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Impact of Titanium Dioxide with Industrial Food Waste on Bio-polymer Matrix of Banana Peel from Agricultural Waste: A Review

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ABSTRACT: Bio-composite of bio-polymer have recently emerged as potential materials for agricultural applications. Bio-composite requires multi-component mixing which involves surface modification, the use of polymer mixtures and the addition of reinforcements or filler. Investigations were made to assess the impacts of normal enduring in the city of Kelantan on the mechanical and morphological properties of a composite made of titanium dioxide on modern food waste, for example, fish bone and egg shell bio-filler. The mechanism of titanium dioxide (TiO_2) will be discussed to investigate how its effects to bio-filler and bio-polymer matrix from agricultural waste. The study of mechanical effects and bio-degradation test were updated as composite films.
Keywords: composite; titanium dioxide; fish bone filler; egg shell filler; agricultural waste; bio-degradation test

1. Introduction

Agriculture is defined as the farming practice that involves the cultivation of soil to grow crops, rear animals, and cultivate fungi or other forms of organic life to provide food, fibre, medicines, fuel, and many more beneficial products for human use. Agriculture contributes to a large quantity of lignocellulose biomass that can be produced from agriculture waste, forest residues, and municipal solid waste. In fact, Malaysia recorded the highest percentage of agricultural waste across the world in 2007 where most of the wastes were originated from oil palm biomass residues such as leaves, fronds, trunks, fruit bunches, kernel shells, and fibres, paddy residue (approximately 830 ktons), banana residue (approximately 830 ktons) and organic waste that includes food waste and paper cardboards (approximately 4653 ktons) [1].Therefore, this of agricultural waste commonly used to be as bio-polymer for varied applications worldwide. The effects of titanium dioxide as additives in bio-filler of fish bone and egg shell fillers were discover.

1.1 Banana peel

Banana peel or also called as banana skin is the outer envelope (cover) of banana fruit. Usually, it becomes a waste of household consumption and banana processing. Due to that reason, disposal of banana peel can contribute to a significant amount of organic waste being generated. Most of banana peel are counted as agriculture waste. Many industries of using banana peel as main ingredients in their food processing such as bakery, banana crispy and crispy banana was throw away this waste in landfill. Despite of treating banana peel as waste, banana peels can be converted into many useful products such as animal food, plant fertilizer, cooking ingredients, encapsulation for functional food and packaging material.

Banana peels consist of high sources of starch which is about 18.5%. The lignocellulosic materials exist as three important components: cellulose, hemicellulose, and lignin. In the meantime, unripe banana naturally consists of more than 70% starch, with the remaining 30% comprised of protein, lipids, and fibre. The polysaccharides in banana peel powder can give extra hydrogen bonding contacts between polymer chains, which is responsible for the film-forming capacity.

1.2 Titanium Dioxide

Titanium dioxide (TiO_2) is a transition metal oxide consisting of three polymorphs; anatase, rutile and brookite. The most stable phase is rutile while anatase is metastable at room temperature. TiO_2 is an inert, inexpensive material and has a high refractive index with UV shielding which makes it useful as paints, plastics and pharmaceuticals. Moreover, polymer nanocomposite containing low TiO_2 content exhibits unique optical, electrical, thermal and mechanical properties, thus making the polymer-TiO_2 nanocomposite a promising new material class. In addition, such composites are also used in active food packaging for antibacterial activity, the breakdown of organic contaminants and the disposal of plastic trash.

The purpose of TiO_2 filler addition in PMCs is not only to improve basic properties such as mechanical, electrical, optical and thermal properties, but also to enhance its functional properties. The important functional properties of TiO_2 include photocatalytic and antibacterial properties. In the presence of light, TiO_2 can generate an electron transition from the valence band to the conductive band, promoting the oxidative capacity of other species by creating active agents such as radicals. Research conducted by [2], [3] and [4] showed that the antibacterial properties of packaging film made of PLA/TiO2 composite can be enhanced by increasing the amount of TiO_2 in the composite.

Addition of TiO_2 with low concentration into polymer can also provide new mechanical, thermal, electrical, optical and barrier attributes to the resulting polymer nanocomposites. This can be seen from the cross-linked wheat starch film as it has represented greater ultimate tensile strength (16.87%) and Young's modulus (8.45%) and lower elongation at break (10.58%) values compared to native wheat starch. This is associated with the formation of either ether or ester inter-molecular linkages between the hydroxyl groups of starch molecules which contributed to more strength structure.Moreover, the thermal stability of improvement can be seen from the degradation temperature after the addition of 0.2% modified TiO_2 into the PLA/starch composite which shows value increased to 357°C and 358°C [4].

TiO_2 has a polar surface, while the polymer matrix is non polar, which makes the surface adhesion between the matrix and the TiO_2 deficient. As a result, TiO_2 particles have a high potential to give good effects on composites for various applications such as wound dressings, food packaging material, bio-degradable UV protective films for agricultural purpose and fruit and vegetable packaging materials.

