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Starch-Based Film Enhancement with Lignin, Nata De Coco and Sunflower Oil: A Mini Review

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Abstract

Much attention has been focused in recent years on research to replace petroleum-based commodity plastics because petroleum-based plastics create an ecological problem with plastic contamination affects the environment especially wildlife. Therefore, biopolymers made from starch is an excellent material to replace petroleum-based plastics in a cost-effective manner, renewable sources, good mechanical and barrier properties also excellent biodegradability. However, starch-based plastics has weak mechanical properties that can limit the application. Therefore, natural fillers/fibres such as lignin, Nata de coco has been added to strengthen the mechanical strength. The addition of natural plasticizers such as sunflower oil provide the benefits to the biopolymer. In this study, four main journal articles have been studied and analysed with the natural fillers/fibres and plasticizers. Based on the reviewed articles, lignin is the suitable choice to enhance starch-based film.

Keywords

Starch-based plastics, Bio-Polymer, Natural fllers/fibers, Plasticizers

Introduction

Due to their non-biodegradability, the increased use of packaging films manufactured from synthetic polyethylene (PE) has contributed to serious environmental issues. Therefore, to overcome this problem, there is a necessary to develop an eco-friendly biodegradable packaging film. Biodegradable films are commonly synthesized from renewable natural resources for examples polysaccharides, protein, lipids, etc. [1]. Biodegradable films which commonly used in food packaging are able to degrade naturally at a varies of sunlight, moisture, oxygen and composting conditions [2]. Among all the natural sources, starch is considered as one of the worthy prospects for future plastics due to its affordable price, availability, renewable and degradable. In addition, starch exhibits thermoplastic behaviour which is suitable to be used for bioplastic film development [1].

Starch has gained attention for the biodegradable film preparation due to being the largest source of polysaccharide its non-toxicity properties. However, starch-based plastic has many disadvantages compared to other polymers such as weak mechanical properties and low stability due to absorption of water [3]. To boost the properties and performance of starch based-plastic, natural fillers such as cellulosic materials and plasticizer were incorporated into the system [4-5].

Natural polyphenol such as lignin is one of the world's most important renewable sources [6]. Lignin provides an antioxidant and antimicrobial properties which improving the longevity of foods [7]. Commercially available lignin is primarily a by-product of pulping or to a lesser extent a process of bio-refinery, such as cellulosic ethanol [8].

Nata de coco is a jelly-like food that are made using *Acetobacter xylinum* to ferment coconut water. It consists of naturally occurring cellulose fibres known as bacterial cellulose. Bacterial cellulose has very good mechanical properties, high tensile strength, biodegradable and able to hold water. Biodegradable plastics manufactured from hydrocolloids like Nata de coco (NDC) has high polarity and

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hydrophilicity which creating higher permeability of water vapor and low oxygen permeability [9].

Using plasticizers such as sunflower oil, which is unsaturated oils, can greatly enhance the of films properties of moisture-barrier, prevent significant alteration of emulsified films in the mechanical properties [10]. Therefore, in order to meet the requirements for biodegradable film while maintaining its function, extended research papers were reviewed about a starch-based film with addition of lignin, Nata de coco and sunflower oil.

Methodology

By conducting the literature review, the methodology approach of four most significant journal articles from Tiara Nur Elfiana, et al. (2018), Rajeev Bhat , et al. (2013), Ruixin Shi & Bin Li (2016) and Volpe (2018) and testing were analyse including FTIR, tensile test, water vapour permeability test, water solubility test and degradation test as in (Table 1). In order to discover relevant articles, keywords such as starch-based biodegradable film, cellulose lignin and vegetable-oils based plasticizers were derived in accordance with the research questions.

Discussion

Tiara Nur Elfiana, Nur IzzaFitria, EndarujiSedyadi, Susy YunitaPrabawati, IrwanNugraha (2018): Degradation Study of Biodegradable Plastic using Nata De Coco as a Filler

In this analysis, biodegradable plastic is made from Ganyong Canna as a base material, glycerol as plasticizer, acetic acid as terminator in polymerization reaction, distilled water as a solvent and modified by nata de coco.

The FTIR spectrum of Ganyong canna and Nata de coco can be seen. It displayed that the OH group is located at wave number 3298.03 cm^{-1} and shifted to 3290.32 cm^{-1} after the addition of nata de coco. The wave number of C-H bonds in Ganyong canna and nata de coco is shown at 2920.01 cm^{-1} and 2916.16 cm^{-1}. While the C-O bond in both components is located at wave number 995.05 cm^{-1} [11].

