

The Utilization of Microcrystalline Cellulose from Waste Coconut Bunches (*Cocos nucifera linn*) as Filler for Cassava Starch Edible Film with Glycerol as Plasticizer

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Abstract. Microcrystalline cellulose (MCC) was prepared from waste coconut bunches (*Cocos nucifera linn*) and was utilized as filler in cassava starch edible film with glycerol as plasticizer. The MCC was added to the starch films with variation of mass: 0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g. Characterization of the MCC with FT-IR, XRD and SEM showed that the MCC contained free OH groups and had a crystalline structure. Analysis of FT-IR for the MCC-starch-glycerol film indicated strong intermolecular hydrogen bonds among starch-glycerol and MCC. The mechanical properties of the film indicated that the tensile strength was 0,317 kg/mm² and elongation was 114.82% in the optimum starch-glycerol film with 0.4 g MCC. XRD analysis showed that starch-glycerol-0.4 g MCC film had a semi-crystalline structure and mainly amorphous structures. SEM analysis showed that the starch-glycerol-0.4 g MCC film had a physical interaction where MCC was attached to the surface of the starch matrix. The lowest water content was 11,50% were obtained on starch-glycerol film with 0.5 g MCC, while the lowest water vapor transmission rate (WVTR) values was 0,008 g/cm².hours were obtained by starch-glycerol film without MCC. Toxicity tests showed that the starch-glycerol-MCC films did not function as antibacterial.

Keywords: microcrystalline cellulose; coconut fruit bunches; filler; cassava starch; edible film

Introduction

Starch has been used widely in the food industry as edible films to substitute for plastics due to the fact that it is renewable, cheap and possesses good physical properties [1]. On the other hand, microcrystalline cellulose (MCC) produced by depolymerization of α -cellulose obtained from plant pulp using an inorganic acid, has been used as fillers and binders for medicine tablets. Some physical properties of microcrystalline cellulose obtained from raw cotton of *cochlospermum planchonii* have been characterised [2]. Jackson, et. al. have used nanocrystalline cellulose for the binding and controlled release of drugs [3].

Recently, oil palm empty fruit bunches have raised environmental problems and therefore have been used as raw material for cellulose pulp production, although it is not in industrial scale yet. Furthermore, Thomas et. al. reported that lignocellulosic biomass from fruit bunch, fruit fibre, leaf stems of coconut (*cocos nucifera* Linn.) have been utilized as substrates for fungi (*Pleurotus sajor-caju* (Fr.) Singer) growth media [4]. It was also reported that cellulose content in the coconut fruit bunches (CFB) is 29% whereas the lignin content is 31%. Abiola has reported flexibility and rate of hydrolysis of coconut empty fruit bunch fibre [5]. Various related researchers have reported the use of cellulose or its derivatives as fillers for edible or degradable polymer films, e.g. Dhanapal et. al. [6] investigated edible films from polysaccharides. Jin and Zhang [7] reported biodegradable polylactic acid polymer films with nisin for use in antimicrobial food packaging. Juliyarsi, et.al. [8] reported the quality of edible film by using glycerol as plastisizer. Whereas Laxmeshwar and Sandep [9], investigated preparation and properties of biodegradable film composite using modified cellulose fibre-reinforced with PVA.

Experimental

Preparation of microcrystalline cellulose (MCC) from coconut fruit bunches (CFB)

The MCC was prepared as reported by Ohwavwhorua dan Adalakun [2]. About 75 gram dried and chopped CFB was reacted with mixture 1 liter of HNO₃ 3.5% and 0.1 gram NaNO₂ at 90°C for 2 hours, washed with distilled water and filtered and then digested with 500 ml of NaOCl 1.75% at 100°C for 30 minutes. Furthermore 10 gram of α -cellulose powder was hydrolised with 200 ml HCl 2.5 N, refluxed at 100°C for 15 minutes. This was then washed with distilled water, dried at 60°C for 4 hours, cooled and ground and shieved at 100 - 120 mesh.

Preparation of edible films based on cassava starch using glycerol as plastisiser at various loading of MCC

Preparation of edible films of cassava starch using glycerol and various concentration of MCC was based on procedure of Bangyekan et.al. [10]. 10 gram of cassava starch was added with 100 ml distilled water mixed thoroughly and then was added with 1.5 gram glycerol and 0.1 gram MCC. The mixture was then heated at 80°C to glutinise and cast on a glass plate (30 cm x 30 cm) which was coated with aluminium foil and the film was dried in open air for 24 hous. The procedure was repeated at various MCC loading of: 0.2 g; 0.3 g; 0.4 g; and 0.5 g based-on 10 g of cassava starch.

