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Mechanical Properties of Blend Films Based on Unripe Plantain Peels Starch/Polyvinyl Alcohol

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Abstract: *Starch from unripe plantain peels was produced. Polyvinyl Alcohol (PVA) reinforced starch films were made using the casting method. The mechanical properties (tensile strength, modulus and elongation) of plantain starch reinforced PVA with different starch loading were investigated. Tensile strength increased up to 15 wt. % before decreasing. Strain decreased as starch content increased, the reverse is the case for elastic modulus. The results were compared with existing theories of reinforcement. The macroscopic behaviour of starch-filled composites is affected by starch loading. A comparison is made between experimental data and different theoretical models, namely Einstein and Guth equations, Parallel and series models, Hirsch's model, Halpin-Tsai, and modified Halpin-Tsai models. Theoretical modelling shows that tensile strength increases with increase in the volume fraction of PPS except the Guth and Series models which values decreased as PPS increased. The best correlation between the theoretical and experimental tensile strength was predicted using the Parallel model of the rule of mixture, followed by the Hirsch equation, modified Halpin-Tsai and Halpin-Tsai models respectively. Guth and Series models agree the least with the experimental values. Notwithstanding all models except Guth and Series models can predict either wholly or marginally up to 0.136 volume fraction or 15% weight of PPS. The Guth model attempted to predict the elastic modulus at a lower volume fraction (0.044) but could not at higher loading. Halpin-Tsai, Parallel, Hirsch and modified Halpin-Tsai theories could predict between 85.19 and 91.74% of the experimental values.*

Keywords: *Strength, Modulus, Starch, Mechanical Theories, Polyvinyl Alcohol.*

INTRODUCTION

Reduction in environmental complications of synthetic plastic necessitates the development of ecologically friendly materials. Fibres have played a prominent role in the production of composite. Nevertheless, with the introduction of fibres, the mechanical properties of composites got improved. The latter is evident in both natural and synthetic composites' properties, which includes: yield strength, hardness, stiffness, tensile strength, elastic modulus etc. Due to this improved mechanical properties, polymer-matrix composites, especially for natural fibres, have received significant attention both in the literature and industrial applications. Reasons for the attention among others are significant processing advantages, low cost and low density (Facca *et al.*, 2006). Fillers from crops like wood flour, Banana flour, cornflour, including corn starch and banana starch have been used to improve the properties of composite materials produced from biodegradable materials (Das *et al.*, 2009; Das *et al.*, 2010; Pelissari *et al.*, 2012; Pelissari *et al.*, 2013; Priya *et al.*, 2014; Pelissari, *et al.*, 2017; Raharjo, *et al.*, 2018). Because of their renewability, crops can be a treasured source of starch. Researchers have isolated starch from various crops such as quinoa (Araujo-Farro *et al.*, 2010), banana (Pelissari *et al.*, 2013; Pelissari *et al.*, 2017), rice (Dias *et al.*, 2010), potatoes (Jain *et al.*, 2018), corn (Priya *et al.*, 2014; Tian *et al.*, 2017) and cassava (Teixeira *et al.*, 2012). Plantain peel waste is a by-product of agricultural waste and can cause environmental problems. Since plantain peel is rich in starch, it is a potential material for reinforcing component in high-performance composites. Research into it will lead to increase commercial value and providing a purpose for its by-product.

Starch-based bio-composites from various sources (Kim *et al.*, 2003; Guohua *et al.*, 2006; Araujo-Farro *et al.*, 2010; Dias *et al.*, 2010; Pelissari *et al.*, 2013; Priya *et al.*, 2014; Tian *et al.*, 2017; Jain *et al.*, 2018) have been made by blending with biodegradable synthetic polymers, an example of which is Polyvinyl alcohol (PVA). PVA has the advantages of being good film-forming polymer, high thermal stability and strong conglutination. Its application can be found in coatings, packing material, drug delivery, and in the materials industry (Azahari *et al.*, 2011). Starch is a biopolymer with relatively low mechanical properties (Lee *et al.*, 2007), the main disadvantage limiting its applications. Research to improve on the properties of PVA/starch blends using various additives have been on the increase. Mechanical properties of starch/PVA bio-composites from different natural plants have been reported (Guohua *et al.*, 2006; Dias *et al.*, 2010; Araujo-Farro *et al.*, 2010; Teixeira *et al.*, 2012; Pelissari *et al.*, 2013; Priya *et al.*, 2014; Tian *et al.*, 2017; Jain *et al.*, 2018). There have been divergent reports on the tensile strength, elastic modulus and strain at breaking point. The variance in properties is ascribed to the volume fraction of starch, method of preparation, source and method of starch extraction, modification, type and amount of plasticizer used. Starch and flour films from unripe plantain bananas of the variety "Terra" (M. paradisiaca) were made by Pelissari *et al.*, (2013). The mechanical properties indicate that the banana flour film compared to the banana starch film has lower values of tensile strength, and Young's modulus, an indication that the flour film is more flexible while the starch film is more resistant and rigid. The presence of protein and lipids in the flour film was attributed to have collaborated with the plasticizer effect and did not contribute to the formation of a stronger network in the film. Tensile strength and per cent elongation of delignified fibre from corn starch at different loading of starch/PVA blend matrix films have been reported (Singha *et al.*, 2015). Starch fibres of 5 to 30 wt. % was added to the starch/PVA blend. The result showed that tensile strength increased on reinforcement with starch cellulosic fibres. At 20% loading, tensile strength and per cent elongation was found to be 40.64 MPa and 214.62%, respectively. The increase in tensile strength was attributed to better adhesion of reinforced fibre and matrix. Contrary to Singha *et al., 2015;* Tiana *et al.*, (2017) reported a decrease in tensile strength, elongation at break and Young's modulus with increasing content of starch. At 50 % starch content, the flexibility of the blend films was high, with the elongation at break more than 1000 %. The same decrease in tensile strength and Young modulus was observed with increase in Relative Humidity, while the elongation at break was improved dramatically, an indication of improved flexibility.

