

Influence of Compounding Methods on Poly(vinyl) Alcohol/Sago Pith Waste Biocomposites: Mechanical and Water Absorption Properties

(Kesan Kaedah Pencampuran ke atas Biokomposit Polivinil Alkohol/Bahan Buangan Empulur Sagu: Sifat-sifat Mekanik dan Penyerapan Air)

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ABSTRACT

Several methods of incorporating sago pith waste (SPW) into poly(vinyl alcohol) (PVA) had been conducted: (i) dry blending (PVA/SPW/G), (ii) blending of SPW and pre-plasticized PVA (pPVA/SPW/G) and (iii) blending of pre-plasticized of both PVA and SPW (pPVA/pSPW). The effect of the compounding method on the mechanical and water absorption properties were investigated. The addition of SPW into PVA greatly reduced the tensile strength and elongation at break. The tensile strength and elongation at break of PVA/SPW composites with identical geometry during compounding stage (powder/powder and pellet/pellet), which were PVA/SPW/G and pPVA/pSPW yielded the highest value. The percentage of water absorbed by PVA/SPW/G (without pre-plasticization) was the highest, followed by pPVA/pSPW and pPVA/SPW/G.

Keywords: Mechanical properties; polyvinyl alcohol; sago pith waste; water absorption

ABSTRAK

Beberapa cara untuk mengadunkan bahan buangan empulur sagu (SPW) ke polivinil alkohol (PVA) telah dilakukan: i) pengadunan secara kering (PVA/SPW/G), ii) pengadunan SPW dan pra-pemplastikan PVA (pPVA/SPW/G) dan iii) pengadunan pra-pemplastikan SPW dan pra-pemplastikan PVA (pSPW/pPVA). Kesan kaedah pengadunan ke atas sifat-sifat mekanik dan penyerapan air telah dikaji. Penambahan SPW ke dalam PVA banyak mengurangkan tegasan tegangan dan terikan pada patah. Tegasan tegangan dan terikan pada patah bagi komposit PVA/SPW dengan geometri yang serupa (tepung/tepung dan resin/resin) semasa peringkat pengadunan, iaitu PVA/SPW/G dan pPVA/pSPW menghasilkan nilai tertinggi. Peratus air diserap oleh PVA/SPW/G (tanpa pra-pemplastikan) adalah tertinggi, ini diikuti oleh pPVA/pSPW dan pPVA/SPW/G.

Kata kunci: Alkohol polivinil; bahan buangan empulur sagu; penyerapan air; sifat mekanik

INTRODUCTION

Recent development of several blends and composites based on PVA and lignocellulosic components derived from agro-industrial waste such as sugar cane, citrus fruits, corn, wheat and wood processing (Chiellini et al. 2004) highlights the potential of utilizing agro-residues in order to achieve sustainable management of agricultural waste. Sago pith waste is an agro-industrial byproduct from sago palms during sago starch extraction. It is a cheap, starchy and fibrous material and represents renewable, abundant and low cost biodegradable filler. Currently, large amounts of the sago waste are allowed to decay naturally in the fields or burnt (Vikineswary et al. 2006).

Starch is a renewable and biologically fully degradable polymer. It is a macromolecular complex of at least two polymeric components, namely linear amylose and branched amylopectin (Tharanathan 2005). By itself, starch is not a thermoplastic material, but at moderately high temperatures (90°C – 180°C), under pressure and under shear, starch granules melt and flow to give an amorphous material called thermoplastic starch (TPS) which can be processed just like a thermoplastic synthetic

polymer by injection molding, extrusion blow molding and thermoforming (Carvalho et al. 2003).

