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To cite this article: T Rihayat *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **788** 012045

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Synthesis and characterization of PLA-Chitosan-ZnO composite for packaging biofilms

T Rihayat^{1,*}, Suryani¹, C N Fitriyani¹, Nurhanifa¹, J P Siregar², J Jaafar², T Cionita³ and Fitria⁴

¹ Departement of Chemical Engineering, Politeknik Negeri Lhokseumawe, 24301, Aceh Indonesia

² Faculty of Mechanical Engineering, Universiti Malaysia Pahang, 26600 Pekan, Malaysia

³ Department of Mechanical Engineering, Faculty of Engineering and Quantity Surveying, INTI International University, 71800 Nilai, Negeri Sembilan, Malaysia

⁴ Departement of Dermato Venereology, Medical Faculty, Syiah Kuala University, 23111, Aceh

*Corresponding author: teukurihayat@yahoo.com

Abstract. This research was conducted to improve the characteristics of PLA-Chitosan-ZnO composites. Composites are synthesized from the matrix of Poly lactic acid by modifying Chitosan and Zinc oxide (ZnO) fillers. The purpose of this study was to look at the mechanical, thermal and morphological characteristics seen from the composite. Basically, the bond between PLA and CS is very weak, so to increase the strength of the bond by entering ZnO; thus advancing overall quality (mechanical, thermal and water absorption) of composites (PLA / CS / ZnO). The mechanical properties of composites are enhanced by the addition of ZnO NP into the PLA / CS matrix. However, the tensile strength, modulus, and breakout extension increased to 2wt% of ZnO NP loading but decreased when ZnO NP content increased by 3wt%. This is consistent with the dispersion of homogeneous ZnO particles in the PLA matrix. Combining ZnO particles increases PLA thermal stability. Thus, ZnO has been shown to have potential as an amplifier in biocomposite synthesis with better integrity, although other approaches, such as the use of compatibilizers in ZnO surface modification, will be needed to improve PLA properties simultaneously. The results obtained in this work can be used on environmentally friendly films.

Keywords. Poly lactic acid; Chitosan; Zinc oxide and biofilm

1. Introduction

Over the years, there has been increasing interest in biosourced renewable energy components to replace petrochemical products [1]. In general, synthetic polymers produced from petrochemical products have low tariff recovery / reproduction and are not easily degraded in the environment. Rapid growth of plastic waste encourages efforts towards biodegradable / biocompatible polymers that can be used as renewable resources for polymer manufacturing and reducing volume synthetic polymer waste.



The popular and important biodegradable polymers are aliphatic polyester [2-3], such as poly (lactic acid) (PLA), poly (glycolate acid) (PGA), poly (ϵ -caprolactone) (PCL) and poly (3 hydroxybutyrate) (PHB). Among polymers, poly lactic acid (PLA) has attracted attention because of its renewable resources, good biocompatibility and good mechanical properties that make it popular in medical implants, in food packaging and industrial biomaterials [4-5]. PLA produced from renewable resources is linear aliphatic thermoplastic polyester and easily decomposes naturally through hydrolytic and enzymatic pathways [6-7]. Figure 1 shows the chemistry structure of PLA.

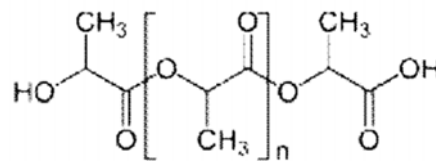


Figure 1. Chemistry structure of PLA.

PLA can also be synthesized by polymerization condensation from lactic acid monomers or by opening polymerization of lactide monomer rings, and monomers are obtained from fermented corn, potatoes, sugar beats, and sugarcane [8-10]. Figure 2 depicts the PLA synthesis method.

