

Thermal and Tensile Properties of PVA and Wood flour Composites

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Abstract

Polymer composites made from synthetic reinforcements are losing acceptability, due to their serious environmental concerns and high cost. The use of natural fibers such as wood flour, rice husk, straw, etc. gain interest for being non-toxic, light weight, reduced energy consumption and their environmental friendliness. In the present work, Poly(vinyl alcohol) [PVA] and wood flour composite films have been prepared by solvent casting method. Thermal analysis of the composite films has been studied at a heating rate of 10 °C min⁻¹, from ambient temperature to 500 °C, in an inert atmosphere. Tensile properties of the composite films were measured with a Universal Testing Machine and the data was also subjected to One-Way ANOVA. Thermal stability of composite films were found to be enhanced upto a certain loading of wood flour, with the modest decrease in tensile strength. Scanning Electron Microscopy is used to study the morphology of the composite films.

Keywords: wood flour, wood polymer composite, thermal stability, tensile strength, ANOVA.

INTRODUCTION

Natural bio-waste materials such as wood flour, rice husk, rice straw, wheat straw, bagasse, fruit peels etc. are menace to modern society. Many of these are burnt to generate energy, producing secondary haze pollution.¹ Wood is the most abundant natural biomass and is a mixture of cellulose, hemicelluloses, lignin and some extractives.² It has been used in making furniture, beam, rafters, plywood etc., which produce a huge amount of wood biomass. So, to deal with this waste biomass and because of its low cost, low abrasiveness, high specific strength and stiffness, biodegradability and relatively low density,^{3,4} it is being utilized by polymer industries to manufacture wood polymer composites (WPC) with polyethylene (PE), polystyrene (PS), polyvinyl chloride (PVC), polypropylene (PP) etc.⁵⁻⁸ Most of these plastics are manufactured from petroleum derivatives that are non-

biodegradable and commonly hydrophobic, resulting in the poor interfacial bonding with polar wood flour and limiting their mechanical performance along with some other important applications.^{9,10} In the past few years, a lot of work has been contributed for the development of environment friendly plastic products, in many agricultural applications like mulch films, greenhouse construction materials, packaging materials etc.,¹¹⁻¹³ and interest has grown to replace them with naturally degradable/biodegradable polymers.^{14,15} Poly(vinyl alcohol) [PVA] is found to be one of the best alternatives to petroleum based polymers, as it is having good film forming ability, biocompatible, biodegradable, non toxic, good chemical resistance and minimal cell adhesion.¹⁶⁻²⁰ Particularly, PVA is compatible with wood flour/fiber and other natural fibers due to its hydrophilic character. Among agricultural applications, mulch films, which apply in the fields, bear high temperature for long period of time, so they required to be thermally more stable and other applications also demand improved thermal stability of composites. To improve the thermal, mechanical, biodegradability and other important properties, PVA matrix based composites with starch, rice husk, chitosan, algae, wood flour etc. are reported in literature.^{5,20-25}

The purpose of the present study is to investigate the possibility of producing thermally stable PVA composites. In the present work, PVA and wood flour composite films were prepared by solvent casting method. Polyethylene Glycol (PEG) was added as plasticizer with its added properties like hydrophilicity, solubility in water, non-toxicity²⁶ and boric acid is also added as cross linking agent.^{21,27} Poplar (*Populus*) is grown in large plantations, regularly cropped²⁸ and one of the vastly used woods.²⁹ So, waste poplar wood flour is used to prepare PVA-wood flour composites. Thermal degradation behaviour of PVA and its composites was studied by TG/DTG analysis. Activation energies of different degradation stages were calculated by using single heating rate methods. Mechanical properties of the composite films were tested at Universal Testing Machine (UTM). The tensile strength data were also subjected to One-Way ANOVA (Analysis of

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Variance). Scanning Electron Microscopy (SEM) is used to study the morphology of the composite films.

EXPERIMENTAL

Materials

PVA (Molecular weight 85000-124000, degree of hydrolysis 86-89%) was supplied by SD Fine Chem. Ltd. PEG-6000 and Boric acid was obtained from Himedia (India). Poplar wood flour was collected from local carpentry shop, washed with deionised water and kept in an oven at 60 °C for 48 hrs. It was powdered, sieved to 75 mesh size and placed in desiccator to avoid absorbing moisture.