Film thickness can influence the permeability of gas, tensile strength and elongation as well [12]. The irregular value of nata de coco plastics is shown by the thickness. On 0.5 g and 1 g of nata de coco pulp, the plastic thickness decreases

Table 1: Methodology based on selected journal articles.

Authors	**Tiara Nur Elfiana, et al. (2018)**	**Rajeev Bhat, et. al (2013)**	**Ruixin Shi & Bin Li (2016)**	**V. Volpe, et al. (2018)**
Title	Degradation Study of Biodegradable Plastic using Nata De Coco as a Filler.	**Producing novel sago starch-based food packaging films by incorporating lignin isolated from oil palm black liquor waste.**	Synthesis and Characterization of Cross-linked Starch/Lignin film.	Uses of sunflower seed fried oil as an eco-friendly plasticizer for starch and application of this thermoplastic starch as filler for PLA.
FTIR	Samples in the form of plastic were placed in set holder and scanned at a wavelength of4000-400 cm^{-1}	No usage of FTIR	Recorded on an Avatar 360 spectrophotometer at wavelength 4000-400 cm^{-1} with a resolution 4 cm^{-1}	No usage of FTIR
Tensile Test	Universal Testing Machine (UTM) ASTM method D.882-02	Using standard method (ASTM,1980) with 5 kg loads with distance between the grips set at 50 mm and cross head speed at 0.40 mm/s	Films were cut 100 mm x 10 mm and determined with Tensile Tester Instron XLDT 1kN (China) with an extension speed of 5 mm/min	10 mm x 5 mm x 200 µm were subjected to Perkin Elmer DMA 8000 with maximum load to 2N and a load rate of 0.1 N/min
Water Vapor Permeability	Using the gravimetric method (ASTM 1983) where the plastic was placed in the mouth of cup with silica gel	Measured by using ASTM E96-95 method with slight modifications	No water vapor permeability testing	No water vapor permeability testing
Water Solubility Test	No water solubility test	Films were cut 2 x 3 cm and placed in a desiccator containing silica gel for 7 days	No water solubility test	No water solubility test
Biodegradation Test	Burying the sample 3 x 3 cm^2 in the soil for 12 days with every two days plastic was taken, washed and weighed	No degradation testing	No degradation testing	No degradation testing

while the 1.5 g and 3 g of nata de coco pulp, increase. The thicker the manufactured plastics, the lower the water vapor transmission value, since the greater the capacity to retain water vapor. In this analysis, the thickness of biodegradable plastic is known from variations of nata de coco ranging from 0.0665 mm to 0.1035 mm.

In order to determine the strength of resistance to plastic weight and elasticity, testing of mechanical properties including tensile strength and elongation is very important. The bonding between hydroxyl (O-H) groups in starch with hydroxyl (O-H) and carboxyl (COOH) groups in cellulose was induced by nata de coco containing cellulose adding tensile strength. The resulting tensile strength of biodegradable plastic in this study is 4.3244 MPa. The resulting value is greater than the research conducted by MeryApriani (2014) using cassava starch with aloe vera to create biodegradable plastics with a tensile strength of 1.53 MPa.

To show the ability of plastic to withstand a number of loads before the plastic is broken, measurement of elongation is very important. The elongation value was around 13.9639%. An irregularity in tensile strength has been shown in this article. This irregularity occurred due to the less homogenous solution where the glycerol broke up the inter-polysaccharide bonds, which occurred unevenly in of nata de coco variations. Therefore, the intermolecular interactions decreased and affect the value of the tensile strength. This interaction occurs because glycerol inserts and removes the hydrogen bonds between polysaccharide molecules so the bonds %plastic molecules is weak [13].

Biodegradation test usings oil media were performed in this study. Observations were carried out visually at the changes in plastic and weighing the decrease in plastic mass. Observations were made for 12 days, where the plastic was removed every 2 days and then washed and weighed. Based on the results, in pure Ganyong canna, the plastic containing nata de coco as filler has more mass degradation than plastics. Depending on how long the plastic was in the soil, the proportion of mass degradation was between 5%-38%. In the early days, degradation process took place more rapidly than on any day. This is because it contains cellulose where nata de coco has ability to absorb water so that the degradation was being faster.

Rajeev Bhat, Nurulismah Abdullah, RozmanHj. Din and G.S. Tay (2013) Producing novel sago starch-based food packaging films by incorporating lignin isolated from oil palm black liquor waste

The main objective of this research was to incorporate lignin isolated from black liquor waste to develop novel, sago-starch based packaging with good mechanical and thermal properties, which is envisaged to find wide applicability for food packaging purposes and be useful to overcome relevant environment issues.

