpolyurethane/montmorillonitenanocomposites". World Academy of Science, Engineering and Technology, 4, 2010, 714-718.

[14]   O. Boura-theodoridou, A. Giannakas, P. Katapodis, H. Stamatis, A. Ladavos, and N. Barkoula, "Performance of ZnO/chitosan nanocomposite fi lms for antimicrobial packaging applications as a function of NaOH treatment and glycerol/PVOH blending". Food Packag. Shelf Life, 23, 2020, 1–9.

[15]   T Rihayat, S Suryani, T Fauzi, H Agusnar, B Wirjosentono, Syafruddin, Helmi, Zulkifli, P N Alam and M Sami. "Mechanical properties evaluation of single and hybrid composites polyester reinforced bamboo, PALF and coir fiber". IOP Conference Series: Materials Science and Engineering, 334, 2018, 1-8.

[16]   Javiera Sepulveda, Carolina Villegas, Alejandra Torresa, Esteban Vargas, Francisco Rodrigueza, Samuel Baltazar, Alejandro Pradad Adrian Rojas, Julio Romero, Simon Faba, María Jose , Galottoa, "Effect of functionalized silica nanoparticles on the mass transfer process in active PLA nanocomposite films obtained by supercritical impregnation for sustainable food packaging". The Journal of Supercritical Fluids, 161, 2020, 104844.

[17]   J. F. S. Bombonatti, A. Y. Furuse, V. D. Silva, T. A. Simões, E. S. Medeiros, J. J. Blaker, N. Silikas, and R. F. L. Mondelli. "Improved mechanical performance of self-adhesive resin cement filled with hybrid nanofibers-embedded with niobium pentoxide". Dent. Mater, 3418, 2019 1–14.

[18]   M. Heydari-majd, B. Ghanbarzadeh, and M. Shahidi-noghabi. "A new active nanocomposite film based on PLA/ZnO nanoparticle/essential oils for the preservation of refrigerated Otolithesruber fillets". Food Packaging and Shelf Life, 19, 2019, 94–103.

[19]   TeukuRihayat, Suryani Salim, Halim Zaini, Salmiyah, Cut Aja Rahmawati, Kurniati, YeniIrawan, Zaimahwati, "Synthesis, characterization and microbial protection of palm oil based polyurethane / bentonite / chitosan as paint and coating material". ICSREE, 1, 2017, 10-13.

[20]   N. K. Chandramohan, "Variation in compressive and flexural strength of the carbon epoxy composites with the addition of various fillers to the epoxy resin". Mater. Today Proc, 6, 2019, 6–10.

[21]   Chi-Hui Tsou, Chen Gao, Manuel De Guzman, Dung-Yi Wu, Wei-Song Hung, Lin Yuan, Maw-ChenrngSuen, Jen-taut Yeh. "Preparation and characterization of poly(lactic acid) with adipate ester added as a plasticizer". Polymers and Polymer Composites, 26, 2018, 446–453.

[22]   A. Akshaykranth, T. V. Rao, and R. R. Kumar, "Growth of ZnOnanorods on biodegradable poly (lactic acid) (PLA) substrates by low temperature solution method". Mater. Lett, 1, 2019, 12–18.

[23]   S. Salim, H. Agusnar, B. Wirjosentono, Tamrin, H. Marpaung, T. Rihayat, Nurhanifa, and Adriana, "Synthesis and innovation of PLA/clay nanocomposite characterization againts to mechanical and thermal properties". Mater. Sci. Eng, 334, 2018, 1–7.

[24]   B. Wirjosentono, R. Siburian, and T. Rihayat. "Modification of PLA/PCL/Aceh's bentonite nanocomposites as biomedical materials". AIP Conf. Proc, 2049, 2018, 1–6.

[25]   Y. Zare and K. Y. Rhee, "Following the morphological and thermal properties of PLA/PEO blends containing carbon nanotubes (CNTs) during hydrolytic degradation". Compos. Part B, 175, 2019, 1–13.

[26]   M. Rahman, S. Islam, and G. Shu, " Development of PLA/CS/ZnOnanocomposites and optimization its mechanical, thermal and water absorption properties". Polym. Test, 68, 2018, 302–308.

[27]   H. Agusnar, B. Wirjosentono, T. Rihayat, and Z. Salisah, "Synthesis and characterization of poly (lactic acid)/chitosan nanocomposites based on renewable resources as biobased-material". J. Phys. Conf. Se, 953, 2018, 1–7.