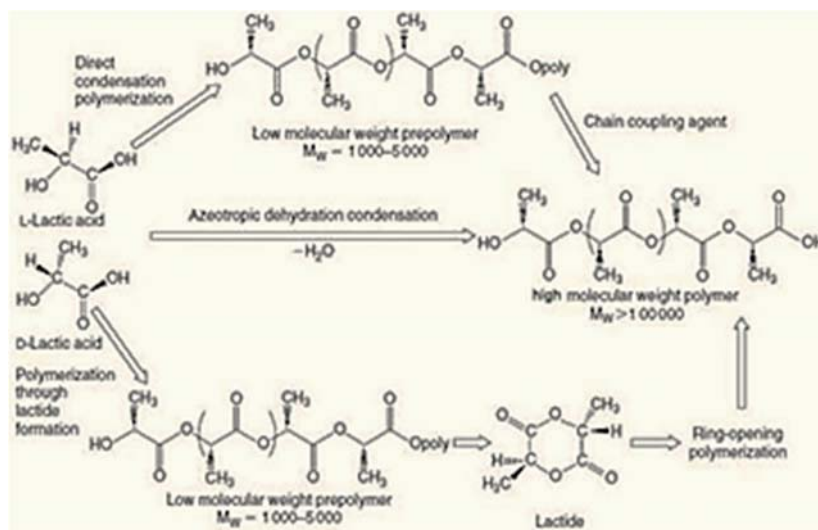


Figure 2. PLA synthesis method.

However, the PLA has several limitations for food packaging applications due to low gas and moisture vapor barrier properties, weak thermal stability, high rigidity, and low toughness and ductility [11]. To overcome these shortcomings, PLA has been mixed with these fillers as nano-clay, nano-cellulose, and nano-metal to improve the properties of films with additional functional properties [12].

PLA is also an attractive choice to improve the stability of chitosan due to its hydrophilic nature. Chitosan (CS) is renewable, natural, non-toxic, edible and biodegradable. From the hydrophilic nature of chitosan, especially pH sensitivity, the stability of chitosan materials is generally lower [13]. To overcome the lack of composites from the PLA-chitosan, metal oxides such as zinc oxide can be incorporated into the composite. Zinc oxide (ZnO) which is often encountered is environmentally friendly and multifunctional inorganic additives which can be considered as fillers for various

polymers providing properties such as antibacterial or intensive ultraviolet absorption [14]. This research was conducted to see from the incorporation of ZnO and chitosan on composites from the PLA matrix to improve morphological, mechanical, and thermal properties in environmentally friendly food packaging films.

Film is a thin layer produced from a material that is combined. Films can be applied to various applications, including those for food packaging films which are usually for meat, bread, fruit and vegetable wrappers.

2. Method

This research uses several chemicals including: poly lactic acid (PLA) (Nature Work TM PLA 3001 D) in the form of pellets obtained from Nature Work LLC, Minnetonka, MN USA. This has a specific gravity of 1.24 g / cm³ and the index of melting point is 15 g / 10 minutes (190 °C / 2.16 kg). Commercial chitosan (Cs) (practical grade 75% DD) from Sigma Aldrich which is used as a filler reinforcement. Zinc oxide (ZnO) from Sigma Aldrich. The solvents used in this study were chloroform obtained from R & M Chemistry. Deionized water for all processes and figure 3 shows the film formation.



Figure 3. Film.

2.1. Synthesis method of composite Chitosan-ZnO PLA

In preparation for the synthesis of PLA-Chitosan-ZnO composites, 10% wt of PLA pellets were added to chloroform each with (1.3 and 6%) Chitosan and (1,2 and 3%) ZnO. Then heated at a temperature of 80 oC until all the pellets are completely dissolved, then added glycerol as a plasticizer as much as 2 ml. After that, the solution is printed in the mold and dried at 40 °C for 24 hours. After that the film formed is released from the mold. Composite was then tested for morphology, mechanical strength and thermal stability. Figure shows the synthesis of Chitosan-ZnO PLA process.



Figure 4. Composite synthesis method of PLA-Chitosan-ZnO.