Literature data on mechanical properties of fibre-reinforced polymer composites have been on the increase, but reports on theoretical modelling of these composites are scarce. The elastic modulus, tensile strength and strain at failure are some of the most important mechanical properties of materials for engineering design. These properties of the material can be affected among other things by type of fibre, the matrix used, fibre orientation and geometry, per cent weight of fibre, the aspect ratio of fibre, type and amount of plasticizer and the degree of interfacial adhesion between the fibre and the matrix. Notwithstanding the above-mentioned factors, properties of agricultural plant fibres depend on other factors such as; nature of the plant, locality grew, age of the plant, extraction methods of fibre, processing method or modification of fibre etc. With the above factors, it is expected that divergent mechanical properties will be reported. Model equations have been propounded (see section 2) to predict the elastic modulus and the tensile strength of materials. Six micromechanical composite models were used by Facca *et al.,* (2006) to predict the properties of the glass, wood, hemp and rice hull fibres reinforced polymer composites. Of all the models applied, modified Halpin-Tsai model could predict the experimental data accurately. In another report Facca *et al.,* (2007) used a modified rule of mixtures (ROM) to predict the properties of hemp fibres, hardwood fibres, rice hulls, and E-glass fibres reinforced polymer composites. The modified ROM strength model was found to adequately predict the tensile strength of the various composites. Kalaprasad *et al.,* (1997) used ten micromechanical composite models (Einstein and Guth equations, modified Guth equation, Parallel and series model, modified Kerner equation, Hirsch's model, Halpin-Tsai model, modified Halpin-Tsai model, Cox model, modified Bowyer and Bader's model) to predict the properties of short sisal fibre-reinforced low-density polyethene composites. All models except Rule of Mixture (series and parallel model) show reasonable agreement with experimental tensile properties of longitudinally oriented composites, specifically at a low volume fraction of the fibre. The Hirsch and the Bowyer-Bader model were found to predict the elastic modulus of the composites. Raharjo *et al.,* (2018) applied Hirsch and the Bowyer-Bader models to predict the tensile strength of randomly oriented zalacca fibre reinforced composite, while Tsai-Pagano, Manera and Cox-Krenchel were used to predict the elastic modulus. For the tensile strength, Bowyer-Bader models could predict marginally at 0.14 volume fraction and 98 % at 0.26 volume fraction. Tsai-Pagano model could predict up to 0.38 volume fraction of the elastic modulus. Using any of the above micromechanical models to predict the mechanical properties of starch reinforced PVA has not been reported. In this research starch from unripe plantain, peels were extracted. Casting method was used to produce films at different loading of starch. The mechanical properties were investigated. Six micromechanical models namely: Einstein and Guth equations, Parallel and series model, Hirsch's model, Halpin-Tsai model, and modified Halpin-Tsai model were used to predict the mechanical properties.

A Theoretical modelling of Mechanical Properties

There is wide-ranging literature dedicated to the modelling of mechanical properties of polymers reinforced natural or synthetic fibres. The modelling is exceedingly significant and sheds light on the relationship between the composite structure and the properties of the composite. The mechanical properties (tensile and elastic) of polymer reinforced composites can be determined from a variety of mathematical models. Properties such as Poisson's ratio, elastic modulus, shear modulus, tensile strength, and relative volume fractions of both matrix and fibre are the important input properties needed to predict the mechanical properties of the composite. In some models, aspect ratio and orientation of fibre play a significant role. Many theoretical models have been reported to model the tensile strength and Young's modulus of composites. These include Rule of mixture (Parallel or Series) model, Halpin-Tsai equation, modified Halpin-Tsai equation, Hirsch's model, Einstein and Guth equations, Cox Model and Guth's Equation and Nicolais-Narkis theory. In this research, the models were limited to: Rule of mixture (Parallel or Series) model, Halpin T-sai equation, modified Halpin-Tsai equation, Hirsch's model, Einstein and Guth equations.

B Rule of Mixtures Model (Parallel and Series model)

The Rule of mixtures model comprises of the parallel and the series models. They are the simplest models used to predict the elastic and tensile properties of composite materials. The applications got across both particulate and fibrous reinforcement.

The parallel and series equations give the maximum and minimum possible values for E_c and T_c. The parallel model assumes iso-strain conditions for both matrix and fibre while series models assume uniform stress in both matrix and fibre. Equations 1 and 2 are the Rule of mixture for modulus and tensile strength (Kalaprasad *et al.*, 1997; Facca *et al.*, 2006; Facca *et al.*, 2007). The role of mixture assumes that the aspect ratio ξ approaches infinity or zero, respectively.

Parallel Model

$$E_c = E_f V_f + E_p V_p \quad (1)$$

$$T_c = T_f V_f + T_p V_p \quad (2)$$

Series Model

$$E_c = \frac{E_m E_f}{E_m V_f + E_f V_m} \quad (3)$$

$$T_c = \frac{T_m T_f}{T_m V_f + T_f V_m} \quad (4)$$

E_m, E_C and E_f are the elastic moduli of matrix, composite, and filler, respectively. V_f and V_p are the volume fractions of filler and polymer. T_c, T_f and T_p, are the Tensile strength of composite, filler and polymer matrix, respectively.

C Halpin-Tsai (H-T) and Modified Halpin-Tsai (MH-T) Models

A semi-empirical equation to predict the elastic properties of short fibres reinforced polymer matrix was developed by Halpin and Tsai (Fornes and Paul, 2003). The H-T models assumed that the particle is isolated, the matrix is isotropic, viscosity is constant, filler well dispersed, has uniform shape and dimension, and is firmly adhered to the matrix. The volume fraction of the filler and its orientation are accounted by using the aspect ratio, $\xi = 2l/D$ where l is the length of the fibre and D the diameter or thickness of the fibre depending on the shape. The Halpin and Tsai equations are given in equations 5-8. The modified Halpin-Tsai equation takes into consideration the maximum packing fraction (ϕ_{max}) of the reinforcement. ϕ_{max}, the maximum packing fraction has a value of 0.785 for a square arrangement of fibre, 0.907 for a hexagonal array of fibres and 0.82 for random packing of fibre (Kalaprasad *et al.*, 1997). The modified Halpin-Tsai equations are shown below (equations 9-11).

$$E_c = E_m \left\{\frac{1+\xi\eta V_f}{1-\eta V_f}\right\} \quad (5)$$

$$T_c = T_m \left\{\frac{1+\xi\eta V_f}{1-\eta V_f}\right\} \quad (6)$$

$$\eta = \frac{E_f/E_m - 1}{E_f/E_m - \xi} \quad (7)$$

$$\eta = \frac{T_f/T_m - 1}{T_f/T_m - \xi} \quad (8)$$

$$E_c = E_m \left\{\frac{1+\xi\eta V_f}{1-\eta\psi V_f}\right\} \quad (9)$$

$$T_c = T_m \left\{\frac{1+\xi\eta V_f}{1-\eta\psi V_f}\right\} \quad (10)$$

$$\psi = 1+\left\{\frac{1-\phi_{max}}{\phi_{max}^2}\right\} V_f \quad (11)$$

E_c = composites' modulus
E_m = the matrix modulus
T_c = composites' Strength
T_m = the matrix Strength
ξ = the shape factor which relates to the filler aspect ratio
V_f = the volume fraction of the filler

D. Nicolais-Narkis Theory and Guth's Equation

The modulus and yield strength of particle-filled composites can be predicted by Guth's equation (Kalaprasad *et al.*, 1997) and Nicolais-Narkis theory (Kalaprasad *et al.*, 1997; Xiano-Lin, *et al.*, 2004) respectively

$$E_c = E_m\ (1 + 2.5\ Vf\ + 14.1\ Vf\ 2) \quad (12)$$

$$\sigma_{yc} = \sigma_{ym}\ (1 - 1.21\ Vf\ 2/3) \quad (13)$$

Guth's Equation is further related to the tensile strength [19], as presented in equation 14.

$$T_c = T_m\ (1- Vf\ 2/3) \quad (14)$$

E, T, and σy are Young's modulus, tensile strength, and yield strength respectively; subscripts *m*, *f*, and *c* denote matrix, filler, and composite, V_f is the volume fraction of filler.

