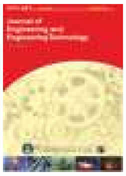

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Investigation into properties of starch-based nanocomposite materials for fruits and vegetables packaging- A review

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A B S T R A C T

The huge environmental impact associated with the use of conventional packaging materials, like polyethylene, has led to the renewed interest in alternative ways of food packaging. Recently, green polymer technology, which involves the application of renewable packaging materials made from biodegradable resources like starch, has been the subject of discussion among stakeholders in food processing and storage. This review was carried out to investigate the mechanical, thermal, barrier and structural properties of biodegradable nanocomposite packaging materials made from starch. Emphasis was given to the application of the starch-based biodegradable packaging materials in fruits and vegetables packaging. The prospect of the new materials in terms of strength, barrier to moisture and oxygen, morphology and thermal stability, with regard to the inclusion of nanoparticles, for this application was highlighted. The information provided will help address the environmental challenges often posed by the conventional materials while at the same time improve the post harvest storage stability of fruits and vegetables through packaging.

1. Introduction

Biodegradable packaging material can be prepared by blending definite proportions of renewable raw materials, like starch, protein and polylactide, with a hydrophilic compound, such as glycerol, urea or polyethylene glycol in hot water maintained at 95oC (Dang and Yoksan, 2015; Fadeyibi et al., 2016a). Choosing any blend of renewable material and hydrophilic compound in the preparation of the packaging materials depends partly on the availability of the raw materials and partly on their application. The type and nature of the biodegradable materials commonly found in most supermarkets, for application in food packaging, are as a result of the availability of the raw materials. For instance, starch, which is readily available and cheaper than either protein or polylactide is often considered ideal material in the formulation of the packaging material (Chung et al., 2010; Huang and Yu, 2006). The huge economic benefits of protein sourced foods to man has rendered the material unattractive for transformation into biodegradable packaging material (Dai et al., 2015). Hence, the packaging engineers preferred starch, which can serve other uses apart from its benefit to man, for application in the formulation of biodegradable packaging materials.

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In order to improve the performance of biodegradable packaging materials organic or inorganic particles with size ranging between 1-100 nm are often added (Mehyar and Han, 2014). The improvement in the physical nature of the packaging materials may be due to large reactive surface area presented by the nanoparticles. Common examples of inorganic nanoparticles used for this application include silver, tin, sodium ion (montmorillonite) and zinc (Tall et al., 2007). The organic nanoparticles commonly used in the food industry include those made from bamboo, sugarcane bagasse and wood sawdust. Each of these nanoparticles, whether organic or inorganic, has been used to modify the matrix of the packaging materials for their latter application in food packaging. The possibility of migration of the nanoparticles into the packaged food has been an issue over the years. Research is till on going to address this using the Toxicity Level Selection Approach (TLSA). There are some metals, like lead, that are naturally toxic, and so it will be unwise to introduce such in packages because of the possibility of migration. Therefore, the toxicity level of metals and non-metals are constantly studied to ascertain which is better placed for this application. Through this approach, zinc and montmorillonite has been reported to be human and environmentally friendly for use as fillers in biodegradable packaging materials (Fadeyibi et al., 2016a; Zhang et al., 2008).

Biodegradable nanocomposite packaging materials have found application in the food industry, particularly in extending the shelf life of agricultural products (Fadeyibi et al., 2016a). The new materials have been proven active in allowing easy gaseous exchange through them and preventing the growth of deteriorating microorganisms. Thus, agricultural products can be packaged conveniently using biodegradable nanocomposite materials to predetermined storage lives without any appreciable quality loss. The choice of a particular material for food packaging is dependent on the properties of the packaging material concern. Even though by default, every biodegradable nanocomposite materials have enhanced physical and mechanical properties (Mehyaret al., 2014), those made from starch are better in terms of strength and are preferred from economic implication. Therefore, this review carried out to investigate the mechanical, thermal, barrier and structural properties of starch-based nanocomposite materials for application in fruits and vegetables packaging.