Preparation of PVA Composite films

PVA/Wood flour composite films were prepared by solvent casting method, with varying amount of wood flour by adding PEG as plasticizer and boric acid as cross linking agent (Table 1). Firstly, PVA (10 % w/v) was dissolved in water at 80 °C, calculated amount of wood flour, PEG and boric acid were added to the hot aqueous solution of PVA and the solution was stirred for 6 hrs. The hot solution was then poured into clean PP dishes, cooled at room temperature and then placed in the vacuum oven at 80 °C for 72 hrs to evaporate the solvent. The films were removed from the dishes and placed in oven at 80 °C for 2 hrs, kept in air tight polyethylene bags until further testing.

Table 1. Composition of PVA, Wood Flour, PEG and Boric acid.

Sample Index	PVA (g)	Wood Flour (% of PVA)	PEG-6000 (% of PVA)	Boric acid (% of PVA)
PVA	2	-	-	-
PVA-PEG	2	-	25	-
PVA10	2	10	25	3
PVA15	2	15	25	3
PVA20	2	20	25	3
PVA25	2	25	25	3
PVA30	2	30	25	3

CHARACTERIZATION METHODS

Scanning Electron Microscopy (SEM) Measurements

The morphologies of PVA and its composite films were observed through SEM analyser (JEOL JSM-6510LV) operated at 15 kV.

Thermal analysis

TGA measurements were performed on STAHL thermogravimetric (TG) analyzer. Thermograms were

obtained at a heating rate of 10 °C min⁻¹ in N₂ atmosphere, from ambient temperature to 500 °C.

Kinetic Studies

With the help of TG data, Activation Energies (E_a) of degradation stages of PVA and its composites were calculated by using single heating rate methods viz. Broido,³⁰ Horowitz-Metzger³¹ and Coats- Redfern.³² Final equations of the methods are given in Table 2.

Table 2. Single Heating Rate Methods to calculate Activation Energies of Degradation.

Method	Considerations	Equation	Plot (Y vs X)
Broido	$y = \frac{w_t - w_\infty}{w_o - w_\infty}$	$\ln\left(\ln\left(\frac{1}{y}\right)\right) = -\frac{E_a}{RT} + const.$	$\ln\left(\ln\left(\frac{1}{y}\right)\right)$ vs $\frac{1}{T}$
Horowitz-Metzger	$\alpha = \frac{w_o - w_t}{w_o - w_\infty}$	$\ln\left(\ln\left(\frac{1}{1-\alpha}\right)\right) = -\frac{E_a}{RT_s^2} \theta$	$\ln\left(\ln\left(\frac{1}{1-\alpha}\right)\right)$ vs θ
Coats-Redfern	$\alpha = \frac{w_o - w_t}{w_o - w_\infty}$	$\ln\left(\frac{g(\alpha)}{T^2}\right) = -\frac{E_a}{RT} + const.$ $g(\alpha) = -\ln(1-\alpha)$	$\ln\left(\frac{g(\alpha)}{T^2}\right)$ vs $\frac{1}{T}$

Tensile Properties

The tensile properties of PVA composite films were measured with Universal Testing Machine (UTM) at a cross head speed of 5 mm min⁻¹. The test samples were cut according to ASTM D882. Prior to testing, samples were conditioned at 50 % relative humidity and 25 °C for 24 hrs. The reported values for tensile properties are averages of five measurements. The tensile strength data were subjected to One-Way ANOVA.

RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM) Measurements

Figure 1(a) represents the SEM image of Neat PVA. It can be seen that it is smoother as compared to that of PVA20 (Figure 1(c)). Homogeneously distributed Wood flour particles can be seen in PVA20, confirming the formation of composite.

