

Table 3: Characteristic thermal decomposition data of PVA and composite films

Sample	First degradation stage				Second degradation stage			
	T _o	T _{max}	T _{end}	MWLR	T _o	T _{max}	T _{end}	MWLR
	(°C)	(°C)	(°C)	(%min ⁻¹)	(°C)	(°C)	(°C)	(%min ⁻¹)
PVA	268.8	325.6	368.8	7.24	388.9	427.6	448.9	7.24
SA-0	262.1	319.8	362.9	8.41	396.9	413.8	436.8	8.07
SA-2	282.1	323.7	362.8	7.80	392.9	415.9	442.9	10.45
SA-4	290.0	331.5	370.9	5.45	390.0	415.9	450.9	13.21
SA-6	288.1	325.6	368.8	6.78	398.9	411.8	438.9	9.90

where T_o, T_{max} and T_{end} stands for onset, maximum degradation and endset temperature respectively.

The weight loss in all the samples, up to about 150 °C results from the evaporation of absorbed water. Degradation of PVA occurs in two steps [37]. For pure PVA and SA-0, weight loss during first degradation stage can be due to the formation of polyethylene resulting from the dehydration and depolymerization of PVA. During the second step after 385 °C the residue resulting from the first stage undergoes the process of intramolecular cyclization and producing some organic volatiles [38]. After 500 °C weight loss percentage was constant (Figure 4a) due to the carbonaceous mass formed during the degradation of polymer which creates layer on the polymer surface and hence prevents its further decomposition [39]. The SA reinforced PVA composites exhibited two stage decomposition like PVA and SA-0. The onset temperature for PVA-SA composites was found to increase with incorporation of fiber in the matrix. A shift of around 20 °C was realized in the first degradation stage of SA-4 with the highest value of onset degradation temperature (T_o) around 290 °C in comparison to PVA. The maximum degradation temperature (T_{max}) and maximum weight loss rate (MWLR) for PVA/composites showed a slight variation during the first degradation stage (Figure 4b). However, these values were found to be significant in the second degradation stage (Table 3).

All the observations apparently showing that the mechanism of thermal decomposition differs for PVA, SA-0 and its composites. The improvement in thermal stability of SA-0 with the addition of fiber is indicated by a shift in its onset degradation temperature to the higher side. The increase in thermal stability can be explained in terms of interaction of fiber with the hydroxyl group of PVA forming a complex as confirmed from the IR spectra of PVA/SA composite films. Moreover, boric acid played an important role as a cross linking agent between PVA and fiber, resulting in the high thermal stability of PVA/SA composite films [31]. Among the composite films, SA-4 showed the highest thermal stability;

followed by SA-6 and SA-2. The reason for observing a decrease in thermal stability from SA-4 to SA-6 can be explained in such a way that at high fiber loading the homogeneous dispersion of fiber could not take place and resulting adhesion between fiber and matrix reduced and hence decreased the thermal stability. The above statement can be generalized by saying that with increase in the fiber loading thermal stability increases up to 10% and the order is SA-4 > SA-6 > SA-2.

Kinetic Study

Kinetic parameters comprising of degradation temperature range and activation energy (E_a) for both the stages were calculated and are summarized in Table 4. It can be inferred that in case of most thermally stable composite SA-4, the activation energy value was less during first degradation stage and high during second degradation stage in comparison to SA-0. This shows that although the degradation of SA-4 occurs at high temperature but once it starts, it degrades much faster in comparison to SA-0 during first degradation stage.

Table 4: Kinetic parameters in the thermal decomposition of PVA and composite films

Sample index	Degradation temperature range (°C)	Activation Energy (kJ/mol) and Regression Coefficient			
		Coats-Redfern	R ²	Horowitz-Metzger	R ²
PVA	268-368	53.94	0.984	62.79	0.986
	388-448	41.78	0.987	37.10	0.995
SA-0	262-362	67.48	0.979	76.80	0.976
	396-436	54.12	0.980	45.51	0.985
SA-2	282-362	63.46	0.983	66.60	0.967
	392-442	57.20	0.968	49.23	0.976
SA-4	290-370	60.65	0.995	66.99	0.986
	390-450	77.92	0.975	73.08	0.986
SA-6	288-368	58.52	0.981	64.37	0.977
	398-438	58.87	0.973	49.74	0.978