2. Properties

2.1 Mechanical properties

Mechanical property of starch-based biodegradable film can be studied using the nanoindentation techniques. This is an indirect measurement of the contact area between an indenter and the specimen. The method provides an avenue of touching the biodegradable film, whose mechanical properties such as elastic modulus and hardness are unknown, with another material of known property. The depth of penetration of the indenter in the film is usually measured in nanometers, thus considering the process as non-destructive because of its relatively smaller area of contact. Gouldstone et al. (2000) studied the discrete and continuous deformation of thin film using the nanoindentation technique. The authors revealed that the response of the film is composed of purely elastic behaviour with intermittent micro-plasticity. Tall et al. (2007) studied nanoindentation of Ni–Ti thin films, and observed that the Young's moduli qualitatively measure the extent of stress-induced phase transformation in the small volumes of Ni–Ti films. The mechanical properties of Cu2O thin films have been studied using nanoindentation techniques (Sheng-Rui et al., 2013). The indentation process usually involves a record of the depth of penetration and the indented area using a known geometry of the indentation tip.

The mechanical properties of biodegradable film of interest include, but are not limited to, the tensile strength, Young's modulus and elongation at the point of break; and they are essential in understanding behaviour of the materials under dynamic loading, especially on high speed transportation (Fadeyibi et al., 2016b). For instance, the tensile strength is an important parameter for proper design of biodegradable packaging films which must show adequate resistance to wearing. The selection of biodegradable film for a specific packaging application is usually based on the mechanical performance of the material (Siracusaa et al., 2008). Moreover, the tensile stress, elongation at the point of break and elastic modulus of biodegradable film are also essential parameters for understanding the stiffness of the material. The mechanical stability of the biofilm can be determined essentially by the structural design of biopolymer material to withstand harsh conditions of the environment. Additionally, biodegradable films have been reported to be stable at ambient temperature, just like the conventional packaging materials, such as the low density polyethylene, polyethylene terephthalate and polyvinyl chloride materials (Auras et al., 2005). The tensile strength, percentage elongation and elastic modulus together with the energy of deformation of biodegradable films have been studied for use in the food packaging application. At the moment, the amount of energy needed for deformation of quite a few kinds of biopolymers, made from polyester, polyester amides, starch and cellulose materials, polylactic acid (PLA) and polyhydroxy acid (PHA), have been quantified from the knowledge of their mechanical stability. In fact, PHA polymer is in the category of most high-priced polymer and together with PLA, used as an alternative packaging material, has found application in food industries because of their stable performances in every feature (Auras et al., 2005).

The degree of degradation of plastics can also be measured with a fair knowledge of the mechanical properties (Orhan et al., 2004; Badmus et al., 2015). Additionally, Jorge et al. (2014) studied the mechanical properties of gelatine nanocomposite films prepared by spreading and investigating the effect of montmorillonite concentration on the properties. The authors revealed that the tensile strength and elastic modulus of the biodegradable films increased with montmorillonite concentration, thus indicating reinforcement of the biopolymer matrix by the nanoparticle. The lower values of resistance and rigidity of the films must be attributed to the plasticizing effect of the absorbed moisture during conditioning. Besides, the elongation at break of the films increased with the montmorillonite concentration. Thus, the nanoparticles contributed to reducing the susceptibility of the nanocomposite material to the environmental relative humidity, and to enhancing the mechanical properties. Sanyang et al. (2015) studied the effect of plasticiser type and concentration on tensile strength of biodegradable films based on sugar palm starch. The authors observed that regardless of the plasticiser type, the tensile strength of the plasticized films decreased with the plasticiser concentration. However, the percentage elongation of the plasticized films significantly decreased at a higher glycerol concentration (45% w/w) due to the anti-plasticization effect of the glycerol. Therefore, mechanical behaviour of nanocomposite material especially when used to transport food on rough roads can be revealed from studying this investigation. Knowledge of this can also be applied in understanding the strength and durability of nanocomposite material prior to packaging.

2.2 *Structural properties*

The structural properties of starch based biofilms are commonly studied using the X-ray diffraction techniques. The effect of starch structures on the starch clay based nanocomposite was studied by Zhou et al. (2007). The authors revealed that the structure of the biofilm is the consequence of the interaction between the starch molecules and the plasticiser. It was also reported by Piyada et al. (2013) that the addition of starch nano-crystals will increase the crystalline peak structure of rice starch films. The authors also revealed that no endemic peaks were observed in the rice starch, and this is capable of restricting the mobility of the starch chain due to the establishment of strong intercalations between rice starch and starch nanoparticles. The presence of diffraction peaks revealed that the materials are mainly intercalated. Tang et al. (2008) and Chung et al. (2010) reported similar behaviour for starch-montmorillonite thermoformed films, but in all cases the nanocomposites presented an intercalated structure. It is often viewed that the polymer will ideally enters the clay gallery and forces apart the layers during the intercalation process, thus widening the spacing of the gallery. This would normally cause a shift in the diffraction peak towards a lower angle, according to Bragg's law. With the succession of more polymers into the clay gallery, the layers are forced further apart to such an extent that the peak of the d-spacing becomes more wider and finally broadens into the baseline, thus revealing a complete exfoliated nanocomposite structure. Ali and Noori (2014) also revealed that the structure of nanocomposite had significantly influenced the physical properties of the nanocomposites, in their study on the barrier properties of biodegradable polymer nanocomposite films due to the dispersion of the titanium in the thermoplastic polymer. Jalalvandi et al. (2012) studied the morphological behaviour of polylactic acid-thermoplastic starch-montmorillonite nanocomposites. The study revealed that the sample with montmorillonite loading 4 phr exhibited exfoliated structure while sample that contained montmorillonite 8 phr exhibited intercalated structure. Thus, the morphology of nanocomposite films, which determines the suitability any material for food (climacteric or non-climacteric) packaging, can be revealed from studying the structural properties.