Thermal Analysis

The inherent characteristics and molecular interaction between the different macromolecules are responsible for the thermal stability of a polymer. TG and DTG curves of PVA and its composite films at heating rate 10 °C min⁻¹ under nitrogen atmosphere are shown in Figure 2. A slight weight loss was observed for each sample at around 150 °C, which

can be due to the loss of physically absorbed water. Thermal degradation of PVA occurs via two different stages,³³⁻³⁵ as confirmed by DTG curve Figure 2(b). Weight loss in the 1st degradation stage is due to the dehydration of PVA and depolymerisation followed by the formation of polyene. During the 2nd degradation stage, intramolecular cyclization reactions produce some organic volatiles.³⁴ Incorporation of wood flour into PVA matrix affected the thermal degradation behaviour of PVA (Figure 2.). Thermal stabilities of PVA wood flour composites were found to be increased with increase in wood flour content upto 20% and then decrease on further loadings. The onset (T_o), endset (T_e) degradation temperatures and DTG maxima (T_{m1} and T_{m2}) of 1st and 2nd degradation stages are listed in Table 3.

T_o (1st stage), of PVA20 is increased by 22.1 °C as compared to virgin PVA (Table 3). This considerable increase in the thermal stability of composite film can be attributed to the compatibility between PVA and wood flour due to their hydrophilic character. Moreover, boric acid played an important role as a cross linking agent²⁷ between PVA and wood flour, resulting the higher thermal stability of composite films.^{21,36} Thermal stability decreases on further loadings, that means 20% is the optimum level of wood flour to be added to PVA.

Table 3. TG and DTG data of PVA and PVA Wood Composite in N₂ at heating rate of 10 °C min⁻¹.

Sample Index	1st Degradation Stage (°C)			2nd Degradation Stage (°C)			MWLR (% min ⁻¹)	Char yield at 480 °C (%)
	T _o	T _e	T _{m1}	T _o	T _e	T _{m2}		
	PVA	261.2	371.4	325.4	387.9	448.4		
PVA-PEG	263.3	356.7	325.4	387.9	447.9	403.2	7.7	11.3
PVA10	264.7	361.1	329.6	392.2	451.9	407.3	5.8	12.2
PVA15	266.9	345.1	313.7	360.8	451.7	407.3	6.9	10.4
PVA20	283.3	345.7	314.4	361.3	437.6	392.3	9.0	10.8
PVA25	251.9	345.6	314.3	361.2	437.6	392.6	8.2	10.1
PVA30	236.0	299.2	314.9	346.4	438.3	362.3	6.1	15.1

Char yield percentages for all composites, including virgin PVA at 480 °C have been reported (Table 3). Relatively, higher char yield for composites as compared to virgin PVA is the adding effect of boric acid.^{36,37}

