Research Article

Preparation and Characterization of Sago Starch filled with Poly (N-vinyl carbazole) (PVK) Nanoparticles

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Received: 15 June 2017 Revised: 14 July 2017 Accepted: 23 July 2017

Abstract

Objective: The aim of present study was to investigate the effects of PVK as fillers on the characteristics and properties of sagu starch solution, water vapour permeability and UV-VIS transmission of the sagu starch. **Material and methods:** The sagu starch filled with PVK was homogenized and incorporated into sagu starch solutions at different concentrations. Introduction of PVK fillers to sagu starch solutions significant increased the viscosity of the solution. **Results and conclusions:** Solubility to different solvents, moisture content was decreased. The sagu starch solutions filled with PVK nanoparticles had 30% UV transmittance. These properties suggest that the prepared biocomposites has the potential as filler in starch based products for use as active materials in packaging and in pharmaceutical and textile industries.

Keywords: sagu starch, PVK, biocomposites

Introduction

For the past decade, nanoscale science and other related technologies has been the leading technology. Composite technologies have been merged with nanoscale science, leading to the development of nanocomposite science and technology. Incorporation of nanoparticles into composite materials has attracted a great deal of attention due to its ability to enhance polymer properties such as thermal and mechanical properties. Nanofillers have excellent interfacial interactions on polymer branches due to their large specific surface area and high surface energy, thus significantly enhancing the properties of sago palm starch. In addition, the use of Poly (N-vinyl carbazole) (PVK) is considered to be a viable method for the prevention of infectious diseases through its antimicrobial properties (Cui, K., et al., 2011).

Sago palm is one of Genus *Metroxylon* belonging to the Family Palmae. The plant accumulates a huge amount of starch in its stem, very often more than 100 kg per plant. Starch is a mixture of two polymers, amylose, a linear (1-4 carbon atom) linked alpha D-glucan and amylopectin a highly branched molecule which consists of short chains of (1-4)-linked alpha-D-glucose with (1-6 carbon atom) alpha-linked branches. All starches are made up of these two polysaccharides. The ratio varies with the starch source but is typically 20:80 amylose to amylopectin.

Polymer biocomposites have received intense attention due to its unique properties, such as adjustable electrical conductivity, robust mechanical properties and the potential to create new materials with much improved characteristics coupled with a good chemical stability. However, effective utilization of the excellent properties of composites depends on the quality of their dispersion and the level of polymer-starch interfacial bonding through covalent or noncovalent method. The combination of the unique properties of sagu starch and organic polymers like poly (*N*-vinyl carbazole) (PVK) make it an interesting material for the development of practical devices. PVK is well known for its exceptionally high thermal stability, high photoconductivity and opto-electronic properties. Thus, the incorporation of sagu starch into the PVK matrix to prepare polymer-starch biocomposites may be one of the best ways to improve the properties of starch. This study made use of high molecular weight PVK to disperse the sagu starch via noncovalent

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interactions. High molecular weight PVK forms a more stable dispersions and that the conducting polymer properties of PVK also have the advantages of producing more enhanced properties of sagu starch-PVK biocomposites. The incorporation of PVK into sagu starch should also increase the mechanical and thermal properties of composite materials and thus increases their environmental stability (Kim., et. al., 2008).

In this work, we report the preparation and fabrication of sagu starch-PVK biocomposites as fillers and its possible application in textiles and packaging were determined. A convenient and facile route for preparing sagu starch filled with PVK biocomposite films is the solution mixing method of the polymer and sagu starch to a suitable solvent. The method for accomplishing this is the prior dispersion of PVK and sagu starch in solvent and with slow and continuous addition of PVK in the sagu solution in order to form sagu starch- PVK biocomposites with the expectation that the sagu starch will be physically wrapped within the PVK polymer matrix which leads to an enhanced mechanical, thermal and electrical property. Here we report an investigation in using mixed solvents on the dispersion, morphology, and structure of sagu starch-PVK biocomposites (Cui, K., et. al., 2011).