2.3. *Thermal properties*

The thermal properties of starch based biofilms are usually expressed as indices of their thermal degradation and stability.
The thermal degradation is the amount of material weight loss with temperature increase; while thermal stability is the required temperature for minimum weight loss on the thermo-gravimetric analyser. Hejri et al. (2012) studied the role of nano-sized TiO2 on the thermal behaviour of starch-poly (vinyl alcohol) blend films. The study revealed that the addition of TiO2 nanoparticles considerably enhanced the thermal stability of the starch-poly (vinyl alcohol) blend films. The enhancement of the thermal stability was attributed to the improvement in the interfacial adhesion and compatibility between the nano-TiO2 and composite, due to the treating effect of plasticiser and film forming process. Also, the improvement in the thermal stability of nanoclay composites was first reported by Zeng et al. (2005). Huang and Yu (2006) noted that introducing inorganic particles improved the thermal stability and thermal resistance of starch-montmorilonite nanoparticles. Studies by the Toyota research team also showed that the heat distortion temperature of nylon-6 nanoparticles increased from 65 to 145oC (Zenget al., 2005) and suggested that the platelet nature of clay nanoparticles hinder the diffusion of volatiles and assist in the formation of char after thermal decomposition and contribution to the improved thermal stability. Sanyang et al. (2015) studied the effect of plasticiser type and concentration on thermal properties of the biofilm based on the starch prepared from sugar palm. The effect of the concentration of plasticiser on the thermal properties of the starch-plasticized films was noticed to be insignificant. This reveals that it does not really matter the type or concentration of the plasticiser used in the preparation of biofilms since the thermal stability would be unaffected. However, the thermal stability of sugar palm starch films slightly decreased as the plasticiser concentration increased up to 45% (Sanyang et al., 2015).

The addition of fillers can also enhance the thermal stability of biofilms. For instance, Taghizadeh and Sabouri (2013) studied the thermal degradation behaviour of polyvinyl alcohol-starch-carboxymethyl cellulose-clay nanocomposites. The authors reported that the thermal stability of montmorillonite blends nanocomposite is higher than that of polyvinyl alcohol blend counterpart, thus suggesting that the addition of montmorillonite improved the thermal stability of polyvinyl alcohol-starch-carboxymethyl cellulose blend. At least four degradation distinct stages were identified in the polyvinyl alcohol-starch-carboxymethyl cellulose-clay blends using thermo-gravimetric analyser, being assigned to the mass loss due to the plasticiser leaching, and to the degradation of the starch, carboxymethyl cellulose and polyvinyl alcohol fractions. Dang and Yoksan (2015) developed and characterised thermoplastic starch chitosan films. The authors observed that the addition of chitosan increased the thermal stability and ultraviolet absorption of the films. Mehyar and Han (2014) studied the physical properties of high-amylose rice and pea starch films as affected by relative humidity and plasticiser and observed that the addition of glycerol into starch films made amylase-rich granules swollen and continuously dispersed between amylopectin rich gels. The authors also observed that the thermal stability of the films increased with relative humidity from 51-90 %. Also, Zhong and Li (2014) studied the effects of glycerol and storage relative humidity on the properties of kudzu starch-based edible films. The authors observed that the thermal stability of the kudzu starch-based edible film increased with relative humidity and glycerol concentration. However, few cases have been reported where addition of fillers negatively affect the thermal stability of biofilms (Ali and Noori, 2014). For instance, the flexible film based on the blend of starch and passion fruit mesocarp flour with nanoparticles, developed and characterised by Nascimento et al. (2012), showed that the addition of clay nanoparticle did not influence the thermal properties of the films. Thus, the stability of nanocomposite material against thermal stress, which may occur when packaged food is subjected to adverse climate, can be revealed from studying the thermal properties.