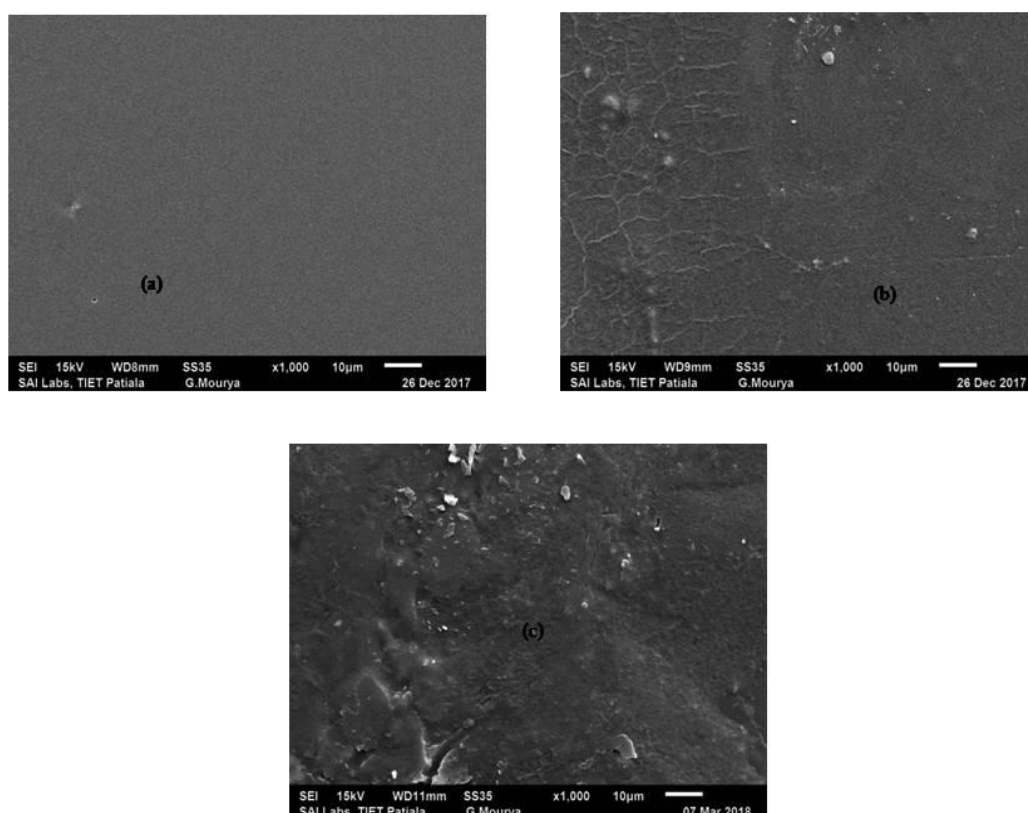


Figure 1. SEM images (a) PVA (b) PVA-PEG (c) PVA20

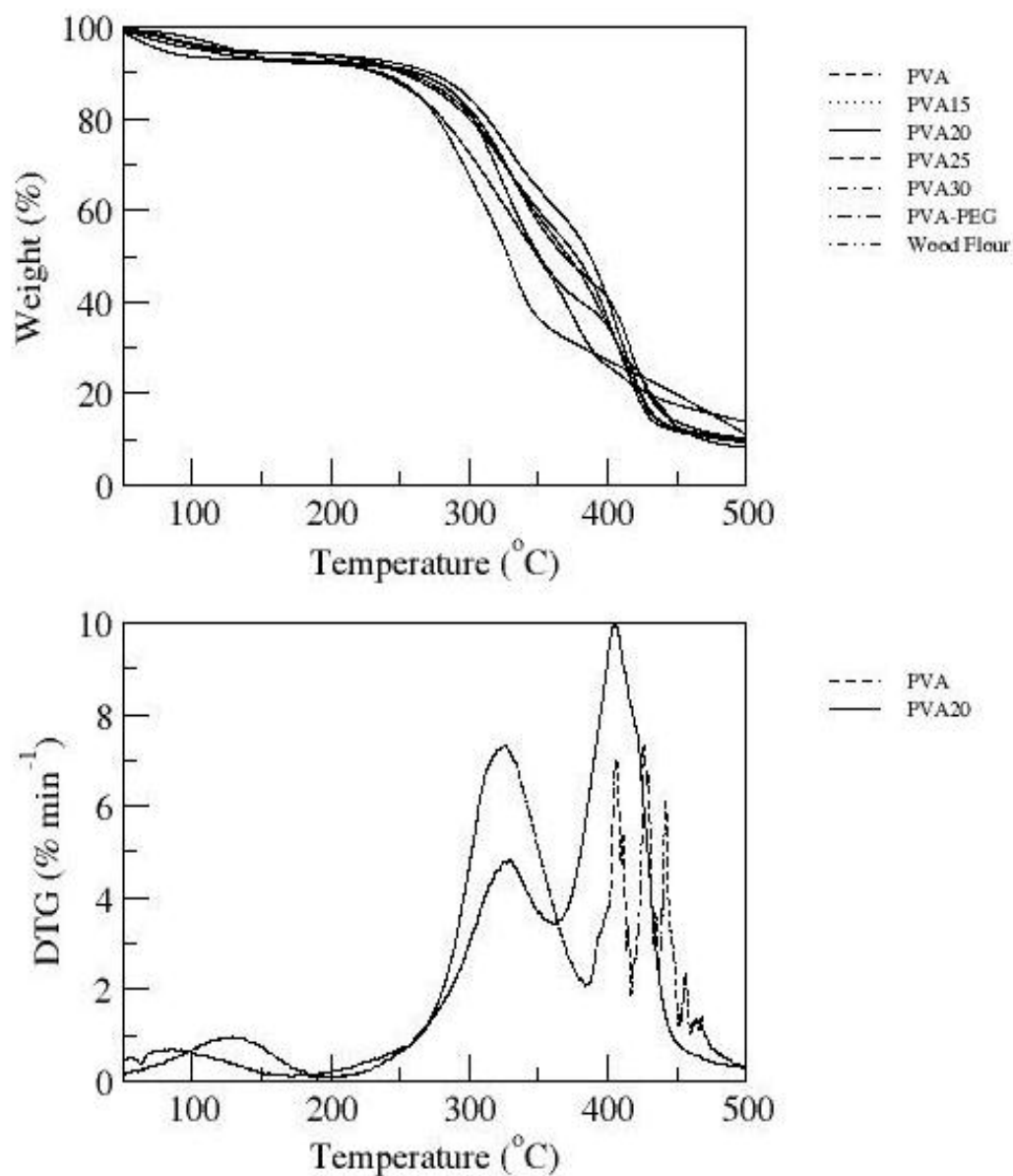


Figure 2. (a) TG curves of PVA and its Wood flour composites (b) DTG curves of PVA and PVA20.

Kinetic Studies

Activation energies of degradation of PVA and its composites films were calculated and are listed in Table 4. All linear plots are having regression co-efficients (R^2) > 0.95. It can be seen that the activation energies calculated using different heating rate methods are in good agreement with each other. Activation energies calculated by all the methods for PVA20

(thermally most stable on the basis of onset degradation temperature) were found to be lower at 1st degradation stage, means once degradation starts, PVA20 degrades at a faster rate than PVA. But the activation energy of 2nd degradation stage for PVA20 was found to be higher than PVA, which might be due to boric acid, which formed some intermolecular cross-linking with hydrogen type bonds of PVA.³⁴

Table 4. Activation Energies of different degradation stages.

Sample Index	1st Degradation Stage			2nd Degradation Stage		
	E _a (kJ mol ⁻¹)			E _a (kJ mol ⁻¹)		
	Broido	Horowitz Metzger	Coats Redfern	Broido	Horowitz Metzger	Coats Redfern
PVA	61.2	60.8	51.4	56.9	40.5	45.6
PVA-PEG	56.2	57.5	46.5	82.9	60.4	71.5
PVA10	48.9	47.3	39.2	61.9	41.8	49.8
PVA15	39.3	54.7	46.3	69.8	51.8	58.6
PVA20	50.6	50.3	36.4	98.8	68.0	72.8
PVA25	45.9	48.4	36.5	80.7	59.8	66.4