Characterisations

Tensile strength (kgf/mm²) and elongations (%) of the films were tested using electro testing machine type MFG SC-2DE based on ASTM D-368-72 type IV. Water contents of the films were measured gravimetrically using an exhausted vacuum oven at 80°C to constant weight, whereas FTIR analysis of the films were carried out using a Shimadzu FTIR spectrometer type 8201PC. Morphology of the films was studied using scanning electron microscopy (JEOL JSM-6510 LV) at 5000 times magnification. The rates of water vapour transmission (WVTR) were measured gravimetrically as reported by Yakubu et. al. [11] and based on ASTM E96.

Results and Discussion

Microcrystalline cellulose (MCC) of coconut fruit bunches (CFB)

From 600 gram chopped coconut fruit bunches (CFB) it was found using the above procedure that 44 gram (yield = 7.3%) of the white microcrystalline cellulose (MCC) was produced (Fig. 1).



Figure 1. White microcrystalline cellulose (MCC) of coconut fruit bunches (CFB).

The white microcrystalline cellulose (MCC) of coconut fruit bunches (CFB) was then characterized using Scanning Electron Microscopy technique. It was shown from the SEM photograph (Fig. 2, magnification 5000 times) that the MCC was in crystalline form (particle diameter 340 μm), which revealed that the amorphous phase of the cellulose has been dissolved during the hydrolysis process using HNO₃ 3.5% and 0.1 gram NaNO₂ at 90°C for 2 hours.

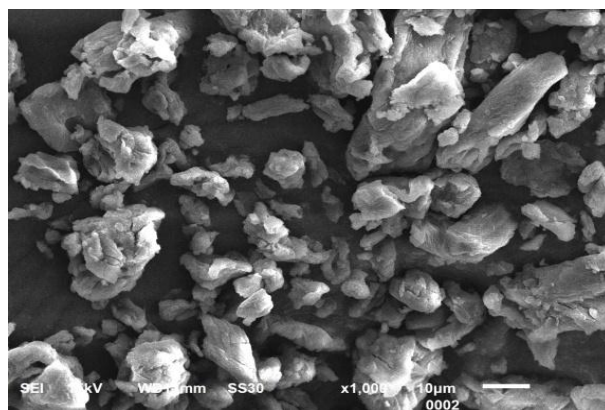


Figure 2. SEM photograph (magnification 5000 times) of microcrystalline cellulose (MCC) of coconut fruit bunches (CFB).

Edible films based on cassava starch with various MCC contents using glycerol as plastisiser

Edible films obtained in this work were shown in Fig. 3a and 3b. Fig. 3a is edible film based on 10 g starch containing 1.5 g glycerol without MCC, which was used as control for the ones containing various loading of the MCC. Contents of the MCC were then varied (from 0.1 g, 0.2 g, 0.3 g, 0.4 g, and 0.5 g in 10 g of starch) and Fig. 3b is that containing 0.5 g of the MCC. It was found that addition of MCC in the edible films up to 0.5 g did not alter visual appearance of the films. These showed that the MCC is compatible with cassava starch matrix in the presence of glycerol as plastisizer as also reported by Yakubu et. al. [11].

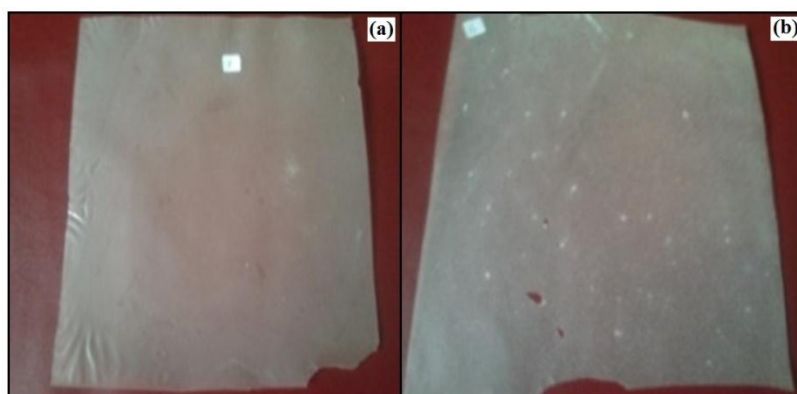


Figure 3. Cassava starch edible films using glycerol as plastisiser without MCC (a), and with 0.5 g MCC (b) on the basis of 10 g of the matrix.