Optical Property

The light absorbance of composite films at wavelengths from 200 and 800 nm were recorded [40] and shown in Figure 5. Virgin PVA and composite films showed the absorbance in the range of 200-300 nm with maximum at 248 for pure PVA and 252 for SA-0. On increasing the fiber loading the absorption region shifted towards the higher wavelengths. At the same wavelength, SA-5 showed the highest absorbance with

maximum obtained at 272 nm. An increase in absorbance/intensity of absorption with addition of fiber is an evidence of occurring electronic interactions in composite films [41]. The enhancement in intensity of composite films showed the localization of SA fiber between PVA chains [13]. However, no significant changes were observed in the absorption spectrum of SA-6 showing that with further loading of fiber homogeneous dispersion could not take place and hence not any observable change in its absorbance value.

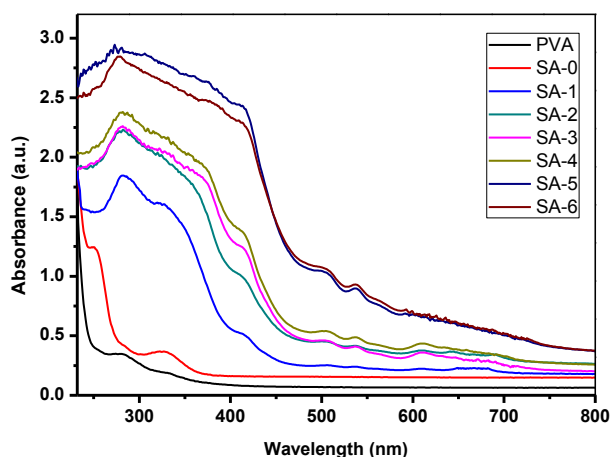


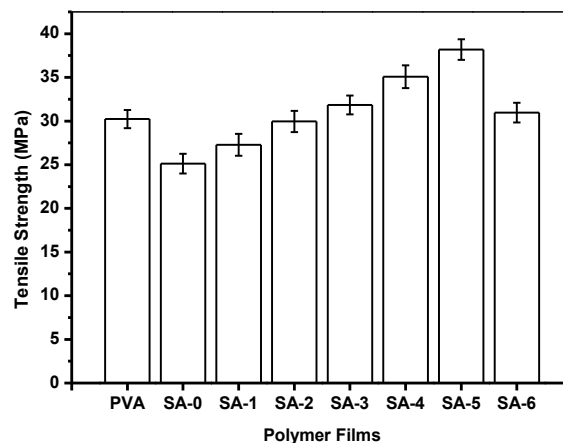
Figure 5: Absorbance spectra of composite films as a function of wavelength (nm)

Mechanical Properties

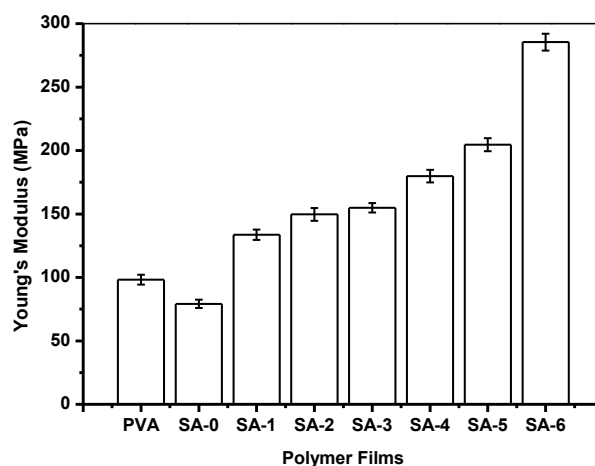
Table 5: Mechanical Properties of Polymer Composite Films

Sample Index	Percentage Elongation	Ultimate Tensile Strength (MPa)	Young's Modulus (MPa)
PVA	161.6± 2.0	30.2 ± 1.0	98.2± 3.8
SA-0	168.0± 2.3	25.1 ± 1.1	79.2± 3.2
SA-1	164.6± 2.6	27.2± 1.2	133.6± 4.1
SA-2	162.3± 2.6	29.9± 1.2	149.6± 4.9
SA-3	148.3± 2.3	31.8± 1.0	154.8± 3.6
SA-4	111.6± 1.8	35.0± 1.2	179.8± 4.9
SA-5	82.0± 2.0	38.1± 1.1	204.6± 5.1
SA-6	72.6± 2.6	30.9± 1.1	285.4± 6.6

The Elongation (%), Ultimate Tensile Strength (UTS) and Young's Modulus calculated from the stress-strain (%) relationship diagrams are reported in Table 5. Tensile strength of polymer composite films was found to improve in comparison to virgin. An addition of SA fiber increased the tensile strength of the films up to 12.5% loading (Figure 6a).