PVA30	45.3	47.5	36.4	50.4	34.3	39.4

Tensile Properties

Ultimate Tensile strengths (UTS) (with standard deviations)

of PVA and its composite films are reported in Table 5. Tensile strengths of PVA film was found to be higher than that of PVA-PEG film, as also reported in the literature.^{38,39}

Table 5. Ultimate Tensile Strength (UTS) of PVA and its Composite films.

Sample Index	PVA	PVA-PEG	PVA10	PVA15	PVA20	PVA25	PVA30
UTS (MPa)	12.74±0.98	3.36±0.51	9.47±1.24	10.16±1.20	8.35±1.26	6.99±1.11	6.53±0.73

However, all the composite films were having improved UTS as compared to PVA-PEG film. It might be due to that boric acid acted as compatibilizer/cross linking agent^{21,27} between PVA and wood flour and might have formed an intramolecular and intermolecular cross-linking with covalent and hydrogen type bonds respectively, of PVA.³⁴ Tensile strengths of composite films showed a modest and irregular decrease with increase in wood flour content. PVA15 was found to have maximum tensile strength among composites

and PVA20 have comparable value of tensile strength, which is found to be thermally the most stable. Tensile strength decreases on further loadings of wood flour in PVA matrix. It might be due to the heterogeneous distribution of wood flour into the matrix.

The tensile strength data were subjected to One-Way ANOVA at a significant level of 0.05 and results are reported in Table 6, which reveals the significant differences between the different compositions.

