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Implementation of Nanofiller for Bioplastic Reinforcement: A Review

Nur Farhana Fadzil[1], Siti Amira Othman[2*]

[1] Faculty Science and Technology, Universiti Sains Islam Malaysia (USIM), Nilai, Malaysia
[2] Faculty Applied Science and Technology, Universiti Tun Hussein Onn Malaysia (UTHM), Johor, Malaysia

*Corresponding Author: sitiamira@uthm.edu.my

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Abstract: *One of the side effect of technology advancement is the inability of nature to decompose substances created by human. Abundant waste of non-degradable plastic on land and oceans have become more increasingly serious issues. Therefore, there are growing research and development on natural-based materials with biodegradable properties. The interaction between biopolymer and nanofiller have attracted attentions for the improved functionality exhibit by them. The novel or improved characters are obtained depending on the type of nanofiller used such as antioxidant, antimicrobial properties, active agent and enhancement of mechanical and thermal properties. These features have great potential for the application in food packaging, medical and tissue engineering.*

Keywords: Bioplastic, nanofiller, food packaging, biodegradable, food packaging

1. Introduction

The annual global plastic production and usage escalates rapidly particularly after the spreading and infectious globally of novel pandemic coronavirus in 2019 (Covid-19). Studies predicting a twofold increase in the number of plastic debris including micro and nano-sized plastic by 2030 (Patricio et al, 2020). However, the excessive use and consumption of single-use plastic including masks, personal protective equipment, medical tools and gloves due to this pandemic are likely to aggravate the predictions. The facts that plastics have become a severe threat as they are difficult to recycle and will remain in the environment, unaltered, releasing toxic substances and gases for hundreds or even thousands of years are undeniable. Therefore, there are prominent impetus in developing biodegradable and bio-based materials from natural sources such as cellulose, starches, proteins, pectin and chitin (Patricio et al, 2020). This bioplastic is also an effective alternative for conventional synthetic petroleum-derived plastic usage which can be applied for food packaging industry, automotive, agriculture and medical field.

In order for the bioplastics could help to reduce the consumption of synthetic polymer, their limitations and drawbacks related to poor mechanical properties, low thermal stability, gas barrier properties and hygroscopic character need to be overcome. One of the promising methods and alternatives to subdue these restraints is by preparing the bioplastic through combination of both organic moieties and nanofillers such as nanoclay (Maulida et al, 2018; Bumbudsanpharoke et al, 2019), nanocellulose, carbon nanotubes (Amri et al, 2018) and inorganic nanofiller (Harunsyah et al, 2017; Agustin et al, 2017). Nanofiller inclusion into natural-based composites not only reinforcing the function but also could act antibacterial agent and active ingredients.

2. Bio-based plastic

Bioplastics are biodegradable plastic made up from natural and renewable feedstocks such as potato, corn, pineapple, jute, hemp, bananas, cassava, citrus waste and many more. These feedstocks greatly come from the fruit and vegetables wastes after their juice processing extraction (Manali et al, 2021). Generally, bio-based plastic can be categorized based on two factors, fossil-based or bio-based, non-biodegradable or biodegradables (Cinar et al, 2020). Bio-based can be further classified into three groups; (i) agro-polymers, valuable compounds such as starch, cellulose and pectin in fruit and vegetables wastes as well as animal's protein. (ii) Polymers from microorganisms, cultured microorganisms under diverse nutrient and environmental conditions for the production of polymer. For example, thermoplastic polymer, polyhydroxyalkanoates (PHA) with hydroxyalkanoic acid as monomer unit can be synthesized intracellularly into insoluble cytoplasmic inclusions using heterotrophic bacteria and also by photoautotrophic microorganisms (such as microalgae). (iii) Biotechnology polymers. This group of polymers implement both bacterial microorganisms and agricultural by-products for the production of polymer. Poly Lactic Acid (PLA) is obtained by conversion process of corn starch or any carbohydrates sources into dextrose, further undergo fermentation/conversion into lactic acid (Acquavia et al, 2021).