[28]   H. Agusnar, B. Wirjosentono, and T. Rihayat, "Thermal degradation of Aceh's bentonite reinforced poly lactic acid (PLA) based on renewable resources for packaging application". AIP Conf. Proc, 2049, 2018, 1–5.

[29]   Suryani, H. Agusnar, B. Wirjosentono, T. Rihayat, and Nurhanifa, "Improving the quality of biopolymer (poly lactic acid) with the addition of bentonite as filler". Mater. Sci. Eng, 222, 2017, 1–7.

[30]   E. Lizundia, M. Cristina, A. Guinault, J. Luis, and S. Domenek, "Impact of ZnO nanoparticle morphology on relaxation and transport properties of PLA nanocomposites". Polym. Test, 75, 2019, 175–184.

[31]   D. Ponnamma, J. Cabibihan, M. Rajan, S. S. Pethaiah, K. Deshmukh, J. Prasad, S. K. K. Pasha, M. B. Ahamed, J. Krishnegowda, B. N. Chandrashekar, A. Reddy, and C. Cheng, "Synthesis, optimization and applications of ZnO/polymer nanocomposites". Mater. Sci. Eng. C, 98, 2019, 1210–1240.

[32]   X. Wang, Z. Huang, M. Wei, T. Lu, D. Nong, J. Zhao, X. Gao, and L. Teng, "Catalytic effect of nanosizedZnO and TiO2 on thermal degradation of poly (lactic acid) and isoconversional kinetic analysis". Thermochim. Act, 672, 2019, 14–24.

[33]   Kamthai, S., &Magaraphan, R, "Development of an active polylactic acid (PLA) packaging film by adding bleached bagasse carboxymethyl cellulose (CMCB) for mango storage life extension". Packaging Technology and Science, 32, 2019, 103–116.

[34]   R. Mansa, C. Huang, A. Quintela, F. Rocha, and C. Detellier, "Preparation and characterization of novel clay/PLA nanocomposites". Appl. Clay Sci, 115, 2015, 87–96.

[35]   A. Anžlovar, A. Kržan, and E. Žagar, "Degradation of PLA/ZnO and PHBV/ZnO composites prepared by melt processing". Arab. J. Chem , 7, 2017, 1–20.

[36]   Y. Chen, L. Xu, X. Wu, and B. Xu, "ThermochimicaActa The influence of nanoZnO coated by phosphazene/triazine bi-group molecular on the flame retardant property and mechanical property of intumescent flame retardant poly (lactic acid) composites". Thermochim. Acta, 679, 2019, 1–8.

[37]   N. Noshirvani, B. Ghanbarzadeh, R. Rezaei, and M. Hashemi, "Novel active packaging based on carboxymethyl cellulose-chitosan-ZnO NPs nanocomposite for increasing the shelf life of bread". Food Packag. Shelf Life, 11, 2017, 106–114.

[38]   R. T. De Silva, P. Pasbakhsh, L. Sui, and A. Yoong, "Applied Clay Science ZnO deposited / encapsulated halloysite – poly (lactic acid) (PLA) nanocomposites for high performance packaging films with improved mechanical and antimicrobial properties". Appl. Clay Sci, 111, 2015, 10–20.

[39]   S. H. P. Priyanka P. Patil, Raghvendra A. Bohara, Jagruti V. Meshram, Shivdas G. Nanaware, "Hybrid chitosan-ZnO nanoparticles coated with a sonochemical technique on silk fibroin-PVA composite film: A synergistic antibacterial activity". Int. J. Biol. Macromol, 9, 2018 1–27.

[40]   R. C. Nonato, L. H. I. Mei, B. C. Bonse, E. F. Chinaglia, and A. R. Morales, "Nanocomposites of PLA containing ZnOnano fibers made by solvent cast 3D printing : Production and characterization". Eur. Polym. J, 114, 2019, 271–278.

[41]   C. Yang, R. Han, M. Nie, and Q. Wang, "Interfacial reinforcement mechanism in poly (lactic acid)/ natural fiber biocomposites featuring ZnO nanowires at the interface". Mater. Des,186, 2020, 1–7.

[42]   F. Croisier and C. Jérôme, "Chitosan-based biomaterials for tissue engineering". Eur. Polym. J, 49, 2013, 780–792.