Materials and methods

Preparation of Materials

Sagu starch was gathered from different study sites in Northern Samar. All the reagents were prepared using analytical grade reagents and distilled water. For the antimicrobial assay, *S. aureus* and *E. coli* was obtained from the culture collection center of the University of the Philippines, Los Banos.

Sagu Starch Isolation

Sagu palm available in the study area are studied. Fresh tubers were washed thoroughly with tap water and grated into a pulp. The pulp was suspended in excess distilled water (1:25 w/v) and homogenized in a blender (Osterizer) at medium speed for 20 minutes at room temperature. The homogenized slurry was strained and filtered through a whatman filter paper. The waste residue was washed washed with 20 mL of distilled water. The resulting milky filtrate was centrifuged for 10 minutes. The starch was dried at 50^0C for 24 hours. The isolated starch was ground in a mortar, sieved through a mesh sieve and stored at room temperature.

Preparation of sagu starch filled with PVK biocomposites films

PVK was dispersed in suitable solvent and stirred for 2 hours. The solution was used to prepare the starch dispersion at 10% (w/w). A mixture of sorbitol and glycerol of total solid was added as plasticizer. Starch and PVK biocomposites were heated to 85^0C and held for 1 hour to allow gelatinization. Upon completion of starch gelatinization, the solution was cooled to room temperature. A portion of the dispersion was cast on a plates to produce 20 x 20 cm^2. The prepared films were dried under controlled conditions (at room temperature) and was kept in a dessicator prior to analysis. Control films were also prepared similarly but without the addition of PVK. Dried films were peeled and stored in a dessicator at room temperature until experimentation. The thickness of each film was measured using vernier caliper. All films were prepared in triplicate.

Characterization of sagu starch and sagu starch filled with PVK biocomposites

Moisture content

Moisture contents of prepared sagu starch samples were determined by drying triplicates of 5 g samples to a constant weight in a drying oven at 105°C.

Apparent amylose determination

Starch from sagu palm (5 mg) were added to 2 mL of DMSO and heated at 85°C for 15 minutes. Distilled water was added to the dissolved sagu starch to bring the volume up to 25 mL. Starch solution (1 mL) was pipetted into a 50 mL volumetric flask and make up to volume. Five millilitres (5 mL) of Iodine was added and the absorbance was read at 600 nm, using a UV-visible spectrophotometer.

Swelling power and solubility

To determine the swelling factor, a starch sample was weighed accurately in a centrifuge tube before 40 mL of distilled water were added. The slurry was heated at 80°C in a water bath for 30 min. subsequently after, the samples were cooled to room temperature and the solution was centrifuged at 3000 rms for 15 minutes. The supernatant obtained was carefully removed, and the swollen starch sediment was weighed. The aliquot of supernatant was evaporated overnight. Analyses were performed in triplicate. Swelling power and solubility were calculated as follows:

$$\text{Swelling power (g/g)} = \frac{Weight\ of\ the\ wet\ sediment(g)}{Weight\ of\ the\ dry\ starch(g)} \quad \text{(Equation-1)}$$

$$\text{Solubility (\%)} = \frac{Weight\ of\ dried\ supernatant\ (g)}{Weight\ of\ the\ dry\ starch\ (g)} \quad \text{(Equation-2)}$$

Water binding capacity

A suspension of starch (dry weight) in 75 ml distilled water was agitated for 1 hr and centrifuged for 10 minutes. The free water was removed from the wet starch which was drained for 10 minutes and the wet starch was weighed.

Thermal analysis

The thermal properties of starch were studied using a thermogravimetric analyzer (TGA). Starch slurries were prepared at 1:3 dry starch/ratios and the samples then were heated from 20 to 120°C at 10°C/min. after the TGA run; samples were stored at 4°C for 7 days for retrogradation studies. Each sample was run in triplicate.

Results and discussion

Starch is one of the natural occuring polymers which is biocompatible, biodegradable and shows bio-adhesion property. It is a polysaccharide that contains amylose and amylopectin. Due to its biodegradability, abundance and low cost, starch has been widely used in various practical applications. Polymer biocomposites have attracted much attention due to their unique properties that are different significantly from their bulk materials. Various synthesis methods have been attempted to prepare starch biocomposites.