FTIR spectroscopy analysis

Fig. 4a-4c are FTIR spectra of the microcrystalline cellulose, the edible films without and containing 0.5 g MCC, respectively. The spectra mainly showed transmittances due to hydroxyl (-OH, 4001-4008 cm⁻¹), (C-H, 3437-3633 cm⁻¹), (C-O, 1151-1168 cm⁻¹) bonds

of the starch, the MCC as well as the glycerol as shown in Table 1. It was revealed that the presence of the transmittances indicated good compatibility between MCC and starch matrix in the presence of glycerol due to hydrogen bonding and other secondary interactions, there was no evidence of chemical reaction between the components.

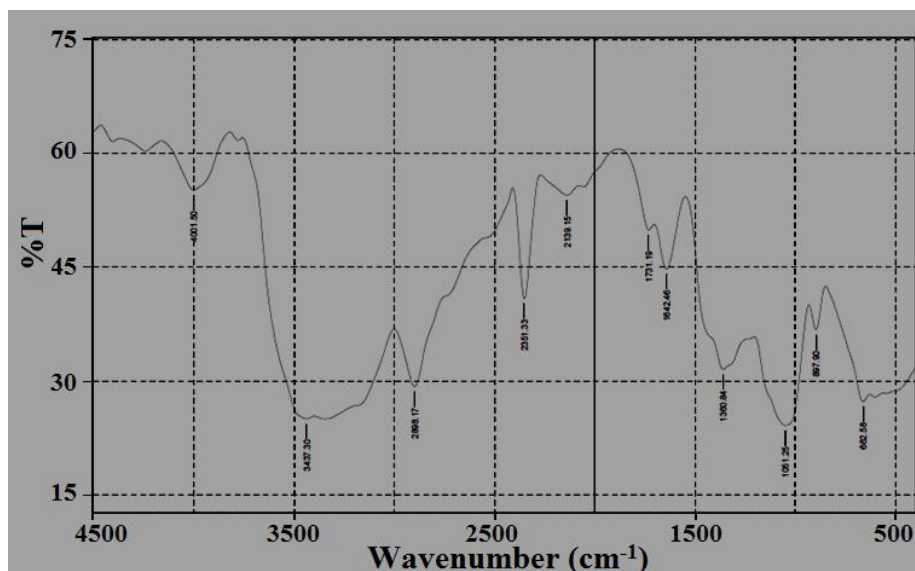


Fig. 4a. FTIR spectra of the microcrystalline cellulose (MCC).

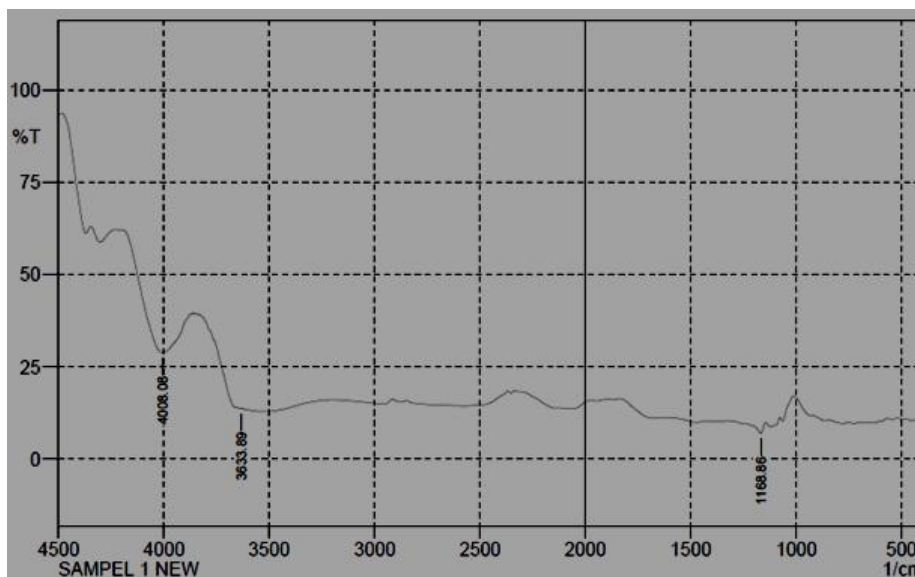


Figure 4b. FTIR spectra of cassava starch edible film with glycerol as a plasticizer without MCC.