(a)



(b)

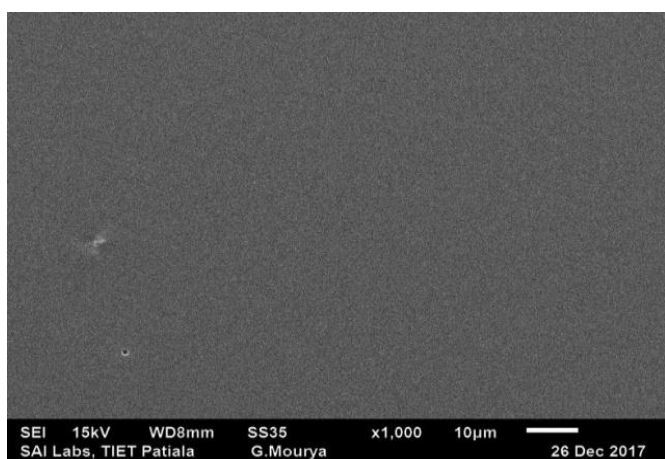
Figure 6: (a) Tensile strength (MPa) and (b) Young's modulus (MPa) of polymer composite films

This implies that PVA-SA composites can withstand much greater stress without undergoing any irreversible deformation. The reason for obtaining high tensile strength can be due to the hydrophilic nature of PVA which results in a strong interface bonding between hydroxyl groups of fiber with PVA [42]. A further addition of fiber (SA-6) led to the significant decrease in UTS. The decrease in tensile strength was due to the super-saturation of particles in the composite films, due to which the enhancement of particle-particle interfacial interaction takes place rather than particle-PVA interaction [43]. It can also be said that with increase in further loading of fiber the nature of adhesion resulted between fiber and matrix was poor which led to an increase in number of void formation in composite film. Due to which enhancement in the formation of micro cracks at the interface of composite film took place and reducing the tensile strength [44]. The decrease in elongation was also observed continuously with an increase in the loading. Young's modulus of the natural fiber reinforced polymer composites generally increases with increasing the fiber amount [6, 45]. In

the present study also, Young's modulus was found to increase continuously up to fiber loading of 15% (Figure 6b) and is an indication of difficulty obtained during stretching the films in an elastic way. It can be inferred that 12.5% loading of SA fiber reinforced in PVA matrix gives the optimum results of tensile strength.

Scanning Electron Microscopy (SEM) Analyses

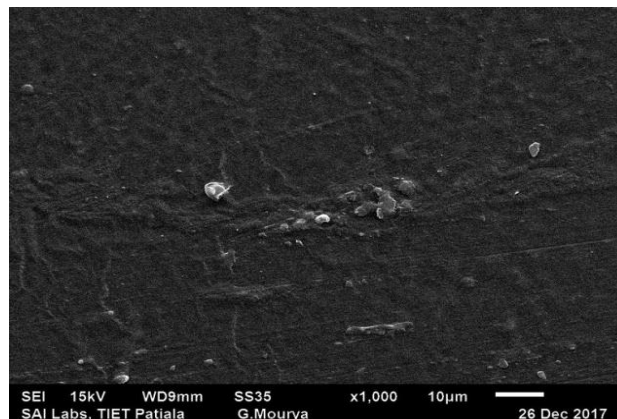
The SEM photographs of the cross-sections of PVA, SA-0, SA-3 and SA-5 are shown in Figure 7. It was observed that surface of pure PVA film was smooth [46] (Figure 7a). An obvious aggregation of PEG was observed in SEM photograph of SA-0 (Figure 7b). On the introduction of fiber, contraction in the surface of the produced film (SA-5) was observed as shown in Figure 7c. Surface roughness was increased with high fiber content. It was also observed that fiber dispersed more homogeneously with its loading up to 12.5% in PVA matrix. On further addition of fiber (SA-6), roughness level and cracking of surface was enhanced, showing that the homogeneous dispersion of fiber can't take place further with high loading (Figure 7d).