Presently, bioplastic and biocompatible polymers are highly in interest as their characteristics features of highly functionalized globular nature (Yaradoddi et al, 2016), biodegradable and sustain the production and consumption cost by increasing the resources efficiency, reducing materials' carbon footprints and minimize the usage of petroleum-based (Veronika, 2019). Biodegradable polymers may recover biologically by composting in the soil or by anaerobic digestion. Besides, they can also be recovered via treatments mechanically and chemically. Abundant amount of fruits waste from the juice processing industry occupies the lands and eventually leads to increasing of municipal solid waste (MWS) especially in urban. These fruits waste confined valuable compounds such as celluloses, pectin and fibers that are suitable for bio-derived polymers creation. Over the past decades, these underutilized fruit wastes have been biorefined into bio-plastic or bio-polymer and been applied for food packaging, medical equipment, pharmaceuticals, automotive and agriculture.

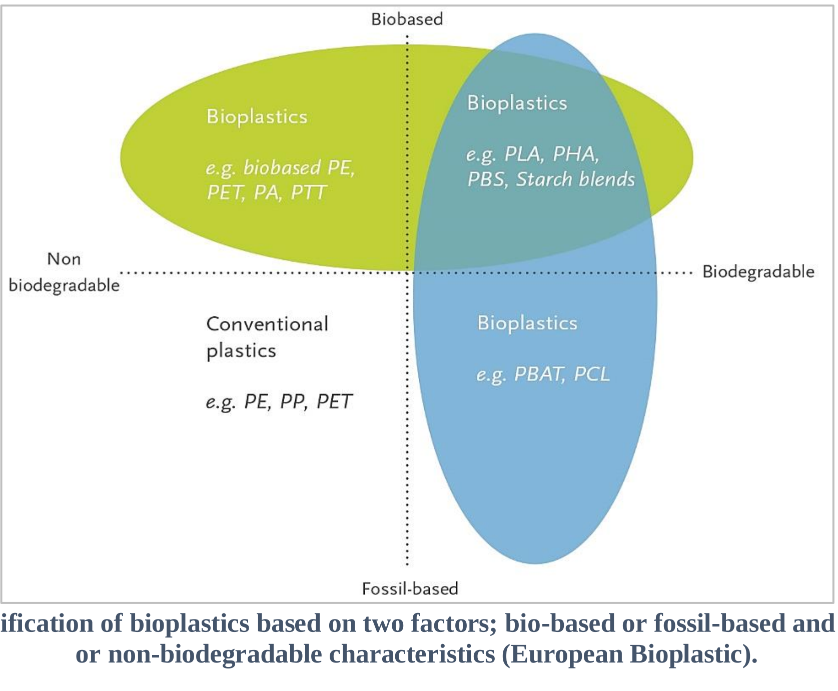

Figure 1: Classification of bioplastics based on two factors; bio-based or fossil-based and biodegradable or non-biodegradable characteristics (European Bioplastic).

3. Nanofiller for bioplastic

Production of bio-based polymers are an alternative for replacing the rising usage of synthetic plastics although it has several limitations and drawbacks such as weak mechanical properties, high hydrophilicity and decomposition susceptibility. The growing interests of nanotechnology presently facilitated the path to use nanofillers in plastic production industry. Therefore, combination of biopolymer and nanofiller are greatly in interests nowadays as the interaction of nanofiller modified biopolymer matrixes which contribute to the improvement of mechanical strength, thermal and also barrier properties of bionanocomposite materials.