Results on the mechanical properties of starch/lignin films showed an increase in tensile strength in incorporation of isolated lignin from black liquor waste compared to the commercial lignin in film. The tensile strength increased corresponding to increase in the isolated lignin from black liquor waste at 1%, 2% and 3% with a value of 3.48 ± 0.15 MPa, 3.76 ± 0.40 MPa and 4.20 ± 0.42 MPa, respectively. Films produced by using 1% and 2% of black liquor waste isolated lignin, has an elastic modulus of 0.36 ± 0.06 MPa/% and 0.39 ± 0.09 MPa/%. Also, films produced by incorporating lignin from black liquor waste at 3% showed greatest improvement compared to other formulations. Above all, addition of 4% and 5% of isolated lignin decreased the elastic modulus values of films. With regard to elongation at break, at 3%, 4% and 5%, a significant decrease in films generated by the addition of isolated lignin from black liquor waste was recorded. However, no significant differences were recorded in films produced by incorporating 1% and 2% of black liquor waste isolated lignin (53.71 ± 4.62 and 50.04 ± 8.43, respectively), with the films found to be more stretchable.

In general, partial miscibility between sago starch and lignin fractions as well as the presence of hydrophilic groups in lignin attributed to improvements in the tensile strength of films. In addition, the presence of hydrogen bonds between lignin and sago starch can be attributed to an increase in tensile strength with a decrease in break elongation [14]. Earlier, decrease in tensile strength and elongation at break at higher concentrations in lignin incorporated films was contributed to lack of uniformity in the distribution of lignin and lignin agglomeration [14]. The decreasing trend observed in tensile strength of sago starch/lignin film above 3% lignin content can be attributed to weakened interfacial adhesion between hydrophilic sago starch and hydrophobic lignin. The mechanical properties of starch/lignin films can also be influenced by the presence of plasticizer such as glycerol, which interacts freely with the starch matrix.

The WVP of 1% and 2% isolated lignin films were 0.011 ± 0.001 g mm/m^2 h kPa and 0.012 ± 0.001 g mm/m^2 h kPa, respectively. Decrease in WVP is considered advantageous when producing food packaging materials requiring efficient barrier properties to minimize moisture transfer between food and outside packaging environment [15]. The observed decrease in WVP in lignin incorporated films is an indication of improved permeability of films towards water vapor. On overall comparison, starch films incorporated with isolated lignin from black liquor waste showed higher WVP compared to starch films incorporated with commercial lignin.

In the present study, water solubility of sago starch films decreased on addition of isolated lignin from black liquor waste or commercial lignin compared to control. These results were expected, as lignin are known to exhibit high hydrophobic properties and are insoluble in water. The water solubility for all the films prepared by using isolated lignin were recorded to significantly decreased, with the values for 1% and 2% isolated lignin being 51.22 ± 0.16% and 50.98 ± 2.80%, respectively. The same trend was observed for films incorporated with commercial lignin. Based on the results of this study, incorporation of black liquor waste isolated lignin and commercial lignin into sago starch film were found to significantly improve the water resistance of the films.

Ruixin Shi, Bin Li (2016) Synthesis and Characterization of Cross-linked Starch/Lignin film

The aim of this work was to develop a cross-linked starch-lignin polymeric film, and to study the effect of lignin on the properties of the starch-based films.

FTIR spectroscopy confirmed the cross-linking reaction between starch and hydroxy-methylated alkali lignin (HMAL). The cross- linked film showed that the characteristic absorption peaks of both, starch and HMAL. The spectrum of the cross-linked showed an intense broad peak at 3414 cm^{-1} (O–H stretching vibration). This was more intense than the corresponding peaks in the spectra of the starch film (3315 cm^{-1}) and Hydroxy-methylated alkali lignin (HMAL) (3422 cm^{-1}), which indicated the formation of inter and intra molecular hydrogen bonds in the cross-linked product. Furthermore, in the spectrum of the cross-linked film, changes in many peaks, characteristic of starch and hydroxy-methylated alkali lignin, suggested a cross-linking reaction. The peak at 1220 cm^{-1} in the spectrum of the cross-linked film, attributed to the C–O stretching vibration of primary alcohol, decreased in intensity significantly, as compared to the peak at 1218 cm^{-1}, in the spectrum of hydroxy-methylated alkali lignin. Meanwhile, the peak at 1035 cm^{-1}, due to C–O stretching vibration, due to C=O stretching vibration of C-O-C as a result of cross-linking. The absorption peak at 1154 cm^{-1}, assigned to deformation vibration of ether linkages in the cross-linked film, also increased significantly, as a result of the cross-linking reaction.

