Effect of thickness and matrix variability on properties of a starch-based nanocomposite supple film

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Abstract

In this research, the effects of matrix variability and thickness on the properties of a flexible nanocomposite film were investigated. The nanocomposite film was prepared from the blends of 1 kg cassava starch, 45–55% (w/v) glycerol and 0–2% (w/v) zinc nanoparticles in thickness ranging from 15 –17 µm. The barrier, mechanical, and thermal properties were determined experimentally. The optimal effects of the thickness and the matrix variability on the properties were determined using Response Surface Methodology. Results showed that the barrier properties increased with glycerol concentration but decreased with thickness. Reduced modulus and tensile strength increased with an increase in the matrix variability. The film was thermally stable up to 60.43 °C with only 2% degradation. The optimal film contains 55% glycerol, 2% zinc nanoparticles with a thickness of 17 µm at a desirability index of 0.95. This can therefore be essential for industrial application.

1. Introduction

Postharvest activities are often associated with some losses in the agricultural value chain. These were estimated to vary between 5-25% in the industrialized nations and 20-50% in developing countries (Ehiem et al., 2009). Abimbola (2014) reported that over 50% of harvested fruits and vegetables in Nigeria get spoilt annually, because of poor packaging, storage, and processing, leading to seasonal shortages and fluctuation in the supply and prices. Most of the materials used in packaging industries are produced from petroleum-based non-degradable monomers. Kirwan et al. (2011) reported a 37% increase in the amount of non-degradable polymer wastes between 1998 and 2005. Consequently, by 2020 the amount is expected to double around 462 million tons. Siracusa et al. (2008) reported that synthetic packaging materials alone have accounted for almost two-thirds by volume of the total packaging wastes the world over. Therefore, there is a need for an alternative packaging material that can help address the problem (Sorrentino et al., 2007). The bio-based film is a good example of an alternative packaging approach. The material has been reportedly used for shelf-life extension of packaged food products (Tharanathan, 2003). Also, since the substrates constituting the material can be degraded on exposure to extreme heat, they could potentially solve the waste problem. The material properties of the biodegradable film can be improved by the addition of nanoparticles (Fadeyibi et al., 2017; Farbodi, 2017). This is made possible with the inclusion of the nanoparticles, with particle size approximately < 100 nm and bonded with the adjacent phases of the starch molecules. Structurally, the characteristics of the packaging material may be largely responsible for its suitability for food applications (Giannelis et al., 1999).

Nanocomposite films have found numerous applications in the packaging of fruits and vegetables (Wu et al., 2005). For instance, the shelf-lives of okra, tomatoes and fresh orange juice have been improved with the nanocomposite film prepared from the blends of low-density polyethylene with silver and cassava starch with zinc nanoparticles (Fadeyibi, Osunde, Agidi, Idah et al., 2016; Fadeyibi et al., 2019). The shelf-life of freshly packaged oranges has been enhanced up to 28 days without any negative effect on its sensory quality with the addition of nano-zinc into the matrix of the packaging material (Emamifar et al., 2011). Motlagh et al. (2006) reported a decrease in the microbial, and mould growth and an increase in the organoleptic parameters of dried barberry in their work on the effects
of polyethylene packages containing micrometre-sized silver particles on the quality and shelf life of the product. Additionally, the application of nanocomposite edible film, made from the blend of cellulose nanofibers with mango purees, has been used for fruits and vegetable packaging (Azeredo et al., 2009). However, the effects of the uniform dispersion of the constituent materials or matrix variability on the physical properties of the nanocomposite film have not been reported. Although Fadeyibi, Osunde, Agidi, Idah et al. (2016) developed and optimized nanocomposite film from the blend of zinc nanoparticle and glycerol, the authors did not report the effect of the matrix variability and thickness on the properties of the film. It is therefore necessary to investigate the effects of these parameters on the behaviour of the film to ascertain the right combination for a specific application. This research was carried out to determine the effect of the thickness, glycerol, and zinc-nanoparticles on the properties of the nanocomposite flexible film using the surface response methodology.

2. Materials and methods

2.1 Preparation of nanocomposite film

Starch was prepared by processing 2 kg of cassava roots using the procedure described by Fadeyibi et al. (2014). The nanocomposite was prepared by mixing the starch (1 kg), glycerol (45-55% w/v), and zinc-nanoparticles (0-2% w/v) to form a thermoplastic film with a thickness in the range of 15-17 µm, as described by Emamifar et al. (2011), Motshekga et al. (2015), Fadeyibi, Osunde, Agidi, Idah et al. (2016) and Fadeyibi et al. (2017). A total of 27 film samples were produced and sealed in the polyethylene packs to avoid possible hydration.