Nanofillers can be classified into four types; clays, organic, inorganic and carbon nanostructures. Natural biopolymers such as chitosan and cellulose are included in the organic nanofillers meanwhile, inorganic agents are divided into metal (e.g., silver) and metal oxide (e.g., CeO_2, TiO_2 and ZnO). Carbon nanostructures is a wide field and thus can be further classified into fullerenes, graphene, nanofibers and carbon nanotubes (Jamroz et al, 2019). These nanofillers can also be classified into three types according to their dimension; nanoplatelets (one nanoscale dimension), nanofiber (two nanoscale dimension) and nanoparticulate (three nanoscale dimension) (Sundarram et al; Jabeen et al, 2015). The selection for physical properties and preparation of nanofiller highly connected with the required application

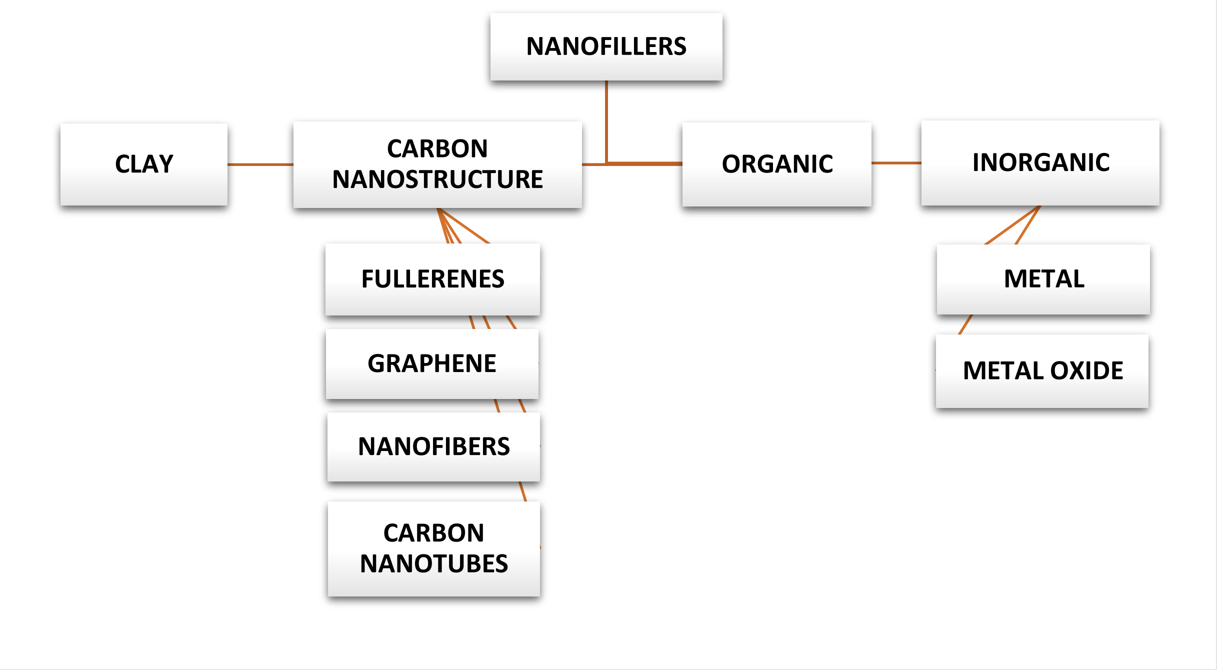

Figure 2: The classification of nanofiller used in biopolymer reinforcement.

Clay and organic nanofiller

Nanoclay is a component composed of phyllosilicates, a compound made up from elements such as oxygen, silicon and other components. The elements are degraded from natural sources, pretreated chemically and exists in the form of platelets or sheets. Nanoclays possess a property of low specific gravity, nanoscale with high aspect ratio. Diverse type of nanoclays is incorporated into polymer to reinforce their characteristics and the most common used nanoclays are montmorillonite (MMT, $MMT\text{-}Na^+$), organophilic MMT (organic modified

MMT, OMMT) and halloysite (Hal) for packaging applications (Bumbudsanpharoke et al,2019).