E Hirch's Model

Hirsch's model is a combination of series and parallel models. Hirsch's model is applicable for particulate and fibrous reinforcements. The Young's modulus and tensile strength can be calculated using the following equations (Kalaprasad *et al.*, 1997; Shindea *et al.*, 2017)

Series model

$$E_c = \chi(E_f V_f + E_p) + (1 - \chi)\ V_p \frac{E_m E_f}{E_m V_f + E_f V_m} \quad (15)$$

$$T_c = \chi(T_f V_f + T_p) + (1 - \chi)\ V_p \frac{T_m T_f}{T_m V_f + T_f V_m} \quad (16)$$

χ is the stress transfer parameter. X is 0.1 for randomly oriented fibres composite.

MATERIAL AND METHOD

2.1 Materials

The following are the major materials used; Unripe plantain, Sodium Hydroxide (NaOH), potassium metabisulfite, Glycerol and Polyvinyl Alcohol (PVA) (4% solution at 20 °C, Mw 850,000, 99% degree of hydrolysis, 23-38cp viscosity), micrometre screw gauge. Weighing device, magnetic stirrer, hot and stirrer device, laboratory oven. An Instron Universal Testing Machine (Instron 1121), fitted with a 10N load Cell is used for the mechanical testing

2.2 Methods

Extraction of starch from plantain peels was carried out with modification as reported elsewhere (Pelissar *et al.*, 2012; Pelissar *et al.*, 2017).

Unripe plantain was obtained from the local market of Calabar Nigeria. The plantain was first washed thoroughly to remove dust and other impurities.
The unripe plantain fruits were peeled to separate the peel from the edible part. The plantain peels were washed thoroughly again with distilled water to remove more dust and impurities, sun-dried, and dried in an oven at 150 °C for four hours to reduce the moisture content. The peels were cut into smaller pieces of between 2 and 8 mm and then blended to smaller particles. These particles are then sieved to obtained particle sizes of approximately 750 μm. The 750 μm particles were washed in potassium metabisulfite solution (1% w/v) for 15 min to prevent oxidation. The particles were dried again in the oven at 150 °C for four hours, soaked in a new potassium metabisulfite solution (ratio of 1:2) for two hours and dried again. The dried particles are soaked in 10 % NaOH solution at an impregnation ratio of 5:2 (mass NaOH: mass plantain peels) and stirring at 40 °C for 4 hours. The obtained slurry was blended again at a speed of 150 rpm for 10 minutes, centrifuged at 3500 rpm for 20 minutes and washed several times with water until a clean waste solution was obtained. The obtained slurry was dried in an oven for 48 hours at 40^{o}C. The obtained starch was sieved by 200 μm sieve and placed in a desiccator in a plastic seal. The composite films were produced by the casting method. To prepare 5 wt.% of PVA aqueous solution 5 g of PVA was added into 100 ml of distilled water at 80 °C and was continuously stirred for 70 minutes using a magnetic stirrer at a very high speed to avoid suspension of PVA particles and hindering the movement of the stirrer. After 70 minutes stirring, plantain peels starch was added at different (5, 10, 15 20, and 25%) starch content. Again, the solution was stirred for 60 min at 80°C. The PVA-starch blends were mixed with 20% wt. of glycerol and heated until a homogenous viscous starch paste was obtained. Depending on the ratio between PVA and starch this process takes between 40 and 60 minutes. The mixture was spread on flat glass for the casting process. Casted mixtures were dried in an oven at 80^{o}C for two hours and at room temperature for an hour, for easy removal from the glass. Obtained films were kept in sealed plastic bags, stored in a dry and cool place until when needed. Table 1 represents the nomenclature of various blended films fabricated.

Table-1 Nomenclature of PVA/PS blended films

Abbreviations	Full name
PVA	Neat PVA film
PVAPS5	PVA blend (5 1w1t.% plantain starch)
PVAPS10	PVA blend (10wt.% plantain starch)
PVAPS15	PVA blend (15wt.% plantain starch)
PVAPS20	PVA blend (20 wt.% plantain starch)
PVAPS25	PVA blend (25 wt.% plantain starch)

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2.3 Characterizations of Composite

A Mechanical Analysis

Mechanical properties were appraised using Instron Universal Testing Machine (Instron 1121), fitted with a 10N load Cell. The tensile test was performed at a crosshead speed of 5 mm/min. Films were conditioned in desiccators under 50% RH, at 25 °C, for 48 h before being characterized for moisture content, mechanical properties, and water vapour permeability. A micrometre screw gauge was used to measure the thickness.

Measurements were taken from three different positions and an average value was used. Between 3 and 5 specimens were tested for each % weight. The mechanical properties were measured according to ASTM D882-02 (2002). Equations 17 and 18 were used to calculate the stress (MPa) σ and strain (%) respectively.

$$\sigma=\frac{F\,(N)}{A(m^2)} \quad (17)$$

$$\varepsilon=\frac{\Delta l\ X\ 100}{l} \quad (18)$$

F= force, A= cross-sectional area, Δl= change in length, l=original length. Six modelling equations; Parallel and Series model of Rule of mixtures, Halpin-Tsai equation, modified Halpin-Tsai, Guth's Equation and Nicolais-Narkis Theory and Hirch's Model were used to predict the elastic and tensile properties of the composite material. The theoretical density of the composites was determined using Equation 19 as reported by Raharjo *et al.,* (2018). Equation 20 was used to calculate the needed volume fraction

$$\rho_c=\frac{1}{\frac{W_f}{\rho_f}+\frac{W_m}{\rho m}} \quad (19)$$

$$V_f=\frac{\frac{W_f}{\rho_f}}{\frac{W_f}{\rho_f}+\frac{W_m}{\rho m}} \quad (20)$$

B Scanning Electron Microscopy Analysis

The fracture surface of PVA-PS composites was examined by scanning electron microscopy (SEM) to investigate the cause and mechanism of fracture. An EVO 60 scanning electron microscope was used to study fracture surfaces. Using a low-vacuum sputtering machine, samples were coated with gold mounted on a silver-paint holder before inserted into the SEM chamber. SEM imaging was employed using an accelerating voltage of 5kV. To prepare specimens for SEM, fracture surfaces were first flushed with distilled water to remove any debris. The film samples were cut into small pieces and dehydrated in a desiccator with silica gel (~0% RH).