Table 6. Analysis of Variance.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Sample Index	6	268.75	44.792	41.56	<0.001
Error	28	30.17	1.078		
Total	34	298.9			

CONCLUSIONS

The PVA/Wood flour composites of improved thermal stability and comparable tensile strength were prepared via solvent casting method. Thermal stability of composites was found to be increased upto 20% loading of wood flour into the PVA matrix. The onset degradation temperature (1st stage), of PVA20 is increased by 22.1 °C as compared to virgin PVA. The percentage char yield of composites calculated at 480 °C, has been found to lie in the ranges 9-16 % and higher char yield for composites as compared to virgin PVA is the adding effect of boric acid. The maximum weight loss rate calculated from DTG shows that there is no significant difference between weight loss rate of virgin PVA and its composites. The results obtained from One-Way ANOVA illustrate the significant differences between the different compositions.

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REFERENCES

- Kojima Y, Minamino J, Isa A, et al. Binding effect of cellulose nanofibers in wood flour board. *J wood Sci.* 2013;59(5):396-401.
- Horvath AL. Solubility of structurally complicated materials: I. Wood. *J Phys Chem Ref data.* 2006;35(1):77-92.
- Nachtigall SMB, Cerveira GS, Rosa SML. New polymeric-coupling agent for polypropylene/wood-flour composites. *Polym Test.* 2007;26(5):619-628.
- Ichazo MN, Albano C, Gonzalez J, Perera R, Candal, MV. Polypropylene/wood flour composites: treatments and properties. *Compos Struct.* 2001;54(2-3):207-214.
- Xu K, Li K, Zhong T, Guan L, Xie C, Li S. Effects of chitosan as biopolymer coupling agent on the thermal and rheological properties of polyvinyl chloride/wood flour composites. *Compos Part B Eng.* 2014;58:392-399.
- Devi RR, Maji TK. Effect of glycidyl methacrylate on the physical properties of wood--polymer composites. *Polym Compos.* 2007;28(1):1-5.
- Ashori A, Behzad HM, Tarmian A. Effects of chemical preservative treatments on durability of wood flour/HDPE composites. *Compos Part B Eng.* 2013;47:308-313.
- Najafi SK. Use of recycled plastics in wood plastic composites--A review. *Waste Manag.* 2013;33(9):1898-1905.
- Duval A, Lawoko M. A review on lignin-based polymeric, micro-and nano-structured materials. *React Funct Polym.* 2014;85:78-96.
- Zhou Y, Fan M, Chen L, Zhuang J. Lignocellulosic fibre mediated rubber composites: an overview. *Compos Part B Eng.* 2015;76:180-191.
- Espi E, Salmeron A, Fontecha A, Garcia Y, Real AI. Plastic films for agricultural applications. *J Plast Film Sheeting.* 2006;22(2):85-102.
- Arora S, Kumar M, Kumar M. Preparation and thermal stability of poly(methyl methacrylate)/rice husk silica/triphenylphosphine nanocomposites: assessment of degradation mechanism using model-free kinetics. *J Compos Mater.* 2013;47(16):2027-2038.
- Arora S, Kumar M, Kumar M. Thermal and flammability studies of poly(vinyl alcohol) composites filled with sodium hydroxide. *J Appl Polym Sci.* 2013;127(5):3877-3884.
- Chiellini E, Cinelli P, Antone SD, Ilieva VI. Environmentally degradable polymeric materials (EDPM) in agricultural applications—an overview.