Sagu starch was isolated from fresh sagu palm. The percentage yield 80.78 % might be an indication of appreciable accumulation of starch in the young palm for conversion of energy during the physiological development of palm. Sagu starch is perhaps the only starch derived from the stem of palm (sagu palm). Sagu palm contains a large amount of starch in its trunk. Normally, during germination arrays of enzymes including amylases developed and remain in an active form. Since no preservatives were used during isolation of starch, there could be a possibility of some amount of starch getting hydrolyzed which might affect the starch yield. Sagu starch yield in this work, after isolation and washing process, relative to other sources of starch like corn and potato as presented in other studies showed a marked loss of starch suggested that the starches had been solubilized by during the treatment. During treatment, starch can undergo changes in the structure and physicochemical properties. These changes could be attributed and depend on the type of treatment, concentration used and the type of starch. Compared to other starch modifications, such as enzyme and acid treatments, very few studies on the introduction of polymers have been conducted.

Characterization studies of starch and starch/PVK biocomposite

Moisture content

Moisture content of sagu starch and sagu starch biocomposites were evaluated in this study. The moisture content was the inherent physicochemical properties of starch and its biocomposites. The results show that in the 20 days of analysis of the moisture content the sagu starch biocomposites is not susceptible to moisture unlike for the pure sagu starch wherein a considerable increase in moisture was observed. Sagu starch is greatly susceptible to moisture and this could be due to the presence of the natural pores and cavities which facilitate the penetration of moisture in the starch granules. But, for the sagu starch biocomposites it presented a lesser susceptibility this could be due to the PVK wrapped around the sagu starch garnules preventing the penetration of moisture to the biocomposites.

Apparent amylose content

The apparent amylose content of the sagu starch and sagu starch biocomposite was employed in this work to gain insight on the effect of the introduction of PVK in the sagu starch in its amylose content. Figure shows the apparent amylose contents for sagu starch and sagu starch -PVK at 0, 10 and 20 days. The amylose contents for sago starch and sagu starch biocomposites, were 29.6%, and 28.2% respectively. Amylose content of the filled sagu starch showed a slight decreased after 20 days of treatment. Apparent amylose content of sago starches did not change during the first 10 days of the introduction of PVK in the biocompoites, but it decreased when after 20 days of after the preparation of the biocomposites. The reduction of apparent amylose content of filled PVK sagu starch could be attributed to the disruption of the amorphous region that contains amylose chains and in addition, the PVK polymer probably affects the amylose rather than the amylopectin molecules and/or regions of the granules suggested that the ions in PVK solution diffuse into the amylose-rich amorphous regions of the granules, break intermolecular bonds, and cause the granules to swell to a higher degree, with a concomitantly higher exudation of amylose. The insignificant canges in apparent amylose content for sago starch-PVK biocompoites during the first 10 days of the experiment suggest that the introduction of PVK as filler did not intensively affect the amorphous region of either starch during this period. It could also be attributed to the large degree of polymerization of sagu starch amylose might slow down the PVK action. In the study of Wang (2014), they suggested that a larger degree of polymerization requires more time to degrade the chain length in starch molecules.