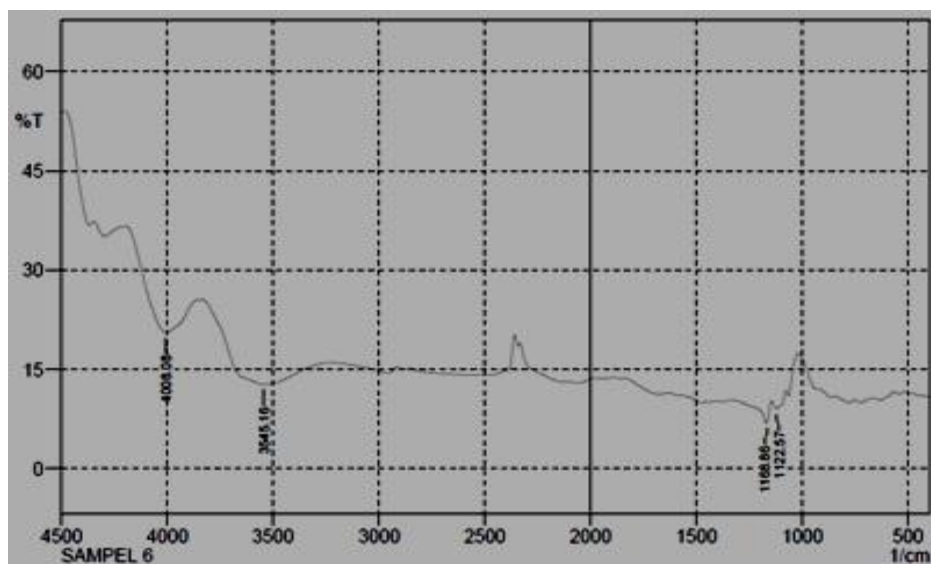


Figure 4c. FTIR spectra of cassava starch edible film using glycerol as a plasticizer containing 0.5 g MCC.

Table 1. Transmittances of FTIR spectra of the MCC, edible films based on cassava starch without and with 0.5 g MCC using glycerol as plasticizer.

Sample	Wave number (cm-1)	Functional groups
Microcrystalline Cellulose	4001.50	Free O-H
	3437.30	Hydrogen bonded O-H
	2898.17	C-H stretching
Edible film without MCC	1051.25	Single bond C – O
	4008.08	Free O-H
	3633.89	O-H stretching
Edible film containing 0.5 g MCC	1168.86	C-O stretching, R-OH primer
	4008.08	Free O-H
	3545.16	O-H stretching
	1168.86	C-O stretching, R-OH primer

Mechanical properties testing

Results of elongation at break (%) as well as tensile strength (kgf/mm²) of the edible films with various ratio of starch/MCC are shown in Fig. 5 and Fig. 6, respectively. It was revealed from Fig. 5 and 6 that the optimum composition of the edible film was a ratio starch/MCC = 10:0.4 in the presence of 1.5 g of glycerol, i.e.: with higher elongation and tensile strength: 114.8% and 0.317 kgf/mm², respectively. It seems that addition of MCC from 0.1 to 0.4 g improved the properties, whereas addition of higher MCC upto 0.5 g

may promote agglomeration of the MCC which inturn interfere compatibility of the films [12].

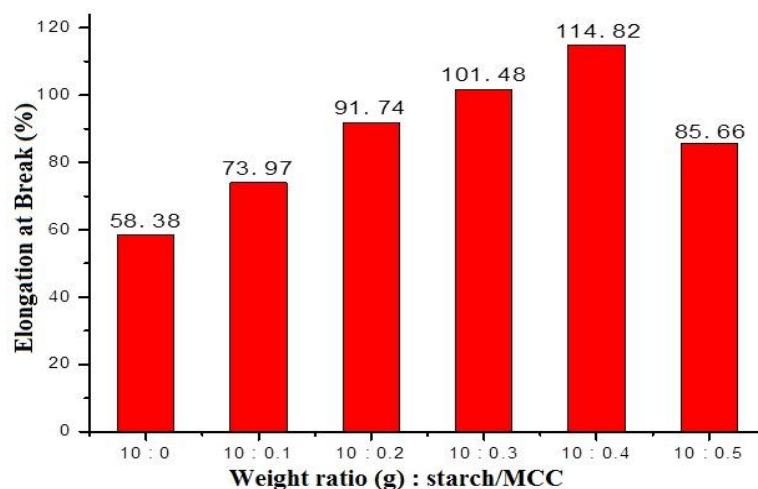


Figure 5. Elongation at break (%) of the edible films with various ratio of starch/MCC (g).