2.2. Physicochemical characteristics

2.2.1. *Fourier transform infrared spectroscopy (FTIR)*. Infrared spectroscopy from polyurethane obtained by KBr pellets using Shimadzu FTIR spectrophotometer. Spectra obtained in the mid infrared region (4000-400 cm⁻¹) at room temperature.

2.2.2. *Scanning electron microscope (SEM)*. An electron gun produces an electron beam and is obtained by an anode. The magnetic lens focuses electrons towards the sample. The focused electron beam scans the entire sample by being directed by the scanner coil. When electrons about the sample, the sample will issue a new electron that will be received by the detector and sent to the monitor. SEM analysis to observe the surface of the object directly.

2.2.3. *Mechanical test*. Tensile properties such as strength and break-up extension of film composites were determined using Shimadzu Universal Testing Machine, according to specific ASTM D 638-02 type 4. This was carried out under tension mode at a single strain level of 0.8 mm / s at room temperature and the results were taken as average of six tests.

2.2.4. *Thermogravimetric (TGA) analysis*. Thermal stability of the sample was determined by thermogravimetric analysis, using Perkin Elmer thermogravimetric analysis at a heating rate of 10 °C / min under a nitrogen atmosphere, from 50 °C to 700 °C. Approximately 2 mg of each sample was analyzed and consequently the sample weight was determined.

3. Result and discussion

3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR is used to see intermolecular interactions and phases in polymers. In this study, interactions between PLA, CS and ZnO were seen by FTIR spectroscopy and displayed in figure. 5 shows a composite mixture of FTIR PLA / CS / ZnO NP with a mixture of chitosan and ZnO. FTIR spectra of biocomposite PLA-Chitosan-ZnO films are presented in figure 5. The following transmittance bands: 1454, 1384 and 1362 cm⁻¹ were assigned to CH deformation, including symmetrical and asymmetrical bending, 1267, 1182, 1129, 1090 and 1045 cm⁻¹ associated with CO stretching and 871 cm⁻¹ assigned to stretch CC, observed. The band transmittance of about 1750 cm⁻¹ corresponds to the carbonyl carbon of the PLA ester group. The ribbons around 2944 and 2995 cm⁻¹ are assigned to stretch CH. This type of absorption band has also been reported in the literature [20]. FTIR spectrum from PLA / CS / 2 wt% ZnO NP. Characteristic absorption bands at 3506.52 cm⁻¹, 2979.77 cm⁻¹ and 1748.82 cm⁻¹ caused by OH bending and stretching, CH asymmetric stretching and C = O stretching vibrations shifting towards lower wave numbers on the merger of ZnO NP. This shows several levels of interaction and formation of PLA / CS / ZnO NP composites. It is also noted that the band intensity at 2979.77 cm⁻¹ and 1748.82 cm⁻¹ increases with respect to the PLA / CS composite spectrum. It implies that some strong interactions between components and dispersions are good at changing the polymer chain arrangement, which then returns in peak intensity.

3.2. Space considerations

Variations in tensile strength and breaking extension of PLA / CS / ZnO composites are functions of optimal dispersion and good inter-component interactions between PLA, CS and ZnO NP. It is reported that uniform dispersion of highly compatible fillers will cause good interactions with the polymer matrix, which then causes an increase in mechanical integrity and thermal stability of the composite [15]. Both tensile strength and tensile modulus of PLA / CS composites showed improvements as ZnO NP incorporated into composites up to a certain ZnO NP. Also, the breakdown extension of the composite showed a stable increase of up to 3wt% ZnO NP loading of PLA / CS / ZnO NP composites. Figure 6 illustrates the mechanical properties of samples.