2.2 Determination of the properties of the film

ASTM Standards procedure was used to determine the water vapour permeability (WVP) while the sorption method was used to determine the oxygen permeability (OP) of the nanocomposite films as described by Motshekga et al. (2015) and Fadeyibi, Osunde, Agidi, Idah et al. (2016). The nanoindenter machine (Nano Mechanical Test System-Hysitron TI750) was used to carry out the mechanical test on the samples of the cassava starch nanofilm at the Physics Laboratory of the Sheda Science and Technology Complex (SHESTCO), Abuja, Nigeria. A record of the depth and area of the indented surfaces were made during this process (Fadeyibi, Osunde, Agidi, Egwim et al., 2016). While indenting, the average values of the reduced modulus, hardness, strain energy, drift rate and tensile strength were measured and recorded.

The thermal properties of the cassava starch nano-zinc oxide films were determined using the Thermogravimetric Analyzer, at the Centre of Genetic Engineering and Biotechnology of the Federal University of Technology Minna. The chillers are set at a temperature of 15°C to maintain the right cooling medium for the TGA equipment. The equipment is then switched on in a range of 30 to 950°C temperature scan while nitrogen gas was released from the cylinder for 30 mins at the pressure, flow, and heating rates 2.5 bar, 20 mL/min and 10°C/ min, respectively. The weight of the crucible was zeroed and a mass of 2 mg of the sample was loaded in the TGA thermo-balance, with continuous weighing as heating progresses. Finally, the program was initiated and the weight (%) and time (min) data were measured as the temperature approached 950°C from the room temperature. The procedure was replicated for all samples of the nanofilm.

2.3 Determination of optimum parameters

Response surface methodology (RSM) was applied to determine the optimum conditions of process variables for the characterized properties of the films, namely mechanical, barrier properties and thermal stability. Data from a previous report and preliminary trials were considered to select the number and range of process variables in the experimental design. The process variables considered were the thickness of the film (A; 15, 16, 17 µm), the concentration of glycerol (B; 45, 50, 55% w/v) and the concentration of zinc nanoparticles (C; 0, 1, 2% w/w), while the dependent response variable chosen were the characterized attributes of the films, as shown in Table 1.

Table 1. Properties of the variables showing allowable ranges and constraints

| Variation | Unit | Allowable Range | Constraint |
|-----------|------|-----------------|------------|
| A         | µm   | 15             | -1 < α ≤ 1 |
| B         | w/w  | 45             | -1 < α ≤ 1 |
| C         | w/w  | 0              | -1 < α ≤ 1 |

2.4 Experimental design

A Box-Behnken Design (BBD), which includes 17 experiments formed by 5 central points, was employed to minimize the cost of running a 3³ full factorial experiment. The layout of the combinations of the process variables and the characterized attributes of the cassava starch nanocomposite films in the BBD are shown in Table 2. The optimization was based on finding the desirability for the objective function (Vargas-Lopez et al., 1990). The objective functions, here are to maximise the reduced modulus, hardness, tensile strength, deformation while minimising the strain energy for mechanical properties. It was also designed to
minimise both the OP and WVP for barrier properties while minimising the thermal stability and weight loss for thermal properties.

3. Results and discussion

3.1 Effect of thickness and matrix variability on the barrier properties of the film

The variations of the effects of concentrations of glycerol and thickness of the films on the WVP and OP of the cassava starch nanocomposite films are shown in Figure 1 and Figure 2. In Figure 1, the OP increases from $4.81 \times 10^{-12}$ to $1.53 \times 10^{-11}$ g/m.Pa.s with an increase in the thickness of the films, a decrease in the concentration of glycerol and an increase in the interaction between the factors. In Figure 2, the WVP increases from $7.97 \times 10^{-11}$ to $3.64 \times 10^{-10}$ g/m.Pa.s with a decrease in the thickness of the films, an increase in the glycerol concentration and an increase in the interaction between the factors. The study of the barrier properties of biodegradable film is common in the food industry because it permits the understanding of the role of oxygen and water in deteriorative reactions. Water acts as a solvent or carrier and causes texture degradation, chemical and enzymatic reactions. Also, the water activity of foods is an important parameter in relation to the shelf-life of the food. In low-moisture foods, low levels of water activity must be maintained to minimize the deteriorative chemical and enzymatic reactions and to prevent texture degradation. When considering a suitable barrier in foods and food packaging the barrier properties of biopolymer films are important parameters (Aydinli et al., 2000; Kang et al., 2010; Kaur et al., 2017).