RESULTS AND DISCUSSION

3.1 Mechanical Behaviour

Results of mechanical properties were compared using ANOVA multiple comparison tests ($p < 0.05$) and were measured according to ASTM D882-02 (2002) standard. The PVA-PPS composite density was measured and calculated based on the Archimedes principle, by ASTM D-638 standard. The theoretical density of the composites was determined using equation 19 (Raharjo *et al.,* 2018). The density of the composite films was calculated to be 1.337g/cm^3, 1.325g/cm^3, 1.313g/cm^3, 1.302 g/cm^3, and 1.29g/cm^3, respectively, for 5%, 10%, 15%, 20%, and 25% weight filler and is presented in Fig. 1. There is no significant difference with theoretical values which are 1.331g/cm^3, 1.323g/cm^3, 1.315g/cm^3, 1.307 g/cm^3, and 1.299g/cm^3, for 5%, 10%, 15%, 20%, and 25% weight filler respectively. The closeness of theoretical and experimental values is due to the absence of voids in the composites.

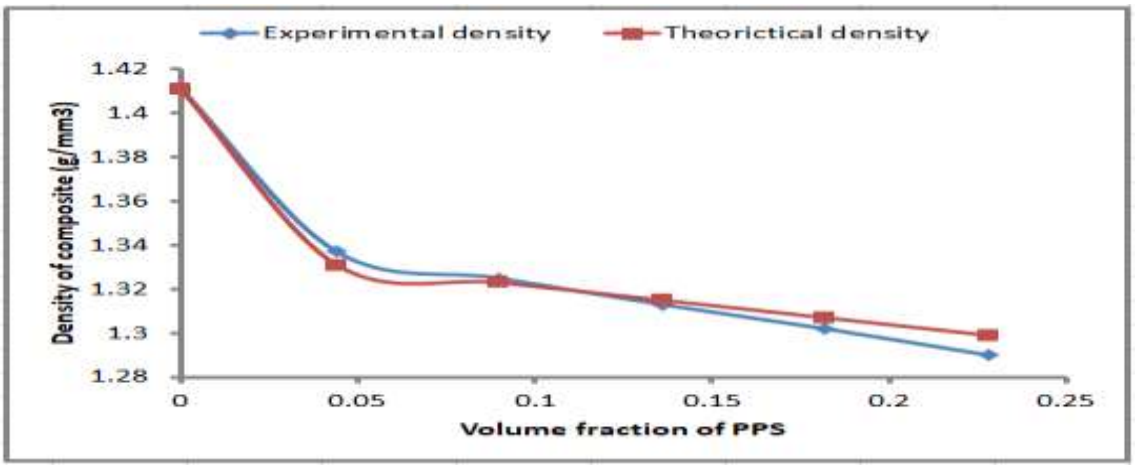

Fig. 1. Experimental and theoretical density of PVA-PPS composite.

Fig. 2 is the stress-strain curves of polyvinyl alcohol reinforced plantain peels starch composite. The figure shows that for PVA curve, at the early stage stress is proportional to strain. As the strain is increased, it reaches its proportional limit, where necking takes place. Then, with the strain increasing, the stress increases gradually at the nonlinear part of the curve. Similar curve pattern has been reported by Ni *et al.,* (2006) and Tiana *et al.,* (2017). The composites films follow the same pattern but with a gradual decrease of the necking area as plantain peels starch increases.

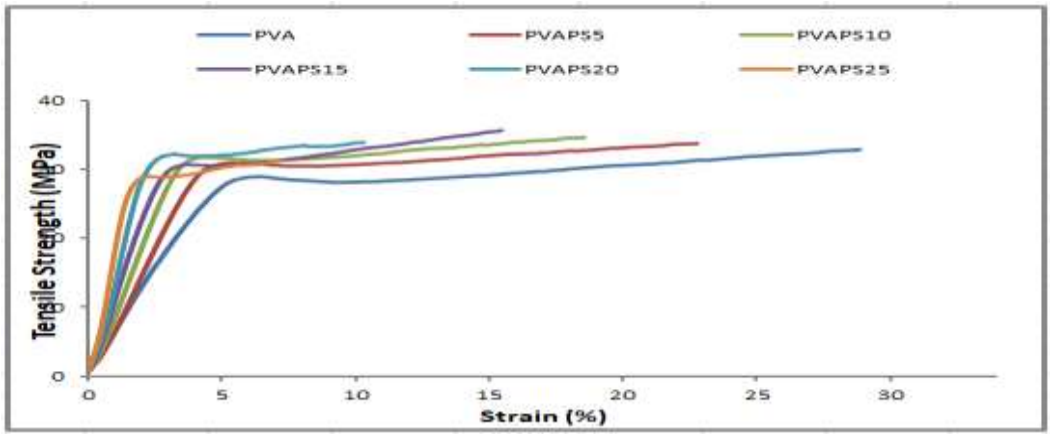

Fig. 2 Stress-strain curves of polyvinyl alcohol reinforced plantain peel starch

Fig. 3 is the mechanical properties of PVA reinforced PPS composites. Generally, starch is primarily known to be a biopolymer with relatively low mechanical properties (Lee *et al.,* 2007) which is the main disadvantage limiting their applications.

Notwithstanding, an addition of PVA will influence the mechanical properties of PVA/starch films due to the flexible C-C backbone and abundant OH groups (Tian *et al.,* 2017). Starch and PVA are harmonious with one other for the reason that both have a large number of hydroxyl groups in their structures which make it easier to take part in extensive intra and intermolecular hydrogen bonding between them (Das, *et al.,* 2009; Das, *et al.,* 2010). From Fig. 3 on blending with starch, tensile strength increased to a maximum of 35.62 MPa at 15 wt.% and then reduced to 31.25 MPa at 25 wt.%. Similar behaviour was also observed for Young's modulus and strain at break. The tensile strength of pure PVA is 32.86 MPa, and this value increases to a maximum of 35.62 MPa at 15 % wt. and decreases to 31.25 MPa at 25% wt. of PPS. The final percentage of increment is 8.40%. The increases in tensile strength with increase in filler contents up to a certain filler loading may be attributed to the likely homogeneous dispersion of plantain peels starch within the PVA matrix and the resulting compatibility. The compatibility is possible due to a large number of hydroxyl groups in their structures as stated earlier.

At higher loading, there is a heterogeneous dispersion of PPS within the PVA matrix leading to an increase in structural defects within the composite resulting in lower mechanical performance (Prachayawarakorn *et al.*, 2013). PVA elongation at break is 28.84%. Addition of PPS decreases to 7.21% at 25 % loading. The maximum percentage decrease is 300 %. The decrease, in elongation at break is an indication that the synthetic polymer blends with a ductile matrix are extremely sensitive to the state of the interface between the matrix and the immiscible filler (St-Pierre *et al.*, 1997). The elastic modulus for PVA increases from 0.59GPa to 2.04 GPa at 25% filler wt.