PVA has been used previously in extruded thermoplastic starch to improve properties such as elongation (Mao et al. 2000) and processability (predominantly through improving melt strength) (Fishman et al. 2006; Mao et al. 2000). In a number of studies, polymer blends were prepared on the basis of poly(vinyl) alcohol (PVA) containing different kinds of natural starch such as corn, potato and sago starch (Khan et al. 2006; Wang et al. 2008; Yun et al. 2006), fibres coconut shell powders, corn fibre and cellulose whisker (Cinelli et al. 2006; Ramaraj & Poomalai 2006; Roohani et al. 2008).

Julinova et al. (2008) studied the influence of technological procedure on mechanical properties and biodegradability when incorporating WAXY starch into PVA. However, the author did not study the method by incorporating starch into pre-plasticized PVA. In this study, several methods of incorporating sago pith waste into PVA had been conducted. The effects of the compounding methods on the mechanical and water absorption properties were investigated.

MATERIALS AND METHODS

MATERIALS

Sago pith waste (SPW) was supplied by Ng Kia Heng Sago Industries Sdn. Bhd. Glycerol with 99.0% purity and a molecular weight of 92.19 purchased from Fisons Scientific Equipment was used as plasticizer. Poly(vinyl alcohol) (PVA) in powder form (fully hydrolyzed, degree of hydrolysis of 99.4-99.8 mole %, 0.7 wt% ash, viscosity 25-30 cps) was supplied by Chang Chun Perochemical Co. Ltd. Calcium stearate (2 phr) used as stabilizer and release agent was purchased from Sun Ace Kakoh (M) Sdn. Bhd.

SAMPLE PREPARATION

The PVA, SPW, glycerol and calcium stearate were mixed according to the composition given in Table 1. The mixing and compounding procedures were studied over three methods. After the compounding stage, the compounded pellets were compression molded using a motor hydraulic press (Motor Hydraulic Lab Press-Guthrie Malaysia) at 120°C for plasticized SPW (pSPW) and 190°C for PVA/SPW blend and plasticized PVA (pPVA). After that, they were cut into standard shapes for further testing. The samples were first applied a contact pressure for 10 min. Then full pressure was applied for another 10 min. A temperature of 120°C was applied to pure SPW because such temperature is already sufficient to melt the pure SPW since it does not contain any PVA. Lower processing temperature leads to lower operating cost and minimizes the possibilities of degradation of SPW. The methods studied were as follows.

TABLE 1. Composition of biocomposites prepared by melt extrusion

Sample	PVA (wt%)	SPW (wt%)	Glycerol (wt%)
pPVA	74	-	26
pSPW	-	65	35
PVA/SPW/G	35	30	35
pPVA/SPW/G	35	30	35
pPVA/pSPW	35	30	35

Method A: PVA/SPW/G Biocomposites from dryblend (powder-powder system) Ground SPW, PVA powder, glycerol and calcium stearate were mechanically mixed in the desired concentration in a laboratory high speed mixer prior to compounding. In the second step, a co-rotating twin screw extruder was used to produce the PVA/SPW/G pellets. The temperature profile from feeding to die was 160/160/160/160°C.

Method B: pPVA/SPW/G Biocomposites with pre-extrusion of PVA (pellet-powder system) The extrudable pPVA/SPW/G composition was obtained by mixing the pre-

plasticized PVA granules (pPVA) with the unplasticized sago pith waste, together with a fixed amount of glycerol, extruding the mixture into pellets of pPVA/SPW/G for subsequent thermoprocessing.

Method C: pPVA/pSPW Biocomposites with pre-extrusion of both PVA and SPW (pellet-pellet system) Both PVA and SPW powder were plasticized individually using the same twin screw extruder. The extrusion condition for SPW was 90/100/110/120°C. Pelletized blends pPVA and pSPW were mechanically mixed and re-extruded to form pellets of pPVA/pSPW.

Tensile Testing Dumbbell specimens (Type V) were cut out from the molded sheet according to ASTM D 638 (2003) and tensile tests were carried out using Tensile Tester EZ 20 kN Lloyd Instrument with a strain rate of 10 mm/min.