2.4 Barrier properties

The most commonly studied barrier properties of starch based biofilms are oxygen and water vapour permeability. The barrier properties of cassava starch film and their plasticising effect have been studied by Suppakul et al. (2013). The authors observed that water vapour transmission rate of the film was gradually reduced with increasing sorbitol content, but drops drastically when the sorbitol content exceeds 40 g/100g. The oxygen transmission rate significantly decreased with rising sorbitol content. The authors concluded that the information can be useful in interpreting the performance of biofilm at different condition of relative humidity and plasticizer content. According to Lopez et al. (2015), who prepared bags from thermoplastic corn starch reinforced with talc nanoparticles for food packaging, the oxygen and water vapour permeability decreased with the addition of talc nanoparticles up to 3%. The barrier properties of the biofilm prepared from the blend of corn starch and taro starch nanoparticles was studied by Dai et al. (2015). The authors observed that the water vapour permeability of the film decreased significantly with an increase in the concentration of taro starch nanoparticles. The gas barrier properties of biodegradable polymer nanocomposite films were studied by Ali and Noori (2014). The study revealed that the oxygen transmission rate decreased with the addition of higher concentration of tin oxide in the biodegradable polylactic acid polymer, which was higher than ordinary polylactic acid in all circumstances.

The oxygen permeability is an important factor in the packaging of fruits and vegetables, especially as it helps in shelf life control (Dolea et al., 2004). Therefore, the oxidation of packaged food is usually retarded and the shelf life extended with relatively insignificant coefficient of the oxygen permeability. The barrier properties of starch-ethylene vinyl alcohol nanoparticles were studied by Amidi-Fazli and Amidi-Fazli (2015). The study revealed that the lowest moisture absorbance was measured in the starch nanocomposite containing 8% nanocrystalline cellulose and the sample containing 7.8% ethylene vinyl glycol and 13% nanocrystalline cellulose. Also, the lowest solubility was observed in the composite containing 10% ethylene vinyl glycol. The authors concluded that addition of nanocrystalline cellulose and ethylene vinyl glycol led to the reduction in the moisture absorption properties of the biofilms. Slavutsky et al. (2012) observed, in their study on the water barrier properties of corn starch-clay nanocomposite films, that water diffusion of rice starch clay based films increased with nanoclay content due to the increase tortuosity of the diffusion path, caused by the nanoparticles. The authors also reported that incorporation of about 5% of the montmorillonite using an adequate dispersion method, improved the water resistance and barrier properties of the corn starch based films. The study further revealed that nanoparticles reduce the damage caused to the properties of the corn starch-clay biofilms by increasing the moisture content. Sanyang et al. (2015) studied the effect of plasticiser type and concentration on barrier properties of biodegradable films. The water vapour permeability increased significantly from 4.86×10^{-10} to 8.70×10^{-10} $gm^{-1}s^{-1}Pa^{-1}$, irrespective of plasticiser types, with the concentration of glycerol. Jalalvandi et al. (2012) studied the absorption behaviour of polylactic acid thermoplastic starch-montmorillonite films. The authors reported that the nano-size montmorillonite particle is also able to block a tortuous pathway for water to enter the starch chain, thus reducing the water uptake and improving the barrier properties of films. It is important to note that having nanocomposite packaging materials with higher degree of water uptake and lower affinity for oxygen is beneficial to its application for food packaging. This is may be possible because of the high surface area of the nanoparticles and the consequent reaction leading to removal of excess oxygen capable of causing food deterioration in storage.

3. Conclusions

This review studied the mechanical, thermal, structural and barrier properties of starch-based nanocomposite materials for application in fruits and vegetables packaging. Emphasis was placed on the roles of the nanoparticles inclusion in the matrix of the materials on their overall service performance and application for minimising post harvest loss of packaged produce. The study showed that nanoparticles have ability to enhance the properties of biodegradable films for food packaging application. Although the mechanism guiding this processes is not yet known, the high surface area to volume ratio of the nanoparticles played key role in making sure that this happen. Migration of traces of residual nanoparticles into packaged food is another point to worry about, as no research has yet addressed this issue completely. There is also the need for shelf-life study for the packaging material because of its ability to degrade fast under adverse climate, as this review has shown. Therefore, unless these gaps are filled the suitability of nanocomposite materials for food packaging will always be queried.

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