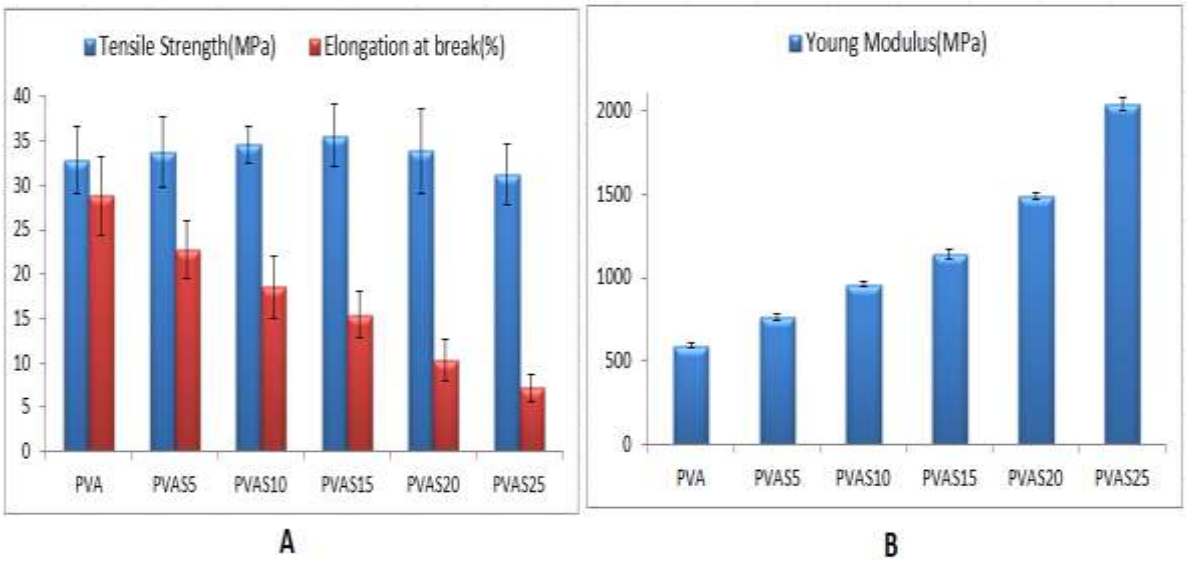

Fig. 3. Mechanical properties of plantain peels starch reinforced PVA

Various authors have reported divergent properties of PVA reinforced starch. The differences in properties are attributed to the method of preparation, temperature, source and method of starch extraction, percentage weight of starch, modification, time taken to process the blend, type and amount of plasticizer used. Tian *et al.*, (2017), reported a decrease in tensile strength, elongation at break and Young's modulus with an increase in corn starch content. Glycerol with hydroxyl groups acts as a plasticizer by entering in between the chains of PVA and starch when mixed with PVA/starch composite and it is expected that the mechanical properties will be enhanced especially at lower volume fraction. Table 2 is the mechanical properties of starch-poly (vinyl alcohol) blended films from different sources as reported in the literature. From the table source of starch, type and percentage of plasticizer and the ratio between matrix and starch greatly affect the mechanical behaviour of composite. The result obtained in this research is in line with reported values as seen in Table 2.

Table-2 Mechanical properties of PVA/starch blended films as reported in the literature

Starch Source	Plasticizer/% added	% wt. of starch	MTS (MPa)	EB (%)	YM(MPa)	Ref
Corn	None	50	16.4	68.74	not given	Priya *et al.*, (2014]
Corn	Glu (0.10%)	50	42.68	134.63	not given	Priya *et al.*, (2014)
Corn	Glu (0.15%)	50	31.81	130	not given	Priya et al. (2014)
Corn	Glu (0.20%)	50	19.32	185	not given	Priya *et al.*, (2014)
Corn	G 10 %	35	≈17.14	≈194.28	not given	Guohua *et al.*, (2006)
Corn	FU=7:3	10	≈23.38	≈1110.86	≈4.39	Tian *et al.*, (2017)
Quinoa	G 21.2 %	4	7.6	58.1	459	Araujo-Farro *et al.*, (2010)
Banana	G 19 %	4	19.3	4.5	2268.7	Pelissari *et al.*, (2013)
Rice	G 30%	50	10.9	2.8	532.8	Dias *et al.*, (2010)
Potatoes	None	10	42.45	6.5	≈1887.64	Jain *et al.*, (2018)
Plantain	G 20 %	15	35.62	15.45	1141.2	This work

FU = Formamide and Urea, MTS=Maximum tensile strength, EB =Elongation at break, YM=Young Modulus, G = glycerol, GLU=Gluteraldehyde

3.2 Modelling of Mechanical Properties.

Tables 3 and Table 4 are the properties of PVA and plantain starch needed for the modelling of the mechanical properties of PVA reinforced plantain peels starch. Fig. 4 shows a comparison of differences in theoretical and experimental tensile strengths of plantain peels starch composites. Theoretical values were calculated using Parallel, Series, Hirsch, Halpin-Tsai, modified Halpin-Tsai and Guth models, as shown in the figure. In all cases, tensile strength increases with increase in the volume fraction of PPS except Guth and Series models whose values decrease as PPS increases. The best correlation between theoretical and experimental tensile strength is predicted using the Parallel model of the rule of mixture, followed by the Hirsch equation, modified Halpin-Tsai and Halpin-Tsai models. Guth and Series models agree the least with the experimental values. Notwithstanding all models except Guth and Series models can predict either wholly or marginally up to 0.136 volume fraction or 15% weight of PPS. Series and Parallel models can be used to describe the strength of both fibrous and particulate reinforced composites (Kalaprasad *et al.,* 1997) and give the minimum and maximum values respectively for tensile strength and Young modulus of the composites. Series model assumes uniform stress while a uniform strain is assumed by the Parallel model. The stress transfer mechanism for continuous fibre reinforced composites is different from that of the short or particulate composite. For a short fibre composite the stress transfer depends on the stress concentration at the ends of the fibre, type and amount of plasticizer, critical length fibre, method of preparation of films, modification of fibre and orientation of fibre, among others. From Fig. 4 irrespective of the volume fraction up to 0.136 (15% weight of PPS), Parallel and Hirsch models agree between 99.15 and 99.82% with the experimental values. For H-T and MH-T models, the percentage agreement with experimental values is between 95.59 and 99.34 % while that of Guth and Series models is between 85.21 and 94.57%. Parallel and Hirsch model's agreement with experimental values is an indication that uniform strain or stress has been achieved in the composite. This is not the case for Series model, at a volume fraction of 0.136 the percentage agreement is 84.39 as against 94.57% for 0.044 volume fraction (5% weight of PPS). At higher volume fraction of PPS (0.136) some of the particulates will be agglomerated in the matrix as seen in Fig.6, hence the uneven distribution of load between aggregated and non-aggregated particulates.