Natural biopolymer nanofibrils containing variety of biopolymer molecules including cellulose, chitosan and chitin are employed as filler for biopolymer production due to the factors of biocompatibility, high durability, ability to degrade and biocompatibility. According to Jamroz et al (2019), nanoscale of cellulose employs as addictive and filler in biopolymer have three types; cellulose nanocrystal, nanofibrallated cellulose and bacterial nanocellulose (BNC). Extraction of short rod and high crystalline cellulose are from cellulose fibrils by acid hydrolysis. It is also known as cellulose nanowhiskers and nanocrystalline cellulose. On the other hand, nanofibrallated cellulose extracted using mechanical method from cellulose fibers producing long, tangled and flexible cellulose filler. This type of cellulose nanofiller also have several terms such a cellulose microfibril, nanofibrillar cellulose, microfibrillated cellulose, cellulose nanofibril and cellulose nanofibril. Bacterial cellulose confined high crystallinity and molecular weight compared to plant-based cellulose. Gram-negative bacteria, *Gluconacetobacter xylinus* are used to extract this BNC. Different type of sources and extraction method are the main factors result to these classifications.

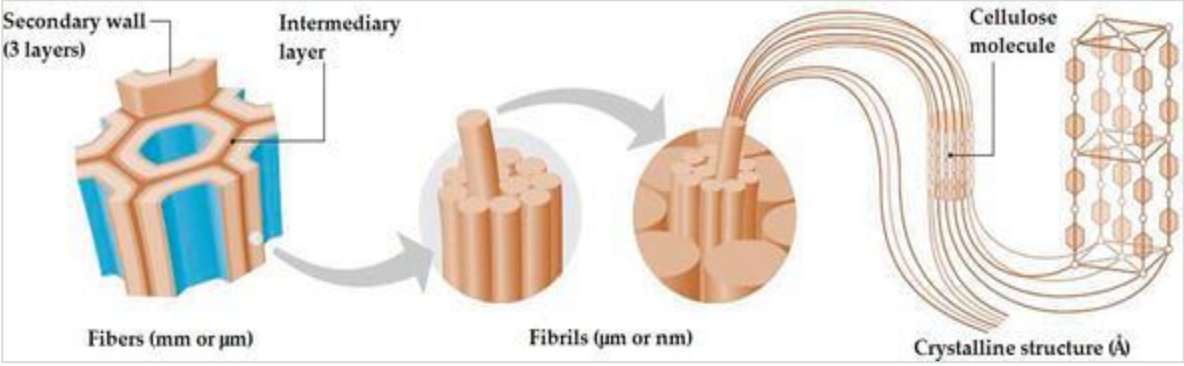

Figure 3: Illustration of crystalline cellulose structure.

Chitosan & chitin are also gained attention as nanofiller for biopolymer. Chitin, the second most abundant polysaccharides on Earth after cellulose. It is mostly accessible in insects and marine invertebrates (e.g., crabs, oysters, lobsters and shrimps) as a primer constituent of exoskeleton and also a component cell walls in certain fungi. These crustaceans confined external shells and other inedible parts about half the body mass and typically discarded as waste. Prominent sources of chitin come from these discarded wastes (Kumar et al, 2020). On the other hand, Chitosan (CS) is the soluble form of chitin obtained from chitin partial deacetylation process forming N-acetyl-glucosamine and α-glucosamine copolymer. Owing the characteristics of attractive surface area, ability to form biofilm, non-toxicity, biodegradable and good antimicrobial activity, chitin and chitosan are employ in various industry including food preservation and packaging.

Inorganic nanofiller

The functionalization of polymer with great success can be achieved by the integration of inorganic nanofiller. In general, this type of nanostructure filler can be classified into metal and metal oxide. These inorganic fillers and additives generally form composite biopolymer electrolyte by bounding with the polymer matrix. There is variety form of filler such as spheroidal, fibrous or porous studied for the purpose of composites enhancement (Sudhakar et al, 2018).

Carbon nanostructure

In recent decades, the unique properties of carbon nanomaterials have attracted tremendous attention among researchers. Some examples of carbon nanostructures are graphene, carbon nanotubes (CNT), carbon black, fullerenes and nanofibers. One of the most outstanding and gained attention is graphene-based material due to their excellent properties in mechanical, stiffness and substantial electron mobility. It has been emerging used as filler for conducting and reinforcing applications. Jabeen et al (2015) state that, graphene has promising future application in electrical devices as well as polymer composites.