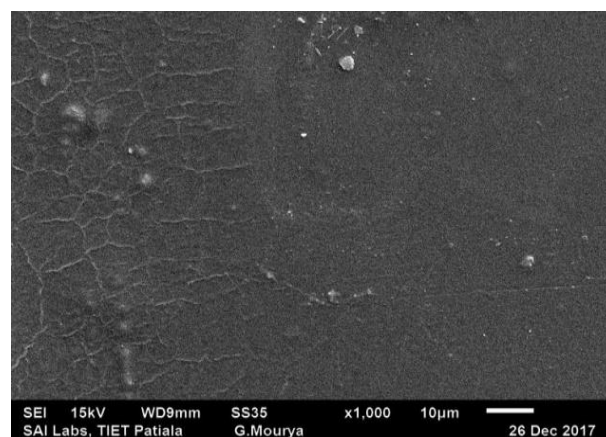
(a)



(b)



(c)



(d)

Figure 7: SEM photographs of (a) PVA and (b) SA-0 and (c) SA-5 and (d) SA- 6

CONCLUSIONS

In this work, PVA has been blended with PEG-6000 (plasticizer), boric acid (cross-linking agent) and *Sterculia alata* leaf fiber to form the polymer composite films and were characterized by different techniques. FTIR studies confirmed the presence of interactions involved in PVA matrix with SA fiber. Polymer films exhibited decrease in water uptake percentage with fiber loading. Soil burial test confirmed fairly good biodegradability of PVA/SA composites in comparison of PVA and SA-0. Addition of fiber enhanced the thermal stability. Tensile strength with 12.5 % loading was found to be maximum. Light absorbance of the composite films against UV light was also found to be improved.

ACKNOWLEDGEMENT

Financial support from the University Grant Commission (UGC), New Delhi as Junior Research Fellowship, award letter no. 21/06/2015 (i) EU-V to Kapil Gulati is gratefully acknowledged. Acknowledgement is also due to Chairman, Chemistry department, Kurukshetra University, Kurukshetra for providing necessary laboratory facilities.