Table-3. Physical and mechanical properties of polyvinyl alcohol (PVA)

Density (g/ cm^3)	Tensile strength at break (MPa)	Elongation at break (%)	Modulus of elasticity (MPa)
1.19	32.86±3.73	28.84±4.41	592.15±16.49

Table-4. Mechanical properties of Plantain starch

Density (g/cm^3)	Tensile strength at break (MPa)	Elongation at break (%)	Modulus of elasticity (MPa)	Aspect ratio
1.34±0.3	19.5±1.4	6.42±0.5	2365±81.54	1.4

Hirsch model is another equation that combined the Series and Parallel models, with the inclusion of a parameter χ. Like Series and Parallel models, the Hirsch model is compatible with particulate and fibrous reinforcements. The theoretical and experimental values can only have 99% agreement of volume fraction up to 0.136 when the value of χ in equations 15 and 16 is 0.99. Bearing in mind the assumption made for Series and Parallel models which are applicable here, it will be right to conclude that at χ= 0.99 uniform stress and strain have been achieved, that is χ is a parameter which defines the

level of stress transfer between matrix and fibre. For a short fibre, the governing indices for the value of χ are fibre orientation, fibre length and stress concentration at the ends of fibre (Kalaprasad *et al.*, 1997). The higher the amount of χ the higher stress concentration at the fibre ends. Stress concentrations at the end of the fibre are influenced by chemical modification carried out before composite formation.

The curves showing the tensile strength values for Halpin-Tsai and the modified Halpin-Tsai equations are shown in Fig. 4. The tensile strength values for both models are not the same. Halpin-Tsai is useful in predicting the properties of composites that contain discontinuous fibres (Kalaprasad *et al.*, 1997). Halpin-Tsai equation has a better correlation with experimental values. Up to 0.136 volume fraction, the percentage deviation from the experimental value is less than 2 % compared to 4.5 % at 0.136 volume fraction for modified Halpin-Tsai equation. The difference in correlation is an indication that the introduction of a factor which determines the maximum packing fraction of fibres affects the tensile strength of particulate fibres. Although Guth equation is used for particulate reinforced polymer composites, Fig. 4 shows clearly, that the predicted tensile strength values are larger than the experimental values. At 0.044 volume fraction the percentage deviation from experimental value is 5.43, this value rose to 16.11% at 0.136 volume fractions.

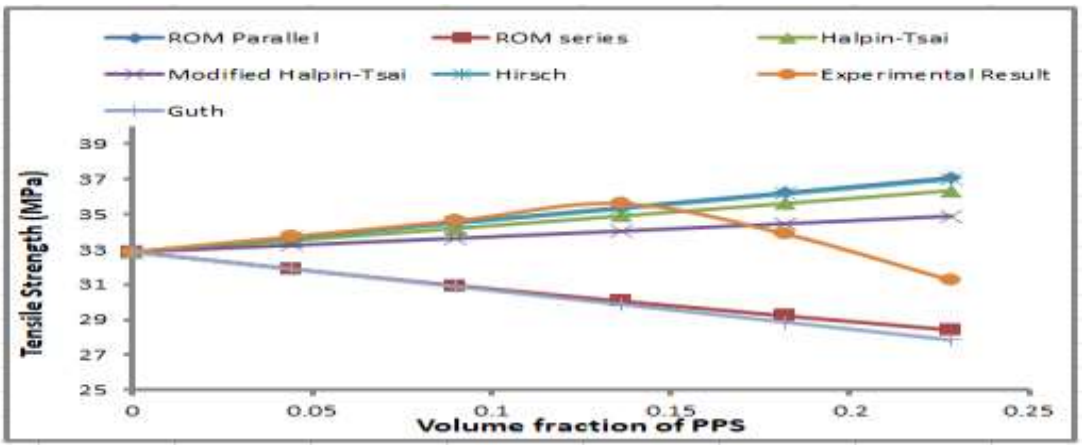

Fig.4. Tensile strength of PVA-PPS composite modelled by Parallel, Series, Hirsch, Halpin-Tsai, modified Halpin-Tsai and Guth

Fig. 5 shows a comparison of the difference in theoretical and experimental elastic modulus of plantain peels starch composites. From the figure, none of the six model equations could give a correlation between theoretical and experimental values. Contrary to the tensile modelling, the Guth model attempted only at 0.044 volume fraction. Guth equation is 99% in agreement with experimental data, followed by Halpin-Tsai, Parallel, Hirsch and modified Halpin-Tsai which has 91.74, 90.89, 90.78 and 85.19% respectively at 0.044 volume fraction. The percentage agreement with experimental values dropped to 87.63, 80.06, 79.84, and 68.65 % for Halpin-Tsai, Parallel, Hirsch, and modified Halpin-Tsai respectively. The constraint of the models used here mainly depends on different factors among which are micro-voids between fibre and matrix during composites formation; this factor is not taken care of in the cause of the model formulation.

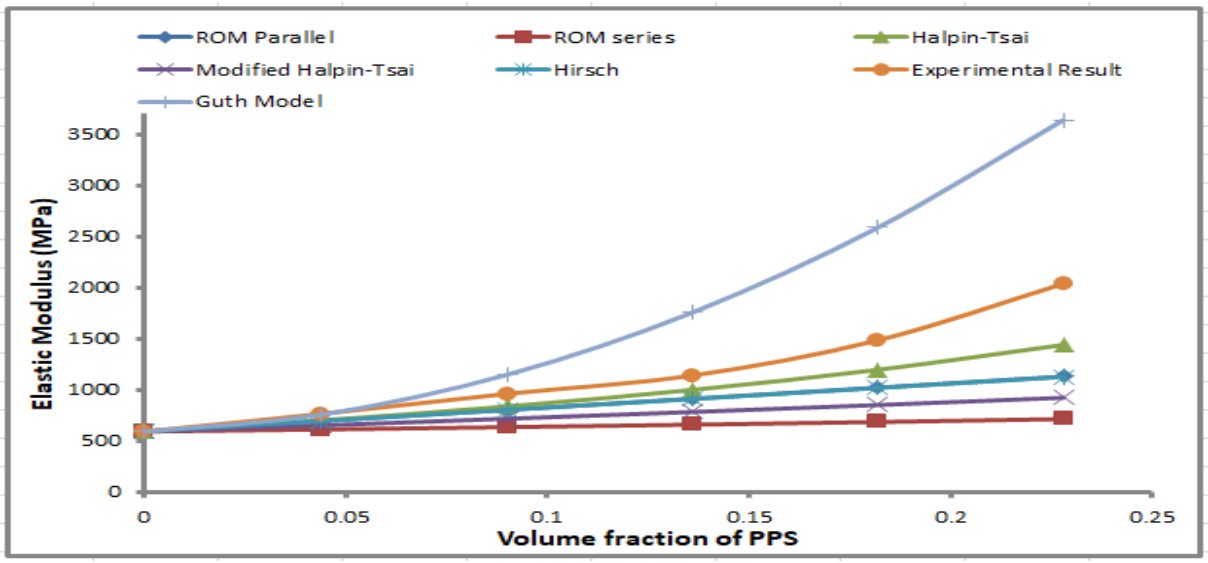

Fig.5 Elastic modulus of PVA-PPS composite modelled by Parallel, Series, Hirsch, Halpin-Tsai, modified Halpin-Tsai and Guth