4. Improvement & application of nanofiller on biocomposite films

One of the key purpose additions of nanofiller in biopolymer is to increase the tensile strength. several factors effected the tensile strength of composite material including the relation between the material's matrix and reinforcement in the composite. In a research by Harunsyah et al (2017), the composition of zinc oxide nanofiller added into the polymer matrix is compared within the composite materials. From the study, the maximum tensile strength of cassava starch bioplastic obtained was 22.30 kgf/mm2 with 0.6% zinc oxide addition and 25% glycerol. Increasing of zinc oxide nanoparticles indicates the rising of tensile strength but declined at a certain threshold as the matrix (starch) have more space for the particles thus influenced the biofilm tensile strength. The percentage of elongation at break could increase while reduced the tensile strength with the presence of glycerol as plasticizer.

In another cases, the mechanical properties of cassava starch-based bioplastic improved by incorporation of graphene oxide. Increased in tensile strength and Young's modulus results by increasing of graphene oxide while less elongation would be. Amri et al (2018) stated that increasing the GO content and mixing time gave and improved in mechanical strength as an outcome due to good composite constituent's homogeneity. Attributed to the hydrophilic properties of GO, as more addition of GO, rate of biodegradation activity eventually increases. The influenced of glycerol and ZnO addition on biodegradability and antibacterial activity onto chitosan-kepok banana peel starch are also studied (Agustin et al,2017). Degradability rate of the bioplastic significantly increasing by the increasing of starch concentration and the antimicrobial activity demonstrated more effective against gram negative (E. coli) contrary to gram positive (S.aureus) bacteria. ZnO capable to exhibit antimicrobial activity effect by soluble species diffusion into agar medium which proven their efficiency as antimicrobial agent. Even so, the presence of ZnO decreased the biodegradability rate of the chitosan-starch bioplastic as the Zn2+ ion act as a bridge and substitute for the lost intra and intermolecular hydrogen bond. Chitosan-starch bioplastic shows great impetus for food packaging application.

Maulida et al (2018) studied that mango seeds starch-based bioplastic reinforced with clay particles increased the tensile strength from 1.567MPa (pure starch) into 5.797MPa. The elongation break is inversely proportional to tensile strength results in reduction in the value. Strong hydrogen bond between hydroxyl groups of both clay filler and starch matrix's interface attribute to the bioplastic improvement reinforced with clay particles. Composition of 6% clay and 25% glycerol was found to be the highest tensile strength. Addition of clay particles causing agglomerates and deflection on the bioplastic. The halloysite nanotubes functionalized cucurbit[6]uril were incorporated into pectin-based bioplastic by Biddeci et al in 2016. The goal for developing a novel nanofiller with high solubility capability towards peppermint essential oil (PO) could be achieved by these hybrid fillers. Both mechanical performances and pectin-based film surface hydrophobicity were enhanced with the hybrid fillers addition with slightly affected thermal behavior. The large inhibition percentage (41%) of free radical DPPH proven the reliable antioxidant activity of the biocomposites.

The relation and thermo-mechanical effect between inorganic nanotubes, Halloysite on Mater-Bi biofilm (Mater-Bi/halloysite) were also studied by Lisuzzo et al (2020). The strain break for Metal-Bi/Hal 10 wt.% nanocomposite much higher compared to the others; 0, 1 & 20% wt. It was clearly proven that concentration of halloysite nanotubes influenced the ultimate elongation of Mater-Bi based film and the ultimate elongation' percentage detected were 30 and 100% (pure and Mater-Bi/Hal biofilm respectively). Further halloysites concentration' addition will only reduce the elongation at break. Nanotube's presence in small quantity confers improved the performance of thermo-mechanical with respect to Mater-Bi. Halloysite contents less than 10%wt showed polymer degradation temperature enhancement up to 4°C. Besides chitosan, eggshell could also act as organic filler for potato-starch derived bioplastic (Kasmuri et al, 2018). Eggshell proved to achieved high Young Modulus value;0.333 N/mm2. There are two type of membrane layers made up from protein fibers, confined in the eggshell. These membranes hold the molecules' bond exist in the bioplastic and it became more rigid. A good bioplastic samples has low water absorption rate and high weight loss result in shorter time to decompose. Eggshell and chitosan exhibit both characteristics mentioned.