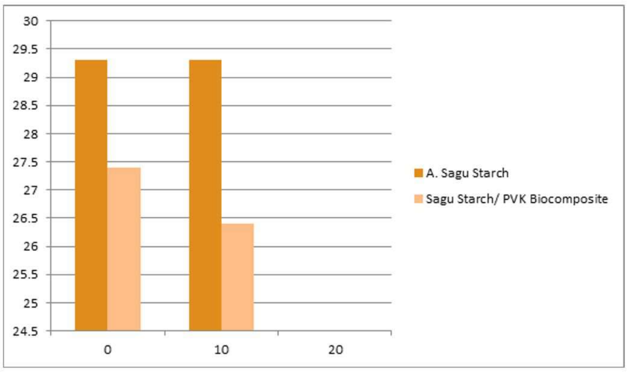

Figure 1. Amylose content of the sagu starch and sagu starch biocomposites

After 20 days of PVK treatment, sagu starch had the highest percentage reduction of amylose content. However, these data might not provide the exact amount of amylose content decrease caused by the incorporation of PVK. The washing process might remove the solubilized starch, together with the supertanant and the remoed solubilezed starch might contain solubilized amylose. The slight decrease, occuring in PVK filled sagu starch, might be due to existence of natural pores and cavities on the surface of sago starch, which could explain the minimum decrease of amylose content of this starch compared to the other sources of starch.

Pasting/viscosity properties

Table 1 also shows the pasting/viscosity characterisics of sagu starch and PVK-filled sagu starch. Results showed that an increasing trend of pasting/viscosity for PVK filled sagu starch. The high viscosity exhibited by sagu starch in this study was due to higher granule rigidity and integrity of the starch which is merely contributed by the presence of amylose. However, for PVK filled sagu starch, the amorphous region of the sagu starch was greatly wrapped by the PVK, thus in this instance increasing the granular structure. Consequently, when shear/force was applied to the starch during pasting, the granules could attain their maximum swelling capacity, resulting in an increase of the starch biocomposites viscosity.

Table 1. Pasting/viscosity properties of the prepared sagu starch and biocomposites.

Sample	Mean Viscosity (mL/min)
Sagu Starch	4.5
Sagu stach/PVK Biocomposites	7.8

A negative correlation between viscosity and amylose content suggest that there was no relationship between starch viscosity and percent amylose content in the starch granule. Breakdown is a measure of the response of starch and PVK filled sagu starch pastes to shear-thinning during the holding period at 95°C. Thus, breakdown viscosity indicates the tendency of starch and starch biocomposites to resist shear force during heating. An increase in breakdown viscosity for PVK filled sagu starch suggests that the granule structure of the filled sagu starch might be due to the presence of the large molecules of PVK which would strenghthen the intermolecular forces within the granules and thereby prevent the physical breakdown of starch biocomposite granules even after holding for a certain period of time at 95 °C. This might explain the increase in breakdown viscosity for PVK filled sagu starch.

Swelling and solubility

The swelling and solubility results illustrate the integrity and rigidity of the starch and starch biocomposites. Swelling is primarily a property of amylopectin and amylose, whereas lipids can inhibit swelling. Table 2 shows the swelling power and solubility of the starch and the sagu starch filled with PVK biocomposites. There was a progressive increase in swelling power of the sagu starch biocomposites compared to that of the sagu starch. The results presented that the increase in swelling power of the sagu starch biocomposites can be attributed to the wrapping of the amorphous region of the sagu starch PVK biocomposites, which probably increase the restraining effect of amylose, thus allow the particles to move freely. The swelling power of sagu starch was increased after the introduction of PVK in this study, in which the sagu starch were protected to rupture which yields a high value of swelling power.

Table 2. Swelling and solubility properties of sagu starch and its biocomposites

Sample	Swelling (G/G)	Solubility (%)
Sagu Starch	8.4	1.3%
Sagu Biocomposites	10.6	1.9%

The solubility of the sagu starch biocomposites shows inconsistent result after 20 days. This inconsistency might be due to the removal of some soluble material during the filtration process after the addition of PVK. From the percentage yield of starch obtained, it shows that some of the soluble components of the biocomposites were removed during the process.

Water Binding capacity (WBC)

The water binding capacity of the sagu starch and sagu starch biocomposites were determined in this study. The WBC of sagu starch showed around 90.45%. The low WBC for sagu starch may be attributed to the involvement of a larger proportion of the hydroxyl groups in forming hydrogen and covalent bonds between starch chains than with water. A larger WBC was observed for sagu starch filled with PVK biocomposites. The results are presented in Table 3.