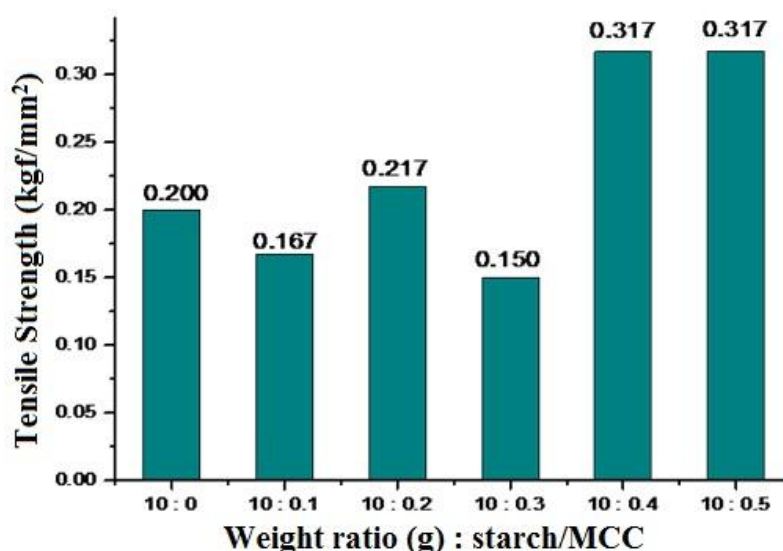


Figure 6. Tensile strength (kgf/mm²) of the edible films with various ratio of starch/MCC (g).

Water content

Fig. 7 showed data of water content (%) against weight ratio of starch/MCC (g), which indicated that addition of MCC upto weight ratio: 10/0.5 (g) decreased water contents from 17.88% to 11.50%. This result was related to the fact that the MCC absorb less water when compared to that of the starch matrix.

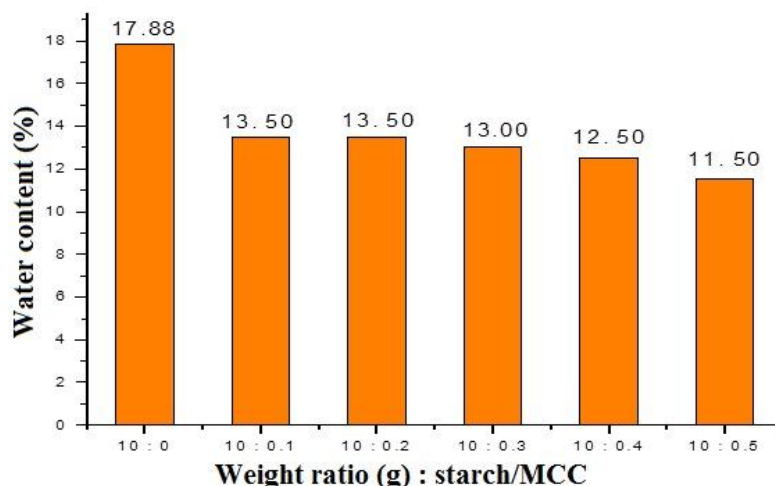


Figure 7. Water content (%) of the edible films with various ratio of starch/MCC (g).

Morphology analysis using SEM

Result of Scanning Electron Micrograph (SEM, magnification 5000 times) of the surface of edible film containing 0.4 g MCC in the presence of glycerol (Fig. 8) indicated that the white MCC particles were covered by the starch matrix. The presence of other white particles may also due to ungelatinised starch. This evidence revealed surface interaction between the MCC particles with starch matrix and glycerol as plasticizer.

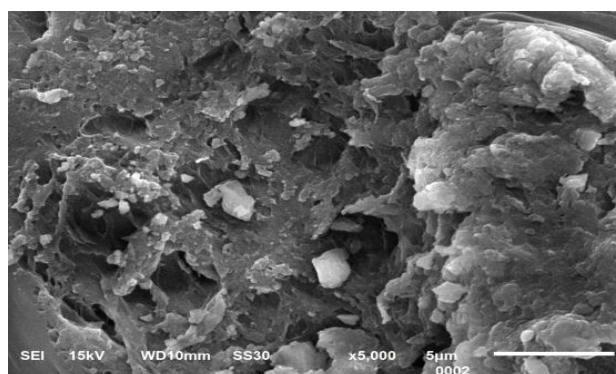


Figure 8. SEM photograph (magnification 5000 times) of edible film based on 10 g cassava starch containing 0.4 g MCC in the presence of 1.5 g glycerol.