3.3 Morphology

The SEM images are shown in Fig. 6. B, D and F are the fractured surfaces of PVA, PVAPS15 and PVAPS25 while A, C, and E are surfaces before fracture. Pure PVA film presents a smooth surface without pores with a compact structure. For the blend films, some particles with diameters of several nanometres appeared (Fig. C and E) but no internal cracking, cavities or disruptions of the interface were observed. This concludes that there is a relatively good interfacial adhesion between the two components, which results in higher mechanical properties as compared to neat PVA up to 15% filler loading. Fractured surface of PVA is a little rough but looks ductile. Also, tough fracture characteristics were observed for the blend films. The fracture surfaces of the blend become gradually tougher and rougher as the PPS content increases. The sample with 25 % PPS showed a less dense structure with traces of agglomeration (Fig. 5F) resulting in low properties. Luduena *et al.*, (2012) reported that agglomeration does not allow the correct matrix–filler interaction, resulting in poor mechanical behaviour due to weaker polymer–filler interfacial adhesion.

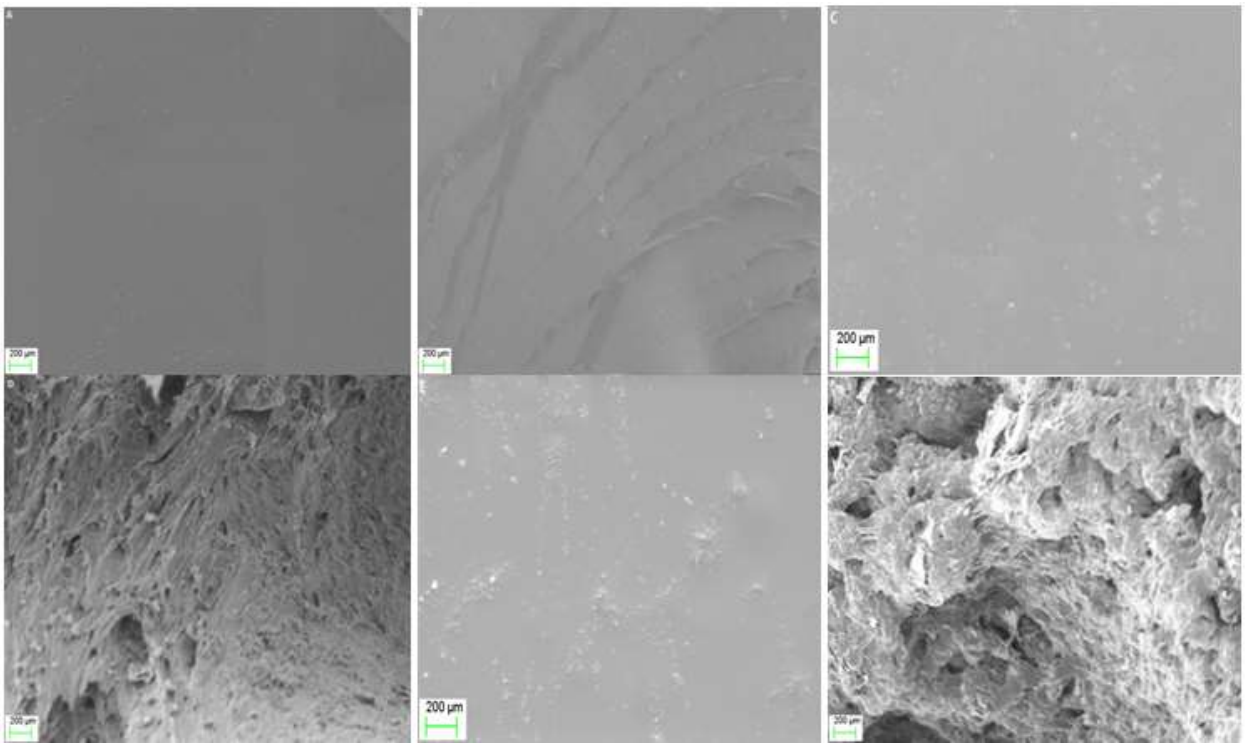

Fig. 6 SEM images of Plantain peels starch/PVA blend films

CONTRIBUTION TO KNOWLEDGE

Different theoretical models of reinforcement namely Einstein and Guth equations, Parallel and series models, Hirsch's model, Halpin-Tsai, and modified Halpin-Tsai models were used to predict the tensile properties and modulus of plantain peels starch (PPS) reinforced Polyvinyl Alcohol (PVA). The best correlation between the theoretical and experimental tensile strength was predicted using the Parallel model of the rule of mixture, followed by the Hirsch equation, modified Halpin-Tsai and Halpin-Tsai models respectively. Guth and Series models agree the least with the experimental values. All models except Series and Guth models can predict wholly or marginally up to 15% weight of PPS. Halpin-Tsai, Parallel, Hirsch and modified Halpin-Tsai theories could predict between 85.19 and 91.74% of the experimental values.

CONCLUSION

A comparison between experimental results and the prediction from theories of mechanical properties (tensile strength, elongation at break, and Young's modulus) of plantain peels starch reinforced Polyvinyl Alcohol (PVA) composites has been presented. The models used were Einstein and Guth equations, Parallel and series model, Hirsch's model, Halpin-Tsai model, and modified Halpin-Tsai. Properties of randomly oriented composites were presented as a function of volume fraction of the starch. All models were applied in both tensile strength and Young modulus. The density of the composite films decreases as plantain peels starch loading increases. There is no significant difference in theoretical values. The tensile strength of pure PVA is 32.86 MPa, and this value increases to a maximum of 35.62 MPa at 15 % wt., and decreases to 31.25 MPa at 25% wt. of PPS. PVA elongation at break is 28.84%, the addition of PPS decreases to 7.21 % at 25 % loading. The elastic modulus for PVA increases from 0.59 GPa to 2.04 GPa at 25 % filler wt. Theoretical modelling shows that tensile strength increases with increase in the volume fraction of PPS except the Guth and Series models whose values decrease as PPS increase. The best correlation between theoretical and experimental tensile strength is

predicted using Parallel model of rule of mixture, followed by the Hirsch equation, modified Halpin-Tsai and Halpin-Tsai models. Guth and Series models agree the least with the experimental values. Notwithstanding all models except Guth and Series models can predict either wholly or marginally up to 0.136 volume fraction or 15% weight of PPS. For tensile modulus, none of the six model equations could give a correlation between theoretical and experimental values. The Guth model attempted only at 0.044 volume fraction giving 99% agreement with experimental data, followed by Halpin-Tsai, Parallel, Hirsch and modified Halpin-Tsai which has 91.74, 90.89, 90.78 and 85.19% respectively. The percentage agreement dropped to 87.63, 80.06, 79.84, and 68.65 % for Halpin-Tsai, Parallel, Hirsch, and modified Halpin-Tsai respectively. The result of modulus modelling reaffirms previous findings that model equations that can predict the tensile strength may not necessarily predict the tensile modulus of the composite.