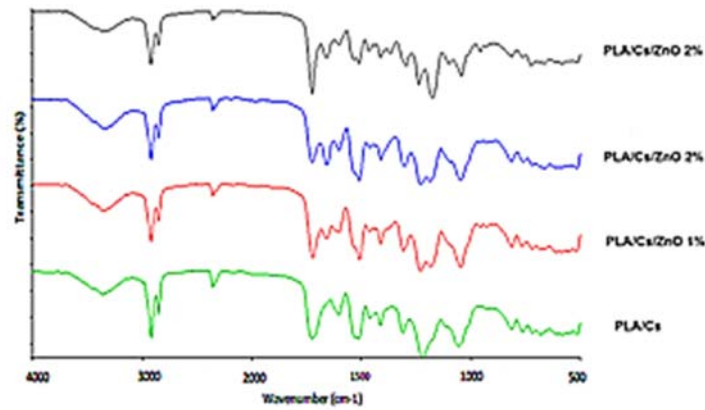


Figure 5. FTIR spectroscopy from biocomposite PLA-Chitosan-ZnO films

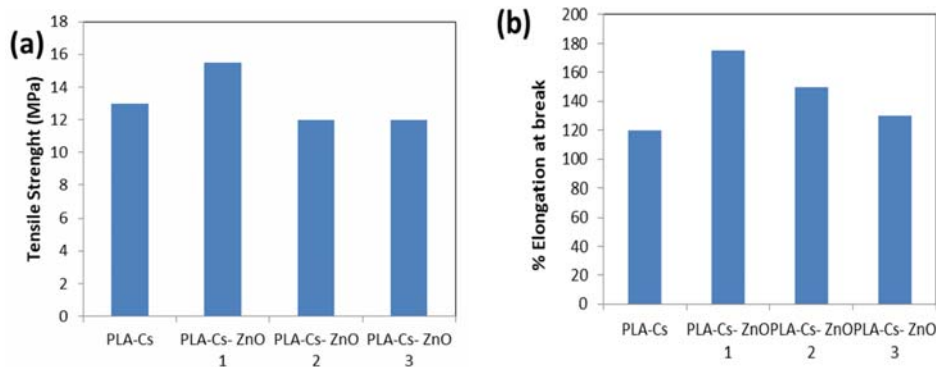


Figure 6. (a) tensile strength of plaque / biocomposite films and (b) tensile modulus of plaque / zoococomposite biocomposite films.

3.3. Thermogravimetric (TGA) analysis

The molecular interactions between macromolecules are different and also some characteristics of components that adhere to the main controlling parameters of thermal stability of polymeric materials. Chains. The division or dissociation of macromolecular bonds takes place when the heat energy provided exceeds the dissociation energy bonds of each chemical bond.

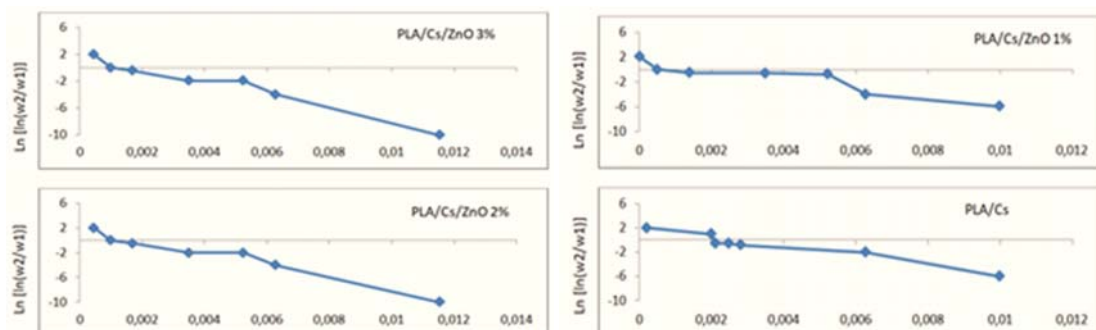


Figure 7. $\ln [\ln (w_2 / w_1)]$ vs. $1 / T$ plot of biocomposite PLA-Chitosan-ZnO film.