REFERENCES

- [1] Winandy J, Williams R, Rudie A and Ross R. Opportunities for using wood and biofibers for energy, chemical feedstocks, and structural applications. *Properties and Performance of Natural-Fibre Composites*. Elsevier, 2008, p. 330-55.
- [2] Yang H-S, Kim H-J, Park H-J, Lee B-J and Hwang T-S. Effect of compatibilizing agents on rice-husk flour reinforced polypropylene composites. *Composite Structures*. 2007; 77: 45-55.
- [3] Väisänen T, Das O and Tomppo L. A review on new bio-based constituents for natural fiber-polymer composites. *Journal of Cleaner Production*. 2017; 149: 582-96.
- [4] Puglia D, Biagiotti J and Kenny J. A review on natural fibre-based composites—Part II: Application of natural reinforcements in composite materials for automotive industry. *Journal of Natural Fibers*. 2005; 1: 23-65.
- [5] Mishra S, Misra M, Tripathy S, Nayak S and Mohanty A. Potentiality of pineapple leaf fibre as reinforcement in PALF-polyester composite: Surface modification and mechanical performance. *Journal of Reinforced Plastics and Composites*. 2001; 20: 321-34.
- [6] Ku H, Wang H, Pattarachaiyakoop N and Trada M. A review on the tensile properties of natural fiber reinforced polymer composites. *Composites Part B: Engineering*. 2011; 42: 856-73.
- [7] Khan T, Hameed Sultan MTB and Ariffin AH. The challenges of natural fiber in manufacturing, material selection, and technology application: A review. *Journal of Reinforced Plastics and Composites*. 2018; 37: 770-9.
- [8] Jayaramudu J, Guduri B and Rajulu AV. Characterization of natural fabric *Sterculia urens*. *International Journal of Polymer Analysis and Characterization*. 2009; 14: 115-25.
- [9] Mohanty A, Tripathy P, Misra M, Parija S and Sahoo S. Chemical modification of pineapple leaf fiber: graft copolymerization of acrylonitrile onto defatted pineapple leaf fibers. *Journal of Applied Polymer Science*. 2000; 77: 3035-43.
- [10] Kengkhetkit N and Amornsakchai T. Utilisation of pineapple leaf waste for plastic reinforcement: 1. A novel extraction method for short pineapple leaf fiber. *Industrial Crops and Products*. 2012; 40: 55-61.
- [11] Paradossi G, Cavalieri F, Chiessi E, Spagnoli C and Cowman MK. Poly (vinyl alcohol) as versatile biomaterial for potential biomedical applications. *Journal of Materials Science: Materials in Medicine*. 2003; 14: 687-91.
- [12] Mallakpour S and Jarang N. Mechanical, thermal and optical properties of nanocomposite films prepared by solution mixing of poly (vinyl alcohol) with titania nanoparticles modified with citric acid and vitamin C. *Journal of Plastic Film & Sheeting*. 2016 ;32: 293-316.
- [13] Mohammad Mahdi Dadfar S, Kavooosi G and Mohammad Ali Dadfar S. Investigation of mechanical properties, antibacterial features, and water vapor permeability of polyvinyl alcohol thin films reinforced by glutaraldehyde and multiwalled carbon nanotube. *Polymer Composites*. 2014; 35: 1736-43.
- [14] Pšeja J, Charvátová H, Hružík P, Hrnčířík J and Kupec J. Anaerobic biodegradation of blends based on polyvinyl alcohol. *Journal of Polymers and the Environment*. 2006; 14: 185-90.
- [15] Sreedhar B, Sairam M, Chattopadhyay D, Rathnam P and Rao D. Thermal, mechanical, and surface characterization of starch–poly (vinyl alcohol) blends and borax-crosslinked films. *Journal of Applied Polymer Science*. 2005; 96: 1313-22.
- [16] Uslu I, Daştan H, Altaş A, Yayli A, Atakol O and Aksu M. Preparation and Characterization of PVA/Boron Polymer Produced by an Electrospinning Technique. *e-Polymers*. 2007; 7.
- [17] Yin Y, Li J, Liu Y and Li Z. Starch crosslinked with poly (vinyl alcohol) by boric acid. *Journal of Applied Polymer Science*. 2005; 96: 1394-7.
- [18] Arora S, Kumar M and Kumar M. Flammability and thermal degradation studies of PVA/rice husk composites. *Journal of Reinforced Plastics and Composites*. 2012; 31: 85-93.
- [19] Nath DCD, Bandyopadhyay S, Yu A, Blackburn D and White C. High strength bio-composite films of poly (vinyl alcohol) reinforced with chemically modified-fly ash. *Journal of materials science*. 2010; 45: 1354-60.
- [20] Sreedhar B, Chattopadhyay D, Karunakar MSH and Sastry A. Thermal and surface characterization of plasticized starch polyvinyl alcohol blends crosslinked with epichlorohydrin. *Journal of Applied Polymer Science*. 2006; 101: 25-34.
- [21] Hu G, Cai S, Zhou Y, Zhang N and Ren J. Enhanced mechanical and thermal properties of poly (lactic acid)/bamboo fiber composites via surface modification. *Journal of Reinforced Plastics and Composites*. 2018; 37: 841-52.
- [22] Jayaramudu J, Reddy DJ, Guduri BR, Rajulu AV. Tensile properties of polycarbonate coated natural fabric *Sterculia Urens*: Effect of coupling agent. *Iranian Polymer Journal*. 2009: 693-1.
- [23] Jeurissen S, Andersen JH, DiNovi M, Folmer D, Schlatter J and Wallin H. Polyvinyl alcohol (PVA)–polyethylene glycol (PEG) graft copolymer. *Who Food Additives Series*. World Health Organization, 2016, p. 88-106.