Water Absorption Water absorption measurement was carried out according to ASTM D 570 (1998) at ambient temperature 23°C at various time intervals up to seven hours (420 minutes). The samples (76.2 × 25.4 × 3.2 mm³) were dried in an oven for 24 h at 50°C, cooled in a desiccator and immediately weighted to the nearest 0.001g. The conditioned specimens were placed in a container of distilled water maintained at 23°C. They were removed at specified intervals and gently blotted with tissue paper to remove the excess water on the surface, and then the weight was recorded. The water absorption value was taken as the sum of the increase in weight on immersion and of the weight of the water-soluble matter according to the following equations:

$$\text{Weight increase, } W(\%) = \frac{(M_2 - M_1)}{M_1} \times 100 \quad (1)$$

$$\text{Soluble matter lost, } L(\%) = \frac{(M_2 - M_3)}{M_1} \times 100 \quad (2)$$

$$\text{Water absorption, } WA(\%) = W + L \quad (3)$$

where M_2 is the weight of the sample after immersion (g), M_1 is the conditioned weight (g) and M_3 is the reconditioned weight (g).

RESULTS AND DISCUSSION

MECHANICAL PROPERTIES

Figure 1 illustrates the stress-strain curves of a specimen of each sample for the native sago pith waste/polyvinyl alcohol (PVA/SPW) composite series. Soft and tough behaviour was observed with the pure plasticized PVA (pPVA) while extremely brittle behavior was observed with the neat plasticized SPW (pSPW). As the PVA was incorporated in the neat SPW, the PVA/SPW materials displayed more ductility. The improvement in the mechanical behavior of a polymer from stiff/brittle to soft/flexible is due to the

increased in molecular mobility. With PVA/SPW blends, the macromolecules developed specific interactions between SPW and PVA which causes ductility in the blend system.

Variation trends measuring tensile strength and elongation at break as a function of different compounding methods are shown in Figures 2 and 3. Overall physical properties in the pure thermoplastic SPW samples were enhanced by the addition of 35 wt% of PVA. For instance, the added PVA increased tensile strength to 4.85 MPa from 1.19 MPa in sample PVA/SPW/G using method A (Figure 2), and increased elongation at break to 84.83% from 19.08% (Figure 3).

Among the three methods, the sample prepared by method B (pPVA/SPW/G) yielded the lowest values of tensile strength and elongation at break. Although different methods were used to the formulations prior to

extrusion, both the PVA/SPW/G and pPVA/pSPW showed a similar tensile strength and elongation at break properties compared to pPVA/SPW/G. In this case, the SPW was believed to be more compatible when blending using method A and C because of the geometrical similarity (powder/powder or pellet/pellet). A slight improvement in the tensile behaviour of PVA/SPW/G and pPVA/pSPW as compared to pPVA/SPW/G may be attributed to the higher formation of hydrogen bonds or chemical interaction between the -OH group of PVA and the -OH group of starch in the PVA/SPW/G and pPVA/pSPW, which will resist and prevent the slippage of molecular chains over the other during stretching in the tensile test (Mishra et al. 2008).

In principle, the extrusion process comprises the forcing of a plastic or molten material through a shaped die