2. Bio-filler from industrial food waste

2.1 Fish bone

Fishing sector has become a major contributor to protein sources for Malaysian. In 2019, the fishing industry contributed 12% of gross output to the agriculture sector. Malaysia has a variety of fish species of both freshwater and marine fish. Fish is consumed as food and commonly used to make fish products such as fish crackers, fish balls, fish cakes, salted fish and fermented fish. About 30% of the market was made up of processed fish for human consumption [5]. Every year, a large amount of fish waste such as fish scales, bones and skins are produced, resulting in the increasing of fish waste production in Malaysia. Countless efforts have been initiated to overcome this problem by converting these fish wastes into useful products.

Bones constitute a significant part of the fish; approximately 10–15% of total fish biomass are bones from the head and vertebrae. Fish meal is produced from fish by-products or whole fish contains about 10% minerals, especially high in calcium and phosphorus, and represents an important source of minerals when included in the feed. The digestibility of minerals from fish meal shows great variation but is generally low, and the presence of phytic acid from vegetable protein sources may further decrease the availability. The level of available phosphorus in feeds for aquaculture might be limited for optimal growth and fish health. For example, three types of nano hydroxyapatite (nHA) from rainbow trout (Oncorhynchus mykiss), cod (Gadus) and salmon (Oncorhynchus Keta) fish bones using thermal calcination management and examined their characterization and biocompatibility. They concluded that nHA derived from rainbow trout and salmon bone materials contained essential mineral ions that improved proliferation, differentiation, cell adhesion and mineralized tissue formation.

On the contrary, fish bone (FB) is also known as one of the main sources of natural hydroxyapatite (HAp). HAp with a chemical formula of Ca10(PO4)6(OH)2 is one of the inorganic components of the hard tissues of living bodies such as bones and teeth. Natural HAp derived from FB is discovered to be beneficial in applications such as orthopaedic and dental implant materials [6]. When compared to commercially available HAp powder, HAp derived from FB is more cost-effective as it can cut the cost of production by five to ten times. This is due to the simple and low-cost method used in extracting HAp from FB. Calcination is the most widely used procedure for HAp extraction. With this procedure, the high-purity powder can be created without causing the chemical composition to degrade. The morphology of natural HAp powder derived from FB using the method is shown in **Fig 1.**

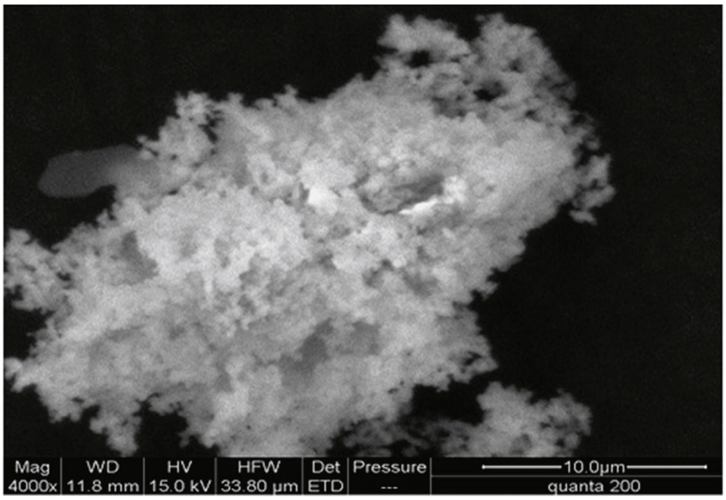

Figure 1: SEM image of natural HAp derived from FB [7].

Incorporation of HAp derived from FB into PMC's filler has been extensively studied by [8] and [9]. According to them, the mechanical strength, biodegradability and biological characteristics of polyester/HAp and HAp/epoxy composites were all satisfactory. Mechanical properties, on the other hand, are not comparable to naturally mineralized bone tissue. The reason for this condition is that the HAp and the polymer matrix may have a poor interaction. HAp derived from FB can also be used as filler in biopolymer composite. According to a recent study by [10] on the HAp/cellulose nanofibre/curcumin biocomposite, the composite has superior thermal properties, biocompatibility, antibacterial properties and high mechanical capabilities which make them useful components for bone tissue engineering application.

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2.2 Egg shell

A large volume of solid waste is produced by the food sector each day, which can end up in lakes, rivers and water drains. Egg shell (ES) has appeared to be one of the major contributors to organic waste because they are widely available and the production is expanding every year. Due to the increasing demand and big market for chicken eggs, it has contributed to a large amount of food waste as their only disposal option is landfills, which can cause the emission of harmful gases such as ammonia, hydrogen sulphide and amines with strong aromas when decomposed. In addition, it is also leading to air pollution due to foul smell and, at the same time attracting mice, rats, flies and pathogens such as Escherichia coli (E. coli) and Salmonella spp. to be grown in eggshell and seashell waste [11].