- [24] Guohua Z, Ya L, Cuilan F, Min Z, Caiqiong Z and Zongdao C. Water resistance, mechanical properties and biodegradability of methylated-cornstarch/poly (vinyl alcohol) blend film. *Polymer Degradation and stability*. 2006; 91: 703-11.
- [25] Bana R and Banthia A. Green composites: development of poly (vinyl alcohol)-wood dust composites. *Polymer-Plastics Technology and Engineering*. 2007; 46: 821-9.
- [26] Sarah S, Rahman W, Majid R, et al. Optimization of Pineapple Leaf Fibre Extraction Methods and Their Biodegradabilities for Soil Cover Application. *Journal of Polymers and the Environment*. 2018; 26: 319-29.
- [27] Coats AW and Redfern J. Kinetic parameters from thermogravimetric data. *Nature*. 1964; 201: 68.
- [28] Horowitz HH and Metzger G. A new analysis of thermogravimetric traces. *Analytical Chemistry*. 1963; 35: 1464-8.
- [29] Kanatt SR, Rao M, Chawla S and Sharma A. Active chitosan-polyvinyl alcohol films with natural extracts. *Food Hydrocolloids*. 2012; 29: 290-7.
- [30] C.A. Finch. Chemical reactions and stereochemistry of polyvinyl alcohol. *Polyvinyl alcohol*, Wiley and Sons, London, 1992, p. 269.
- [31] Lum YH, Shaaban A, Mohamad N, Dimin F, Yatim NM. Boric acid modified starch polyvinyl alcohol matrix for slow release fertilizer. *e-Polymers*. 2016 Mar 1;16(2):151-8.
- [32] Ooi ZX, Chan KL, Ewe CY, Muniyandi M, Teoh YP, Ismail H. Evaluation of Water Affinity and Soil Burial Degradation of Thermoplastic Film Derived from Oil Palm Ash-filled Polyvinyl Alcohol. *BioResources*. 2017 Apr 24;12(2):4111-22.
- [33] Yang H-S, Yoon J-S and Kim M-N. Dependence of biodegradability of plastics in compost on the shape of specimens. *Polymer degradation and stability*. 2005; 87: 131-5.
- [34] Ooi Z, Ismail H, Abu Bakar A and Aziz N. Effects of jackfruit waste flour on the properties of poly (vinyl alcohol) film. *Journal of Vinyl and Additive Technology*. 2011; 17: 198-208.
- [35] Shaini VP, Jayasree S. Isolation and characterization of lipase producing bacteria from windrow compost. *Int. J. Curr. Microbiol. App. Sci*. 2016;5(5):926-33.
- [36] Pradhan S, Mohanty S, Nayak SK. In-Situ Aerobic Biodegradation Study of Epoxy-Acrylate Film in Compost Soil Environment. *Journal of Polymers and the Environment*. 2018 Mar 1;26(3):1133-44.
- [37] Zhou X-Y, Jia D-M, Cui Y-F and Xie D. Kinetics analysis of thermal degradation reaction of PVA and PVA/starch blends. *Journal of Reinforced Plastics and Composites*. 2009; 28: 2771-80.
- [38] Gilman J, VanderHart D and Kashiwagi T. Fire and polymers II: materials and test for hazard prevention. *ACS Symposium Series*. 1994, p. 161.
- [39] Singh R, Kulkarni SG and Channe SS. Thermal and mechanical properties of nano-titanium dioxide-doped polyvinyl alcohol. *Polymer bulletin*. 2013; 70: 1251-64.
- [40] Mallakpour S and Dinari M. Enhancement in thermal properties of poly (vinyl alcohol) nanocomposites reinforced with Al₂O₃ nanoparticles. *Journal of Reinforced Plastics and Composites*. 2013; 32: 217-24.
- [41] Aziz SB, Ahmed HM, Hussein AM, Fathulla AB, Wsw RM, Hussein RT. Tuning the absorption of ultraviolet spectra and optical parameters of aluminum doped PVA based solid polymer composites. *Journal of Materials Science: Materials in Electronics*. 2015 Oct 1;26(10):8022-8.
- [42] Bhatnagar A and Sain M. Processing of cellulose nanofiber-reinforced composites. *Journal of Reinforced Plastics and Composites*. 2005; 24: 1259-68.
- [43] Nath DC, Bandyopadhyay S, Boughton P, Yu A, Blackburn D, White C. Chemically modified fly ash for fabricating super-strong biodegradable poly (vinyl alcohol) composite films. *Journal of Materials Science*. 2010 May 1;45(10):2625-32.
- [44] Thwe MM, Liao K. Effects of environmental aging on the mechanical properties of bamboo-glass fiber reinforced polymer matrix hybrid composites. *Composites Part A: Applied Science and Manufacturing*. 2002 Jan 1;33(1):43-52.
- [45] Malkapuram R, Kumar V, Negi YS. Recent development in natural fiber reinforced polypropylene composites. *Journal of Reinforced Plastics and Composites*. 2009 May;28(10):1169-89.
- [46] Chen Y, Cao X, Chang PR, Huneault MA. Comparative study on the films of poly (vinyl alcohol)/pea starch nanocrystals and poly (vinyl alcohol)/native pea starch. *Carbohydrate Polymers*. 2008 Jul 4;73 (1):8-17.