3.2 Effect of thickness and matrix variability on the mechanical properties of the film

3.2.1 Reduced modulus of the film

The variation of the reduced modulus of the cassava starch nanocomposite films with the concentration of glycerol, thickness of the films and their interaction is shown in Figure 3. The reduced modulus increases from 2.24 to 185.2 MPa with an increase in the concentration of glycerol, a decrease in the thickness of the films and an increase in the interaction of both factors. The best prediction among all the treatment combinations of the films was 59.91% glycerol, 16.29 µm and 1% of the zinc nanoparticles with a reduced modulus of 113.56 MPa. The reduced modulus can be regarded as a basic property of a material, which determines the deformation response to an applied load. In polymer nanocomposites, one of the most important theoretical efforts is to predict the reduced modulus. Therefore, the nearest film closer to the desired optimal reduced modulus, among the available treatments, was the one containing 55% glycerol and 1% of the zinc nanoparticles with a thickness of 17 µm.

3.2.2 Hardness of the film

The variation of the hardness of the cassava starch nanocomposite films with the concentration of glycerol,
thickness of the films and their interaction is shown in Figure 4. The hardness increased from 1.01 to 765.56 MPa with an increase in the thickness, irrespective of the concentration of the glycerol or the interaction between both factors. The best prediction among all the treatment combinations of the films was 55% glycerol, 16.27 µm and 1.24% zinc nanoparticles with a hardness value of 15.88 MPa. The hardness of the film is an indication of its stability at the sub-atomic scale level, and this can enhance its application in food packaging. In particular, Gersappe (2002), who studied the effect of particle size on the mechanical properties of the biodegradable film, reported an increase in the toughness with particle size variability. Adnan et al. (2007) reported an enhanced toughness of amorphous polyethylene nanocomposites with the inclusion of fullerene buckyball fillers. In the presence of spherical nanoparticles, Sen et al. (2005) reported an increase in the elastic region during the deformation and the hardness of most plastic nanocomposites. Therefore, the nearest film closer to the desired optimal hardness, among the available treatments, was the one containing 55% glycerol and 2% of the zinc nanoparticles with a thickness of 17 µm.

3.2.3 Strain energy of the film

The variation of the strain energy of the cassava starch nanocomposite films with the concentration of glycerol, thickness of the films and their interaction is shown in Figure 5. The strain energy increases from 14.54 to 11878 pNm with an increase in the concentration of glycerol, a decrease in the thickness of the films and the interaction between both factors. The best prediction among all the treatments combinations of the films was 55% glycerol, 17 µm and 1% of the zinc nanoparticles with strain energy of 158.433 pNm. Therefore, the nearest film closer to the desired optimal strain energy, among the available treatments, was the one containing 55% glycerol and 1% of the zinc nanoparticles with a thickness of 17 µm.

3.2.4 Drift rate of the film

The variation of the drift rate of the cassava starch nanocomposite films with the concentration of glycerol, thickness of the films and their interaction is shown in Figure 6. The drift rate increases from 7.48 to 25.55 nm/s with an increase in thickness of the films but decreases with an increase in the concentration of the glycerol and interaction between the variables. The best prediction for the combination among all the treatments of the films was 49.13% glycerol, 16.93 µm and 0.54% of the zinc nanoparticles with a reduced modulus of 25.35 nm/s. Drift rate can be described as the time-dependent creep behaviour, occurring due to the action of a static load on the nanocomposite film. The drifting may also take place under stress, provided the applied force is not sufficient to cause the material to yield. The results of many studies have shown that the addition of nanoparticles into biofilms may significantly improve the drift resistance of the biodegradable material (Pérez et al., 2008; Dasari et al., 2009). The findings of Yang et al. (2006), who investigated the tensile creep resistance of polyamide nanocomposites reinforced with clay nanoparticles, corroborates the findings of the present study. Also, the finding of Ohji (1996), who reported a delayed fracture behaviour under tensile loading at high temperatures for silicon nitride, silicon carbide, and alumina carbide nanocomposites, is in line with this research. The results showed that silicon carbide had an excellent creep resistance, even at very high temperatures, and the creeping effects were well described by a diffusive crack growth model. Moreover, the dispersion of silicon carbide nanoparticles into an alumina matrix led to a dramatic improvement in creep resistance when compared to alumina with equivalent grain size. This improvement was attributed to the impedance of grain boundary sliding, induced by the presence of intergranular silicon carbide nanoparticles. Therefore, the nearest film closer to the desired optimal drift rate, among the available treatments, was the one containing
50% glycerol and 1% of the zinc nanoparticles with a thickness of 17 µm.