The TGA (thermogram) of PLA and PLA / ZnO biocomposite films is graphically presented in figure 7(a). In general it is believed that the introduction of inorganic components into organic materials can improve their thermal stability. In the PLA-Chitosan-ZnO biocomposite film, the increase in thermal stability can be attributed to ablative and reassembly of ZnO, which may appear on the surface of biocomposite films, creating a physical protective barrier on the surface of the material and on the other hand, volatilization may also be delayed by the labyrinth effect of ZnO layers, in biocomposite films. Analogous thermal behavior was also observed by Wu, et al. [16] From the TGA data, it was clear that ZnO was able to increase the char residue of PLA / ZnO biocomposite films from 0.3 to 19.3 percent. The activation energy for thermal degradation also revealed information about the thermal degradation properties of composites.

3.4. Morphological analysis (SEM)

The surface morphology of the PLA-Chitosan-ZnO composite in the film layer was observed under SEM. In PLA-Chitosan-ZnO samples at all concentrations it can be observed that some of the surfaces are smooth. The most significant observation is that in the case of PLA-Chitosan-ZnO 2, star-like fish structures were observed (see figure 8(f)), which also trapped the matrix in such a way as to increase tensile strength and improve toughness. But with increasing loading of ZnO, poor dispersion in the PLA matrix, with some presence interrupted from agglomerated ZnO, as confirmed in figure 4 (g and h).

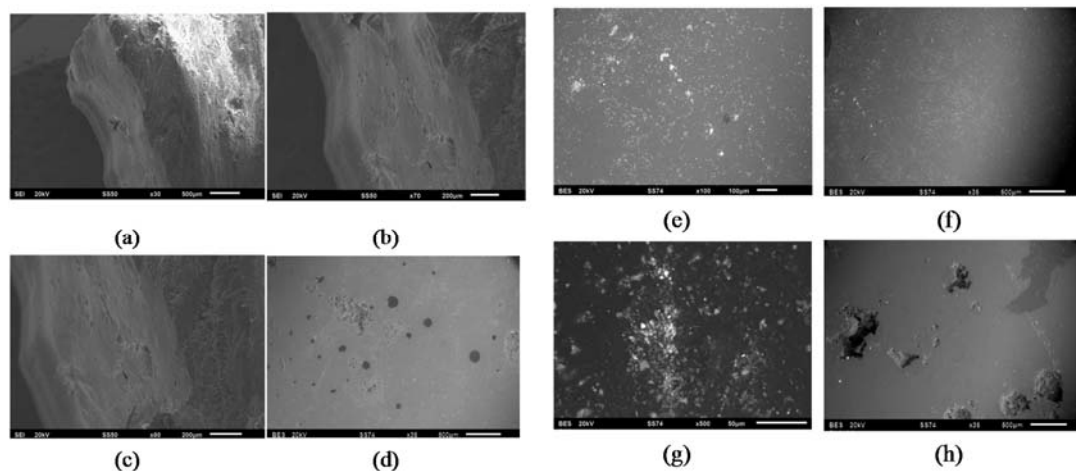


Figure 8. Sem images of zno, pla and pla / zno biocomposite films (a and b) are different magnifications from ordinary rectangular zno; (c) smooth pla 0; (d) smooth zno spread on pla zno 1; (e) zno good bond in pla zno 1; (f) starfish unique to the morphology of pla 2; (g) zno is agglomerated on pla 2 and (h) zno is agglomerated on pla 3.

4. Conclusion

In this work, an analysis of the characteristics of PLA-Chitosan-ZnO composite films. The results showed that ZnO had been successfully entered into the PLA / CS matrix as the FTIR spectrum showed good attractiveness and interactions between PLA, CS and ZnO in the composite. This improvement is ascribed to the superior relationship between composite components. Also, composites can be seen from good tensile strength. However, the thermal stability of the composite deteriorated with the addition of ZnO NP into PLA / CS composites. the extension of the break from the composite shows a stable increase of up to 3wt% ZnO NP composite PLA / CS / ZnO loading.

5. Acknowledgement

The authors express their gratitude and thanks to the Ministry of Research, Technology and Higher Education for Financial Support through the “Penelitian Terapan – 2019”.

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