CONFLICT OF INTEREST

The research work is original and there is no conflict of interest.

REFERENCES

Azahari, N.A., Othman, N., Ismail, H. (2011). Biodegradation studies of polyvinyl alcohol/corn starch blend films in solid and solution media. *Journal of Physical Science* 22, pp. 15-31

Araujo-Farroa PC, Podadera G, Sobral PJA, Menegalli FC. (2010). Development of films based on quinoa (Chenopodium quinoa, Willdenow) starch. *Carbohydrate Polymers* 81, pp. 839-848.

Das, K., Ray, D., Bandyopadhyay, N.R., Gupata, A., Sengupta, S., Sahoo, S., Mohanty, A., Misra, M. (2010). Preparation and characterization of cross-linked starch/poly (vinyl alcohol) green films with low moisture absorption. *Industrial and Engineering Chemistry Research* 49, pp. 2176-85.

Das, K., Bandyopadhyay, N.R., Ray, D., Mitra, D., Sengupta, S., Sengupta, S.P., Mohanty, A. K.., Misra, M. (2009). Physico-mechanical and morphological study of starch/polyvinylalcohol based biocomposite films reinforced with microcrystalline cellulose. *Journal of Biobased Material and Bioenergy* 3, pp. 1-8.

Facca, A.G., Kortschot, M.T., Yan, N. (2006). Predicting the elastic modulus of natural fiber reinforced thermoplastics. *Journal of Applied Science and Manufacturing, Composite Part A,* 37, pp. 1660-1671.

Facca, A.G., Kortschot, M.T., Yan, N. (2007). Predicting the tensile strength of natural fiber reinforced thermoplastics. *Journal of Composites Science and Technology,* 67, pp. 2454-2466.

Fornes, T., Paul, D. (2003). Modelling properties of nylon 6/clay nanocomposites using composite theories. *Polymer,* 44, pp. 4993-5013.

Guohua, Z., Ya, L., Cuilan, F., Min, Z., Caiqiong, Z., Zongdao, C. (2018). Water resistance, mechanical properties and biodegradability of methylated corn starch/poly(vinyl alcohol) blend film. *Polymer Degradation and Stability,* 91, pp. 703-711.

Jain, N., Singh, V.K., Chauhan, S. (2018). Dynamic and creep analysis of polyvinyl alcohol-based films blended with starch and protein. *Journal of Polymer Engineering*, pp.1-13.

Kim, D.H., Na, S.K., Park, J.S. (2003). Preparation and characterization of modified starch-based plastic film reinforced with short pulp fibre. II Mechanical properties. *Journal of Applied Polymer Science,* 88, pp. 2108-2117.

Kalaprasad, G., Joseph, K., Thomas, S., Pavithran, C. (1997). Theoretical modelling of tensile properties of short sisal fiber-reinforced low-density polyethylene composites. *Journal of Materials Science,* 32, pp. 4261-4267.

Lee, S-T., Park, C.B., Ramesh, N.S. (207). Polymeric foams: science and technology. Taylor & Francis, New York .

Luduena, L., Vazquez, A., Alvarez, V. (2012). Effect of lignocellulosic filler type and content on the behavior of polycaprolactone based eco-composites for packaging applications. *Carbohydrate Polymer,* 87, pp. 411-421.

Ni, W., Wang, B., Wang, H, Zhang, Y. (2006). Fabrication and Properties of Carbon Nanotube and Poly (vinyl alcohol) Composites. *Journal of Macromolecular Science, Part B: Physics,* 45, pp. 659-664.

Prachayawarakorn, J., Chaiwatyothin, S., Mueangta, S., Hanchana, A. (2013). Effect of jute and kapok fibers on properties of thermoplastic cassava starch composites. *Material and Design,* 47, pp. 309-315.

Pelissari, F.M., Andrade-Mahecha M.M., Sobral, P.J.A., Menegalli, F.C. (2017). Nanocomposites based on banana starch reinforced with cellulose nanofibers isolated from banana peels. *Journal of Colloid and Interface Science,* 505, pp. 154-167.

Priya, B., Gupta, V.K., Pathania, D., Singha, A.S. (2014). Synthesis, characterization and antibacterial activity of biodegradable starch/PVA composite films reinforced with cellulosic fibre. *Carbohydrate Polymers,* 109, pp. 171–179

Pelissari, FM, Andrade-Mahecha M.M., Sobral, P.J.A., Menegalli, F.C. (2013). Comparative study on the properties of flour and starch films of plantain bananas (Musa paradisiaca). *Food Hydrocolloids,* 30: pp. 681-690.

Pelissari, FM, Andrade-Mahecha M.M., Sobral, P.J.A., Menegalli, F.C. (2012). Isolation and characterization of the flour and starch of plantain bananas (Musa paradisiaca). *Starch/Starke,* 64, pp. 382-391.

Raharjo, W.P., Soenoko, R., Purnowidodo, A., Choiron, M.A. (2018). Experimental and micromechanical modelling of randomly oriented zalacca fibre/low-density polyethylene composites fabricated by hot- pressing method. *Cogent Engineering,* 5, pp.1-14

Singha, A.S., Priya, B., Pathania, D. (2015). Cornstarch/Poly(vinyl alcohol) Biocomposite Blend Films: Mechanical Properties, Thermal Behavior, Fire Retardancy, and Antibacterial Activity. *International Journal of Polymer Analysis and Characterrization,* 20, pp. 357-366.

Shinde, S.S., Salveb, A.V., Kulkarnic, S. (2017). Theoretical modeling of mechanical properties of woven jute fibre reinforced polyurethane composites. *Materials Today: Proceedings,* 4, pp. 1683-1690.

St-Pierre, N., Favis, B.D., Ramsay, B.A., Ramsayt, J.A., Verhoogt, H. (1997). Processing and characterization of thermoplastic starch/polyethylene blends. *Polymer,* 38, pp. 647-655.

Teixeira, E.M., Curvelo, A.A.S., Corrêa, A.C., Marconcini, J.M., Glenn, G.M., Mattoso, L.H.C. (2012). Properties of thermoplastic starch from cassava bagasse and cassava starch and their blends with poly (lactic acid). *Industrial Crops and Products,* 37, pp.61–68.

Tiana, H., Yana, J., Rajulu, A.V., Xianga, A., Luo, X. (2017). Fabrication and properties of polyvinyl alcohol/starch blend films: Effect of composition and humidity. *International Journal of Biological Macromolecules,* 96, pp. 518-523.

Xiano-Lin, X., Liu, Q., Li, R. K., Zhou, X., Zhang, Q., Yu, Z. Mai, Y. (2004). Rheological and mechanical properties of PVC/CaCO3 nanocomposites prepared by in situ polymerization. *Polymer,* 45, pp. 6665-6673.