This study determined the water absorption rates of the cross-linked films. In contrast to the results obtained by [16], cross-linked films had higher absorbability rate compared to the starch film which showed that the addition of lignin to the starch matrix made the film more hydrophobic.

The ultimate stresses and elongation ratios of the films showed a consistent a clear pattern for any discussed above. The sample however, the sample became very brittle, and more lignin powder remained insoluble, which was apparent. It was found that there was also a maximum ultimate stress and elongation ratio for films made under conditions corresponding to the maximum water uptake. Under optimized conditions, the ultimate stress of the films was 1.19 T 0.02 MPa and the elongation ratio was 114.5 2.5%, which were 2.2 times and 2.8 times than that of the starch film, respectively.

The moisture absorption of both starch and cross-linked film has increased with increased humidity. It shown that the moisture absorption of the cross-linked film was obviously greater than that of the starch film at a fixed relative humidity. This following two factors may be related to this: The first was the creation of the network structure due to the reaction between the polymers and the cross-linking agent. The structure of the network in the film resulted into water molecules being more strongly adsorbed on the film surface, which allowed the water molecules have the ability to gradually penetrate into the film. Secondly, compared to the starch film, more hydrogen bonds by different functional groups with water molecules could be formed by the cross-linked films. These groups included starch hydroxymethyl groups, hydroxy-methyl alkali lignin, and glycerol, together with ether groups, formed in the cross-linking reaction. In addition, some hydrophilic surrounded by polymeric chains were exposed to water molecules because of the cross- linking reaction between the polymers. All these factors encouraged the absorption of water molecules and resulted in an increase in the rate of water absorption and moisture absorption by the cross-linked films.

V. Volpe, G.DeFeo, L. De Marco, R. Pantani (2018) Uses of sunflower seed fried oil as an eco-friendly plasticizer for starch and application of this thermoplastic starch as filler for PLA

The innovation proposed in this work is to replace into the starch plasticization process part of the glycerol with a sunflower seed oil resulting from the frying process in a fast food. The so plasticized Thermoplastic starch (TPS) was compared to the TPS plasticized with only glycerol and then mixed to the poly(lactic) acid (PLA) The replacement of a certain percentage of glycerol with fried edible sunflower oil as plasticizer for starch results in an improvement in material properties of the TPS.

In this work, the possibility of adopting fried sunflower seed oil as a plasticizer was decided to be studied. Oil is, in particular, the waste from the fast -food frying process. The use of this oil can be twice advantageous as reducing the cost of the plasticizer and reusing a waste product according to the research.

Small hydrophilic molecules such as amino acids, glycolic or polyols are commonly plasticized into corn starch powder. Among these, glycerol, a substance that is rather costly because of the laborious production process is the most commonly used. As stated above, the innovation proposed in this work is to replace part of glycerol with fried oil into the starch plasticization in order to reduce the costs of glycerol and simultaneously reuse a waste product. In particular, to compare, their plasticizing capabilities, different percentages of glycerol were replaced by raw and fried oil.

Uniaxial tensile elongation was applied to the films, from which elastic modulus and maximum stress were evaluated. There is a lower modulus of thermoplastic starch with only glycerol than the one with oil. With the oil/glycerol ratio, the elastic modulus increases to a maximum value, corresponding to an oil/glycerol ratio equal to 0.5. The maximum stress presents a similar trend, TPS with fried oil having a larger modulus and a larger maximum stress with respect to raw oil thermoplastic starch. It can therefore be concluded that the substitution of a percentage of glycerol with specially fried edible sunflower seed oil as plasticizing for the starch results in improved thermal stability and mechanical properties of TPS.

Conclusion

In conclusion, the high performance of starch-based biodegradable using the additional natural fillers/fibres such as cellulose and nata de coco and also plasticization with sunflower oil has also been reviewed. According to the four

research paper articles, the improvement of starch based biodegradable film can be made from the addition of natural fillers/fibres and the addition of natural plasticizer made from vegetable oil. It showed that the lack properties of starch-based film can be modified to make excellent mechanical and barrier properties, affordable biodegradable film. Based on the articles chosen, a film made from lignin as written by Bhat, et al. in 2013 is the most suitable to add in starch-based film for future reference plastics. This is because, it has higher tensile strength and elastic modulus, lower water vapor permeability and lower water solubility.

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