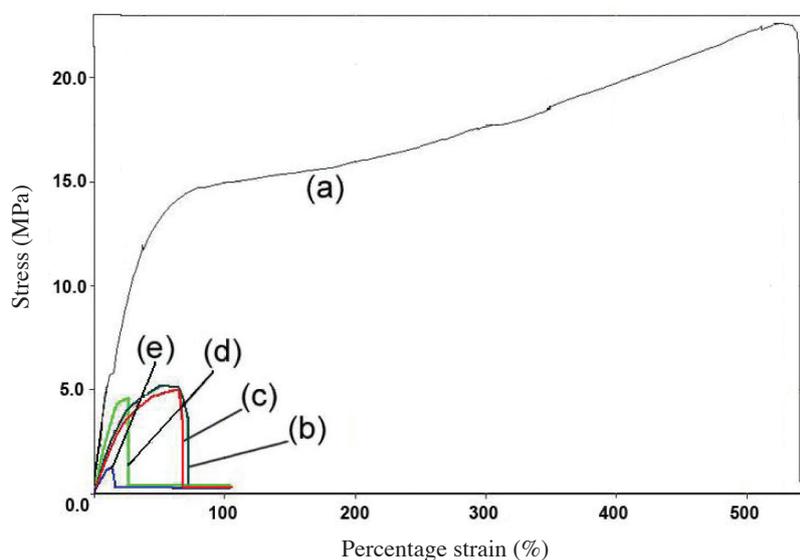


FIGURE 1. Stress-strain curves: (a) pPVA (reference), (b) pPVA/pSPW (method C), (c) PVA/SPW/G (method A), (d) pPVA/SPW/G (method B) and (e) pSPW (reference)