Table 3. Water binding capacity property of sagu starch and sagu starch/PVK biocomposites

Sample	Mean WBC
Sagu Starch	90.45
Sagu Biocomposites	108.54

Thermal properties

To confirm the formation and mixing and macromolecular interactions of sagu starch filled PVK solutions, TGA analysis of sagu starch and sagu starch filled with PVK were conducted. The TGA thermograms of the samples were recorded under N_2 atmosphere scanned in the range 20-900^{0}C is shown in Figure 2. TGA thermogram of sagu starch filled PVK exhibited 2 degradation steps as presented in Figure 2.

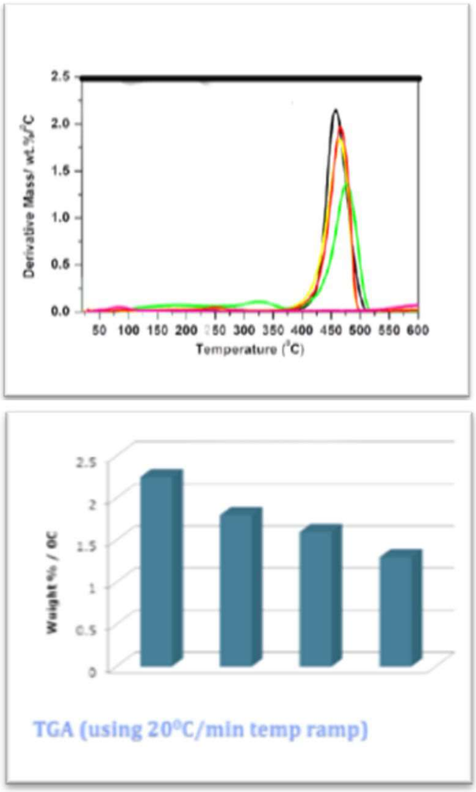

Figure 2. Thermal properties of sagu starch and sagu starch/PVK biocomposites

The 1st degradation step takes place at 250^{0}C and then the polymer showed a fast 2nd degradation step reaching a 90% weight loss at 378^{0}C and almost total degradation at 402^{0}C. It is evident in the graph that the sagu starch exhibited a small stability showing a 98% weight loss after heating the composite to 82^{0}C. The thermal stability sagu starch is enhanced with the incorporation of PVK biocomposites. This can be explained by the sagu starch near the PVK chains may degrade more slowly, which helps to shift the decomposition temperature to the higher side. Other possible reason is the increased thermal stability of the polymer biocomposites due to the effect of higher thermal conductivity of PVK that facilitates heat dissipation within the composite. An improvement of the thermal stability can be associated with a better wrapping/preparation of biocomposites, since it hinders the flux of decomposition product and thus delay the decomposition. It is important to point out that the extent of interaction between sagu starch and PVK filled biocomposites could be responsible for the higher thermal stability of the composites. These results indicate that the addition of PVK in sagu starch showed to be more thermally stable as compared to pure sagu starch. In this study, sagu starch filled with PVK showed a significant increase of thermal stability compared to the other polymer biocomposites. This is an interesting finding because we assumed that the natural features of sagu starch granules would allow more OH ions to diffuse into PVK chains, thus providing stability and increasing the thermal stability. Severe interaction of the amorphous region of sagu starch filled with PVK might have increase the ability of the OH ions to interact well with PVK chains, resulting in a higher thermal degradation.

In this study, the results have shown that the physicochemical properties of the sagu starch and sagu starch filled with PVK were affected to a certain degrees when they were incorporated with PVK fillers. The results can be usefully applied to the development of novel products with improved attributes.

Conclusions

In this study, we prepared PVK-sagu starch biocomposites. The specific characteristic of the prepared biocomposites plays a key role in the basic properties of the sagu starch films filled with PVK. After the incorporation of PVK, we observed significant differences in the film properties, especially in water permeability, and UV-VIS. The said prepared biocomposites may have great potential in the medical and packaging industries.

The fabricated films cannot go beyond the commercially available biocomposites materials. But once the abovementioned recommendations are met, the prepared films could be applied to a variety of areas, including electronics and biomedical sciences for commercial applications.

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