So far, ES has shown promising properties in various of applications, including animal feed, human nutrition, ink-jet printing paper-coated pigments, natural heavy metal absorbents, dye-effluents removal, bone substitute and filler for polymer-based composites. A study has shown that the micro-porous structure of eggshell powder has appropriate physical properties to be used as a reservoir for drugs and chemicals. The large market of ES can be seen by the total production of chicken egg around the world in 2013 including Malaysia as shown in Table 1.

Table 1. Countries of leading chicken egg producers in Asia [12].

Country (chicken egg production in million metric tonnes)	
Mainland China (24 446)	Iran Isl Rep (665)
Japan (2522)	Thailand (668)
India (3835)	Malaysia (664)
Turkey (1031)	Pakistan (649)
Indonesia (1224)	Korea (615)

Total production of all countries = 36320

ES can be used as a reinforcing agent in polymer-based composite to reduce cost and enhance physical, mechanical and thermal properties [13]. Yet, the final performance of the composite is determined by the types of fillers used, the composite's distribution, the interfacial interaction between the polymer and the fillers, the ratio and size of the fillers and the presence of the coupling agent. Table 2 shows the summary of the effects of filler on particle size and distribution, filler composition on processing, mechanical properties and thermal properties of a polymer-based composite.

Table 2: Effect of ES characteristics on properties of composites.

Factor	Properties	Reference
ES particle size and distribution	Mechanical properties (tensile strength, hardness values and impact energy)	[14]
ES particle size and distribution	Thermal properties	[15]
ES content	Mechanical properties (flexural strength, hardness)	[16]
ES particle size and distribution	Processing	[17]
ES content	Mechanical properties (tensile strength, hardness)	[18]

High content of $CaCO_3$ has made ES a suitable option for bio-sources mineral fillers in a composite. It can exhibit strong photocatalyst as well as good antibacteria activity. On the other hand, HAp can also be derived from ES. HAp is often used as filler in many PMCs as it has excellent biocompatibility with human bones. Despite the fact that composite development based on ES and synthetic polymer has been extensively explored, the knowledge on the compatibility of biopolymer matrix and ES filler has not been fully discovered. Thus, the study on ES filler with biopolymer sources such as banana peel should be further investigated. Moreover, high filler content commonly produces inhomogeneous distribution which contributes to poor interfacial bonding with bio-polymer matrix. This finding is confirmed by [19] study. They explained that the optimum content of ES varies with the nature of the materials for composite. Hence, research on the effect of ES filler concentration in composite should be pursued.

3. Mechanism of titanium dioxide (TiO2) with bio-filler in bio-polymer matrix

After adding TiO_2, relatively less agglomeration occurs. All composite morphologies have spherical and porous particle shapes. The addition of TiO_2 led to an increase in the density of the composite layer [20]. After calcination and grinding of egg shell fillers, the final particles become nanosized with less agglomeration tendency. Calcined egg shell nanopowder utilized as co-sorbent or support with the prepared TiO_2 photocatalyst exhibits enhanced photocatalytic degradation efficiency as compared to the bare TiO_2 nanoparticles. The solvothermal derived TiO_2 nanocrystals supported on ground nano-sized egg shell waste exhibited enhanced photocatalytic activity as compared to the as-prepared TiO_2 nanoparticles [21]. From the study by current research, the interaction between nano-TiO_2 can prevent random agglomeration of fillers, thereby enhancing the functional properties of bio-composites [22]. The support mechanism for this bio-polymer with TiO2 and bio-filler as in Figure 2. Less area of roughness or significant aggregation observed in the WBP matrix resulted in a very good dispersion of TiO_2 particles.

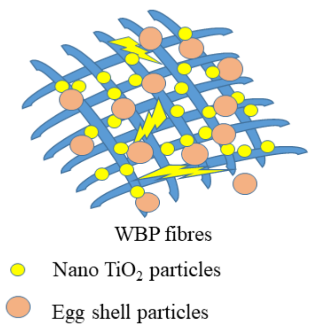

Figure 2: Nano-TiO2 particles interactions in WBP-ES-TiO_2 composite

4. Conclusions

In conclusion, the water repellent action and thermal properties of the WBP-ES and WBP-FB composites were enhanced by the inclusion of TiO_2 particles, however the strength of the composite films was somewhat decreased. An additional benefit of adding TiO_2 was the potential for a light-weight bio-composite film. The characteristics of the HA that develop are significantly influenced by the presence of TiO_2. Furthermore, employing disc diffusion and optical density techniques, the HA-TiO_2 composite demonstrated good antibacterial activity. These findings show that the synergistic combination of TiO_2 and HA from eggshells has advantageous characteristics for antibacterial action. When compared to the as-prepared TiO_2 nanoparticles, the solvothermal-derived TiO_2 nanocrystals supported on ground nano-sized egg shell waste shown increased photocatalytic activity. The combined action of nano-egg shell support and TiO_2 nanoparticles is credited with the effective dispersion of TiO_2 that offers high specific surface area.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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