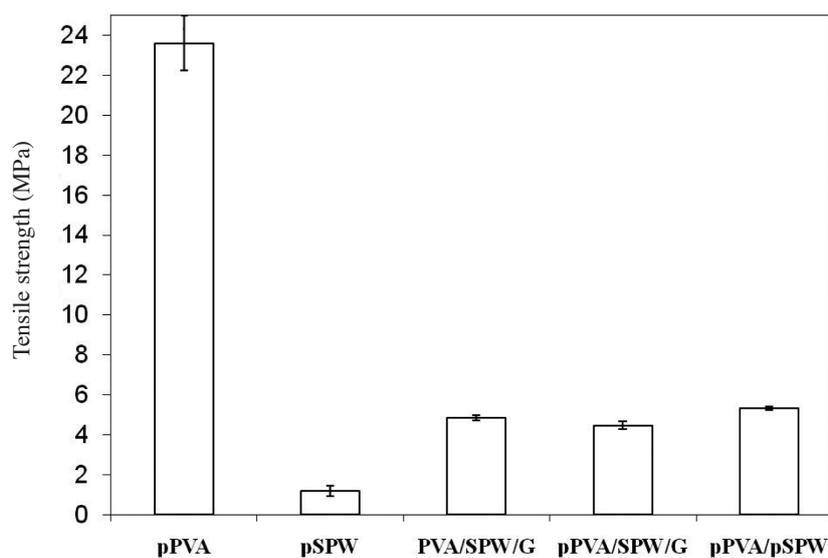


FIGURE 2. Tensile strength of pPVA, pSPW and their composites

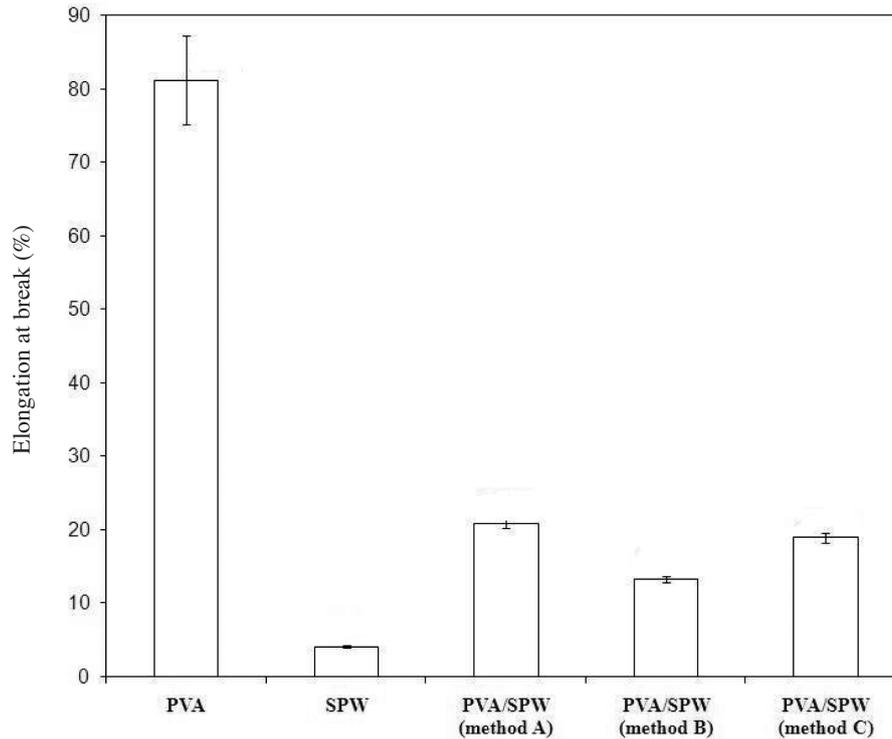


FIGURE 3. Elongation at break of pPVA, pSPW and their composites

by means of pressure. Destructurization, homogenization and plastification of native starch was performed in one step by extrusion on a twin screw extruder. The lower elongation at break and tensile strength obtained with the method B with respect to the incorporation of a powdery material into a preplasticized system could be explained by the conformation of macromolecules. In this method, the materials with identical geometry can favor self-associations between PVA macromolecules and SPW macromolecules (random coil chain) instead of the desired SPW/PVA interactions. Thus, this material has a loosely-packed structure.

It appears that during the tensile test under applied stress, the macro-molecular chains may undergo three steps which are uncoiling, stretching and slippage. The macromolecules reduced the continuity of the composite thereby decreasing the flow of the continuous phase PVA during the stress transfer. On the contrary, the extrusion using technique A and C (PVA/SPW/G and pPVA/pSPW) can force the PVA macromolecules to be stretched out in a linear conformation, thus interacting with SPW chains (H bonds). Highly-packed structure could be obtained with the desired PVA/SPW interactions.

WATER ABSORPTION

Figure 4 illustrates the percentage of water absorbed from a compression sheet of the formulations. In order to compare the water absorption properties with reference systems, pure plasticized PVA and SPW were prepared using the same procedures as for PVA/SPW blends and their water uptake were analyzed. As can be seen from

the figure, the percentage of water absorbed of SPW was the highest because starch is a hygroscopic material. Soaking the specimens caused a catastrophic change in the appearance of the SPW specimens where the SPW bars were almost dissolved in the water at 75 min of immersion period. The water uptake of pPVA showed a linear behaviour. PVA is a water-soluble synthetic polymer but high degree of hydrolysis increases the crystallinity and the crystallization tendency (Orefield et al. 1994), making fully hydrolyzed grades of PVA (98.0-99.0 mol%) less soluble in water. Thus, pure plasticized PVA in this case behaved as the most water resistant material. The pPVA, PVA/SPW/G, pPVA/SPW/G and pPVA/pSPW specimens appeared slightly swollen but still intact at the end of immersion period. The PVA/SPW composites reached equilibrium after 300 min immersion period. Noticeable decrease in water uptake was observed with the addition of PVA in the SPW. This can be explained by the consumption of water binding sites (Follain et al. 2005), which had been occupied by glycerol and PVA. The formation of hydrogen bonds between the two polymers reduced the capacity to absorb water.

Among those methods, the method A (PVA/SPW/G) yielded the poorest water resistance. The initial percentage of water absorbed for method B and C (pPVA/SPW/G and pPVA/pSPW) was almost the same up to 180 min, afterwards the PpSp showed higher tendency of water uptake than the pPVA/SPW/G. The hydroxyl groups of the SPW and PVA, being the hydrophilic one, could interact directly with the water molecules making a very compatible system.