3.3.5 Tensile strength of the film

The variation of the tensile strength of the cassava starch nanocomposite films with the concentration of glycerol, thickness of the films and their interaction is shown in Figure 7. The tensile strength increases from 0 to 0.4 µN/mm² with an increase in the concentration of glycerol but decreases with an increase in the thickness of the films. The best prediction for the combination among all the treatments of the films was 55% glycerol, 16.27 µm and 1.27% zinc nanoparticles with a reduced modulus of 0.23 µN/mm². Accurate quantification of the tensile strength of the individual component in the matrix of the film is essential for the understanding of the overall elastic performance of the nanocomposite material. In a related investigation, Suter et al. (2007) studied the tensile strength of the individual clay platelets in a composite matrix. Similarly, Capaldi et al. (2006) and Patel et al. (2018) reported that the average modulus and strength of a crystalline octacyclopental polyhedral film increase with an increase in the concentration of the nanoparticles. The above-predicted properties may be applicable to micromechanical models suitable for tensile strength prediction. Therefore, the nearest film closer to the desired optimal tensile strength, among the available treatments, was the one containing 55% glycerol and 2% of the zinc nanoparticles with a thickness of 17 µm.

3.3 Effects of thickness and matrix variability on thermal properties of the film

3.3.1 Thermal stability of the film

The variation of the thermal stability of the cassava starch nanocomposite films with the concentration of glycerol, thickness of the films and their interaction is shown in Figure 8. The thermal stability increases from 59.70 to 60.43°C with a decrease in the concentration of glycerol and an increase in the thickness of the films. The best prediction among all the treatments combinations of the films was 49.29% glycerol, 17 µm and 2% of the zinc nanoparticles with the thermal stability of 60.14°C. Therefore, the nearest film to be chosen closer to the desired optimal thermal stability, among the available treatments, is the one containing 50% glycerol and 2% of the zinc nanoparticles with a thickness of 17 µm.

3.3.2 Weight loss of the film

The variation of the weight loss of the cassava starch nanocomposite films with the concentration of glycerol, thickness of the films and their interaction is shown in Figure 9. The weight loss or degradation increases from 97.71 to 99.03% with the concentration of glycerol and the thickness of the films. The best prediction among all the treatments combinations of the films was 49.65% glycerol, 16.59 µm and 1% of the zinc nanoparticles with a weight loss of approximately 97.73%. Therefore, the nearest film closer to the desired optimal weight degradation at a higher temperature, among the available treatments, is the one containing 50% glycerol and 1% of the zinc nanoparticles with a thickness of 17 µm.

4. Conclusion

The development of biodegradable nanocomposites requires a thorough understanding of the phenomena, and an accurate prediction of the materials’ properties and behaviours over a different combination of the matrix variables. The Surface Response Methodology was used to determine the optimal effects of the thickness and matrix variability on the properties of the nanocomposite film. The OP and WVP of the nanocomposite film were found to increase with an increase in the glycerol concentration and a decrease in the thickness. The reduced modulus increases from 2.24 to 185.2 MPa with an increase in the concentration of glycerol, a decrease in the thickness of the films and an increase in the interaction of both factors. The hardness
increased from 1.01 to 765.56 MPa with an increase in the thickness, irrespective of the concentration of the glycerol or the interaction between both factors. The strain energy increases from 14.54 to 11878 pNm with an increase in the concentration of glycerol, a decrease in the thickness of the films and the interaction between both factors. The drift rate increases from 7.48 to 25.55 nm/s with an increase in the thickness of the films. The thermal stability increases from 59.70 to 60.43°C with a decrease in the concentration of glycerol and an increase in the film thickness. The optimal film contains 55% glycerol, 2% zinc nanoparticles with a thickness of 17 μm with a desirability index of 0.95.

Conflict of interest
The authors declare no conflict of interest.

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