Water vapour transmission rate (WVTR)

Results of water vapour transmission rates (WVTR, g/cm².hour) of the edible films measured using the above procedure are shown in Fig. 9. WVTRs for the edible films containing 0-0.5 g MCC did not show any considerable differences (0.008-0.012 g/cm².hour). It seems that this result is related to better compatibility and interaction

between MCC and the starch matrix, Garcia et.al. [13]. Optimum WVTR was also due to hydrophilic interaction between MCC and the starch matrix, Siracusa [14].

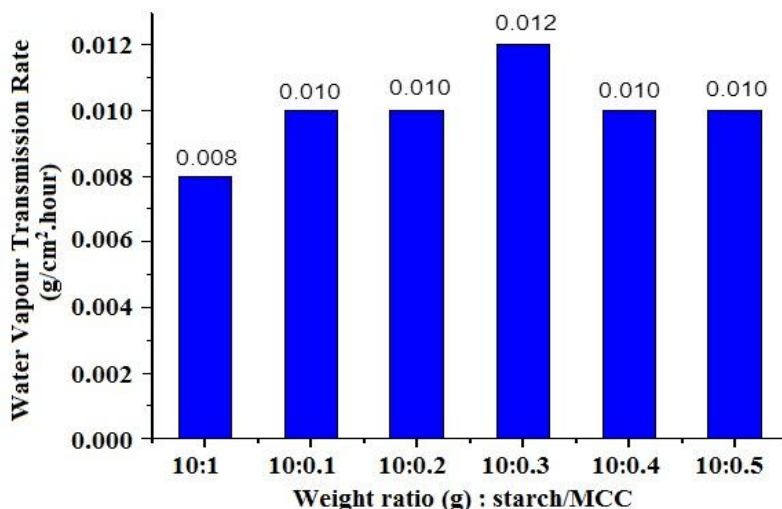


Figure 9. Water vapour transmission rate (WVTR, g/cm².hour) against weight ratio of starch/MCC (g) of the edible films.

Conclusion

Microcrystalline cellulose (MCC) of coconut fruit bunches (CFB) can be used as filler for cassava starch-based edible films in the presence of glycerol as plastisiser. Addition of the MCC weight ratio starch/MCC = 10/0-10/0.5 g improved elongation at break and tensile strength, decreased water content and did not show any considerable differences on their WVTR. These results were due to good physical interaction between the MCC and the starch matrix.

- [1] T. Bourtoom, *Int. Food Res. J.* **2008**, *15*(3), 237.
- [2] F. O. Ohwoavwoorhua. and T. Adedokun, *Trop. J. Pharm. Res.* **2005**, *4*(2), 501.
- [3] J. K. Jackson, K. Letchford, and B. Z. Wasserman, *Int J of Nanomed.* **2011**, *6*, 321.
- [4] G. V. Thomas, S. R. Prabhu, M. Z. Reeny, and B. M. Bopalala, *World J. Microb. Biot.* **1998**, *14*, 879.
- [5] A. A. W. B. O. Abiola, Master's Degree Thesis, Department of Mechanical Engineering. Blekinge Institute of Technology. Sweden, 2008.
- [6] S. Dhanapal, R. Kavitha, Yazhini and Banu, *Food Sci. Qual. Man.* **2012**, *3*, 9.
- [7] T. Jin and H. Zhang, *J. Food Sci.* **2008**, *73*(3), 127.
- [8] I. Juliyarsi, S. Melia, and A. Sukma, *Pak. J. N.* **2011**, *10*(9), 884.
- [9] S. Laxmeshwar and S. Sandep, *International Scholarly Research Network ISRN Polymer Science*, **2012**. Article ID 154314.
- [10] C. Bangyekan, D. Aht-Ong, K. Srikulkit, *Carbohydr. Polym.* **2006**, *63*, 61.
- [11] A. Yakubu, M. U. S. Tanko, S. D. Mohammed. *Adv. Appl. Sci. Res.* **2011**, *2*(6), 532.
- [12] D. R. Lu, X. M. Xiao, S. J. Xu, *Express Polym. Lett.* **2009**, *3*(6), 366.
- [13] M. A. Garcia, M. N. Martino, and N. E. Zaritsky, *J. Food Sci.* **2000**, *65*, 941.
- [14] V. Siracusa, *Int. J. Polym. Sci.* **2012**, *2*, 1.