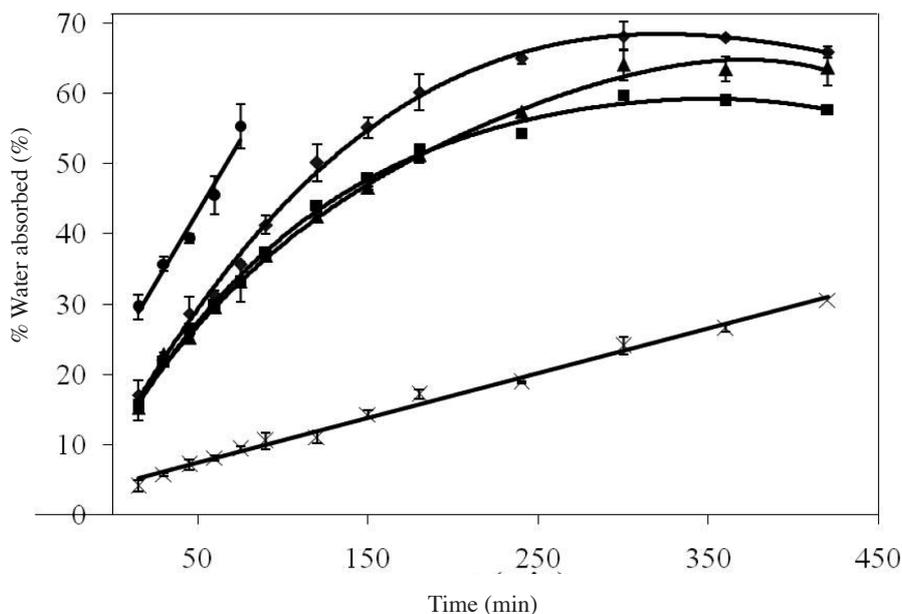


FIGURE 4. Percentage of water absorbed at various interval times. •: pSPW (reference), ◆: PVA/SPW/G (method A), ▲: pPVA/pSPW (method C), ■: pPVA/SPW/G (method B), x: pPVA (reference)

When the materials were immersed in water, there was a leaching of glycerol, leaving more freely available hydroxyl groups to interact with water molecule (Zhang & Sun 2004). It was expected that the glycerol was less tightly bound in PVA/SPW/G composite (without preplasticized) compared to pPVA/SPW/G and pPVA/pSPW composites. With pre-plasticization, the heat treatment results in the elimination of bound water, which in turn enhanced the alignment order of the polymer chains (Gohil et al. 2006). A decrease in the hydroxyl groups results in a loss in the polar nature of the compound and as a result the solubility of the polymer in water decrease. This explains the higher water uptake of PVA/SPW/G compared to the preplasticized systems (pPVA/SPW/G and pPVA/pSPW). It is believed that the pPVA/pSPW composite was not well covered by the continuous PVA matrix, thus increased the hydroxyl groups and exposed more water binding sites than that of pPVA/SPW/G.

CONCLUSION

From the viewpoint of tensile properties, the tensile strength and elongation at break of PVA/SPW composite with identical geometry during compounding stage (powder/powder and pellet/pellet), which are PVA/SPW/G and pPVA/pSPW yielded the highest value. The difference in the tensile properties between these two composites is negligible. The percentage of water absorbed of the PVA/SPW/G (without pre-plasticization) was highest, followed by pPVA/pSPW and pPVA/SPW/G. This is because the glycerol was loosely bound in the system causing more freely available hydroxyl sites to interact with water molecule when PVA/SPW/G was immersed in water.