- Polimery*. 2002;47(7-8):538-544.
15. Kasirajan S, Ngouajio M. Polyethylene and biodegradable mulches for agricultural applications: a review. *Agron Sustain Dev*. 2012;32(2):501-529.
 16. Chabba S, Netravali AN. 'Green' composites Part 2: Characterization of flax yarn and glutaraldehyde/poly (vinyl alcohol) modified soy protein concentrate composites. *J Mater Sci*. 2005;40(23):6275-6282.
 17. Rosa MF, Chiou B, Medeiros ES, et al. Effect of fiber treatments on tensile and thermal properties of starch/ethylene vinyl alcohol copolymers/coir biocomposites. *Bioresour Technol*. 2009;100(21):5196-5202.
 18. Uslu I, Dacstan H, Altacs A, Yayli A, Atakol O, Aksu ML. Preparation and Characterization of PVA/Boron Polymer Produced by an Electrospinning Technique. *e-Polymers*. 2007;7(1).
 19. Hoshiro H, Nishiyama M, Yamamoto R. Long-term Durability of Kuralon (PVA fiber) in alkaline condition. In: *Proceedings 10th International Inorganic-Bonded Fiber Composite Conference*. ; 2006.
 20. Sreedhar B, Sairam M, Chattopadhyay DK, Rathnam PA, Rao D V. Thermal, mechanical, and surface characterization of starch--poly (vinyl alcohol) blends and borax-crosslinked films. *J Appl Polym Sci*. 2005;96(4):1313-1322.
 21. Arora S, Kumar M, Kumar M. Flammability and thermal degradation studies of PVA/rice husk composites. *J Reinf Plast Compos*. 2012;31(2):85-93.
 22. He P, Bai S, Wang Q. Structure and performance of Poly (vinyl alcohol)/wood powder composite prepared by thermal processing and solid state shear milling technology. *Compos Part B Eng*. 2016;99:373-380.
 23. Lee HW, Karim MR, Park JH, et al. Poly (vinyl alcohol)/chitosan oligosaccharide blend submicrometer fibers prepared from aqueous solutions by the electrospinning method. *J Appl Polym Sci*. 2009;111(1):132-140.
 24. Ozaki SK, Monteiro MBB, Yano H, Imamura Y, Souza MF. Biodegradable composites from waste wood and poly (vinyl alcohol). *Polym Degrad Stab*. 2005;87(2):293-299.
 25. Arora S, Lal S, Sharma C, Aneja KR. Synthesis , thermal and antimicrobial studies of chitosan / starch / poly (vinyl alcohol) ternary blend films. *Der Chem Sin*. 2011;2(5):75-86.
 26. Herold DA, Keil K, Bruns DE. Oxidation of polyethylene glycols by alcohol dehydrogenase. *Biochem Pharmacol*. 1989;38(1):73-76.
 27. Yin Y, Li J, Liu Y, Li Z. Starch crosslinked with poly (vinyl alcohol) by boric acid. *J Appl Polym Sci*. 2005;96(4):1394-1397.
 28. Roberts M, Reiss MJ, Monger G. *Advanced Biology*. Nelson Thornes; 2000.
 29. Arora S, Kumar M, Kumar M. Catalytic effect of bases in impregnation of guanidine nitrate on Poplar (Populus) wood. *J Therm Anal Calorim*. 2012;107(3):1277-1286.
 30. Broido A. A simple, sensitive graphical method of treating thermogravimetric analysis data. *J Polym Sci Part A-2 Polym Phys*. 1969;7(10):1761-1773.
 31. Horowitz HH, Metzger G. A new analysis of thermogravimetric traces. *Anal Chem*. 1963;35(10):1464-1468.
 32. Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. *Nature*. 1964;201(4914):68.
 33. Shie JL, Chen YH, Chang CY, Lin JP, Lee DJ, Wu CH. Thermal pyrolysis of poly (vinyl alcohol) and its major products. *Energy & fuels*. 2002;16(1):109-118.
 34. Gilman JW, VanderHart DL, Kashiwagi T. Thermal decomposition chemistry of poly (vinyl alcohol). *ACS Sym Ser*. 1994;599:161-185.
 35. Thomas PS, Guerbois JP, Russell GF, Briscoe BJ. FTIR study of the thermal degradation of poly (vinyl alcohol). *J Therm Anal Calorim*. 2001;64(2):501-508.
 36. Gao M, Yang S, Yang R. Flame retardant synergism of GUP and boric acid by cone calorimetry. *J Appl Polym Sci*. 2006;102(6):5522-5527.
 37. Hirata T, Werner KE. Thermal analysis of cellulose treated with boric acid or ammonium phosphate in varied oxygen atmospheres. *J Appl Polym Sci*. 1987;33(5):1533-1556.
 38. Abd Alla SG, Said HM, El-Naggar AWM. Structural properties of γ -irradiated poly (vinyl alcohol)/poly (ethylene glycol) polymer blends. *J Appl Polym Sci*. 2004;94(1):167-176.
 39. Abdel Tawab K, Magida MM, Ibrahim SM. Effect of Ionizing Radiation on the Morphological, Thermal and Mechanical Properties of Polyvinyl Alcohol/Polyethylene Glycol Blends. *J Polym Environ*. 2011;19(2):440-446.