A novel matrix composite of wheat gluten and shrimp shell waste as filler successfully prepared by Thammahiwes et al (2017). Incorporation of shrimp shell powder into the biofilm improved the tensile strength and achieved its maximum with 2.5 wt% (6.53MPa) shrimp powder content which is twofold than pure biofilm. Excess powder content results in agglomeration and reduce its strength. Further comparison demonstrated that high mineral content and layer structure changes of shrimp shell powder after calcination process are more effective at improving these tensile, morphology and thermal properties.

Table 1: Examples of bioplastic film with the addition of nanofiller.

BIO-BASED POLYMER	FILLER	EFFECT ON BIOPLASTIC WITH NANOFILLER ADDITION	REFEERENCE
Cassava starch bioplastic	ZnO	• Optimum formulation composition achieved tensile strength of 22.30kgf/mm2, with 0.6% zno and 25% plasticizer concentration. • Best elongation at break's value is 122.80% with 0.6% zno and 30% glycerol concentration.	(Harunsyah et al, 2017)
Chitosan-Kepok banana peel starch bioplastic	ZnO	• ZnO proven to be great antimicrobial agent by decreasing the microbial growth. • Glycerol enhanced the biodegradability of the bioplastic; potential for food packaging application	(Agustin et al, 2017)
Cassava starch bioplastic	GO	• High tensile strength of 3.92 mpa, 13.22% elongation value & 29.66mpa young's modulus from bioplastic produced by 15% go and 60 minutes mixing time.	(Amri et al, 2018)

Mango seed starch bioplastic	clay	• Improved tensile strength into 5.797mpa from 1.567mpa (pure starch bioplastic). • Addition of clay reduce the water uptake in bioplastic	(Maulida et al, 2018)
Pectin-based bioplastic	Halloysite Nanotubes-cucurbit[6]uril (HNT/CB[6])	• Enhanced mechanical performances and the pectin-based film's surface hydrophobicity. • Thermo-tuneable antimicrobial activities.	(Biddeci et al,2016)
Mater-Bi based bioplastic	Halloysite Nanotubes (Hal)	• Increase strain break with 10wt% of halloysites. • Improved the thermo-mechanical performances up to 4°c with nanotubes content lower than 10wt%.	(Lisuzzo et al, 2020)
Wheat Gluten bioplastic	Shrimp shell powder	• Tensile strength increased twofold with 2.5 wt% shrimp shell powder compared to pure wheat gluten bioplastic. • Calcined shrimp shell powder shows better degradation activity.	(Thammahiwes et al, 2017)
Potato starch-based bioplastic	Eggshell	• Increased tensile strength by 4.94% due to fibre presence in the membrane layers. • Reduction of 10.95% of water absorption • High rate of weight loss in biodegradability (21.06%) in 20 days	(Kasmuri et al, 2018)
	Chitosan	• Enhanced the tensile strength by 1.28%. • Reduction of water absorption up to 27.59%. • Weight loss in biodegradability increased by 7.9%	

5. Conclusion

The application of nanofiller in biopolymer materials is being more prevalent because of its functional property reinforcement and enhancement. It can be concluded that nanofiller increased the mechanical properties, thermal stability, act as antimicrobial and antioxidant agent. Additional features offer by nanofiller inclusion depends in the type of filler used, percentage of composition and also rely on the required application. These combinations could be used as an alternative for synthetic petroleum-based polymer. Further studies and research still need to be done to investigate their effect in a long-term period.

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