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REFERENCES

- Carvalho, A.J.F., Zambon, M.D., Curvelo, A.A.S. & Gandini, A. 2003. Size exclusion chromatography characterization of thermoplastic starch composites. Part 1. Influence of Plasticizer and Fibre Content. *Polymer Degradation and Stability* 79: 133-138.
- Chiellini, E., Cinelli, P., Chiellini, F. & Imam, S.H. 2004. Environmentally degradable bio-based polymeric blends and composites. *Macromolecular Bioscience* 4: 218-231.
- Cinelli, P., Chiellini, E., Lawton, J.W. & Imam, S.H. 2006. Properties of injection molded composites containing corn fibre and poly(vinyl alcohol). *Journal of Polymer Research* 13: 107-113.
- Fishman, M.L., Coffin, D.R., Onwulata, C.I. & Willet, J.L. 2006. Two stage extrusion of plasticized pectin/poly(vinyl alcohol) blends. *Carbohydrate Polymers* 65: 421-429.
- Follain, N., Joly, C., Dole, P. & Bliard, C. 2005. Properties of starch based blends. Part 2. Influence of poly vinyl alcohol addition and photocrosslinking on starch based materials mechanical properties. *Carbohydrate Polymers* 60: 185-192.
- Gohil, J. M. Bhattacharya, A. & Ray, P. 2006. Studies on the cross-linking of poly(vinyl alcohol). *Journal of Polymer Research* 13: 161-169.
- Julinova, M., Dvorackova, M., Kupec, J., Hubackova, J., Kopicilova, M., Hoffmann, J., Alexy, P., Nahalkova, A. & Vaskova, I. 2008. Influence of technological process on biodegradation of PVA/WAXY starch blends in an aerobic and anaerobic environment. *Journal of Polymers and the Environment* 16(4): 241-249.

- Khan, M.A., Bhattacharia, S.K., Kader, M.A. & Bahari, K. 2006. Preparation and characterization of ultra violet (UV) radiation cured biodegradable films of sago starch/PVA blend. *Carbohydrate Polymers* 63: 500-506.
- Mao, L., Imam, S., Gordon, S., Cinelli, P. & Chiellini, E. 2000. Extruded cornstarch-glycerol-polyvinyl alcohol blends: Mechanical properties, morphology and biodegradability. *Journal of Polymers and the Environment* 8(4): 205-211.
- Mishra, S., Bajpai, R., Katare, R. & Bajpai, A.K. 2008. On the mechanical strength of biocompatible semi-IPNs of PVA and polyacrylamide. *Microsystem Technologies* 14(2): 193-198.
- Orefield, A.F., Allentown, J.F.N. & Macungie, FLM. 1994. *U.S. Patent No. 5, 362, 778*. Washington DC: U.S. Patent and Trademark Office.
- Ramaraj. B. & Poomalai, P. 2006. Ecofriendly poly(vinyl alcohol) and coconut shell powder composite films: Physico-mechanical, thermal properties and swelling studies. *Journal of Applied Polymer Science* 102: 3862-3867.
- Roohani, M., Habibi, Y., Belgacem, N.M., Ebrahim, G., Karimi, A.N. & Dufresne, A. 2008. Cellulose whiskers reinforced polyvinyl alcohol copolymers nanocomposites. *European Polymer Journal* 44: 2489-2498.
- Tharanathan, R.N. 2005. Starch - value addition by modification. *Critical Reviews in Food Science and Nutrition* 45: 371-384.
- Vikineswary, S., Abdullah, N., Renuvathani, M., Sekaran, M., Pandey, A. & Jones, E.B.G. 2006. Productivity of laccase in solid substrate fermentation of selected agro-residues by *pycnoporus sanguineus*. *Bioresources Technology* 97: 171-177.
- Wang, J., Lu, Y., Yuan, H. & Dou, P. 2008. Crystallization, orientation morphology and mechanical properties of biaxially oriented starch/polyvinyl alcohol films. *Journal of Applied Polymer Science* 110: 523-530.
- Yun, Y.H., Na, Y.H. & Yoon, S.D. 2006. Mechanical properties with the functional group of additives for starch/PVA blend film. *Journal of Polymers and the Environment* 14(1): 71-78.
- Zhang, J.F. & Sun, X. 2004. Physical characterization of coupled poly(lactic acid)/starch/maleic anhydride blends plasticized by acetyl triethyl citrate. *Macromolecular Bioscience* 4(11): 1053-1060.

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