




Research Article

Preparation and characterization of polyvinyl alcohol–starch composites reinforced with pulp

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Abstract

Herein, we have investigated the reinforcing potential of starch and cellulose pulp in a matrix of polyvinyl alcohol (PVA). Polyvinyl alcohol, starch, and pulp fibers having different compositions were constructed in order to achieve better reinforced composite films. Various techniques were utilized for extract the physical, mechanical as well as thermal properties. The magnitudes of tensile strength were reduced with rising of starch content in PVA. Tensile strength values of (PVA + starch) mixtures were enhanced with the enhancement of pulp fibers content. The properties of bulk density and water absorption revealed the significant impact of starch and pulp fibers. The obtained result of thermal stability of PVA was superior which was reduced by addition of starch content; therefore, regained with the insertion of pulp fibers content in PVA–starch matrix.

Keywords Polyvinyl alcohol · Composite · Physical property · Mechanical property · Thermal property

1 Introduction

Polymers which degrade after disposal by the action of living organisms are biodegradable [1]. Various types of commercial polymers as well as composites are utilized for a number of industrial and daily purposes which are mainly constructed from non-biodegradable components. After the termination of these materials, cannot be squandered smoothly and exploited as waste; therefore exerts a variety of significant damaging causes on the environment [2]. If the material used to fabricate some product is not degradable, it causes serious environmental hazard or pollution. In this circumstance, developing and spreading eco-friendly/environment friendly materials is a worldwide concern during past few decades to keep fresh the environment and save the environmental resources. Now a days, water soluble and biodegradable polymers got importance as an alternative source of material for using it

in many purposes [3]. Natural fibers are cheap, biodegradable and available in our surroundings and can be used to produce biodegradable composites, therefore assist to assured our environment [4]. Manufacturing of biodegradable composites from such biodegradable plastics will enhance the demand of such materials.

Polyvinyl alcohol (PVA) is a biodegradable polymer that has received significant attention because of its ability to decompose in relatively short timeframe [5]. But PVA is a costly commercial raw material. To lower down the cost of product without any compromise or partial compromise with its properties, people are using composites of PVA. Composites are produced by blending biodegradable polymers with natural fibers to produce bio-based or biodegradable polymer composite that exhibit unique and stable characteristics [6]. Bio-plastics are one type of plastic materials which can be extracted from reproducible biomass origins such as vegetable, micro biota, corn

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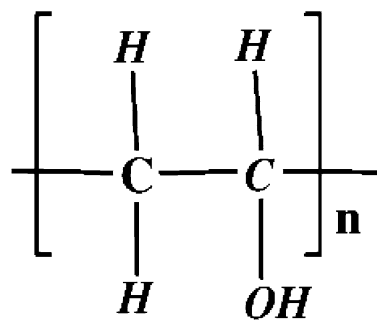


starch, oil, and pea starch whereas conventional plastics are obtained from petroleum sources. According to literatures, these materials may be utilized either as explicit replacement for typical plastics or as blends with typical plastics [7]. Achieve any kinds of plastics bio-based or petroleum-based are technically bio-degradable.

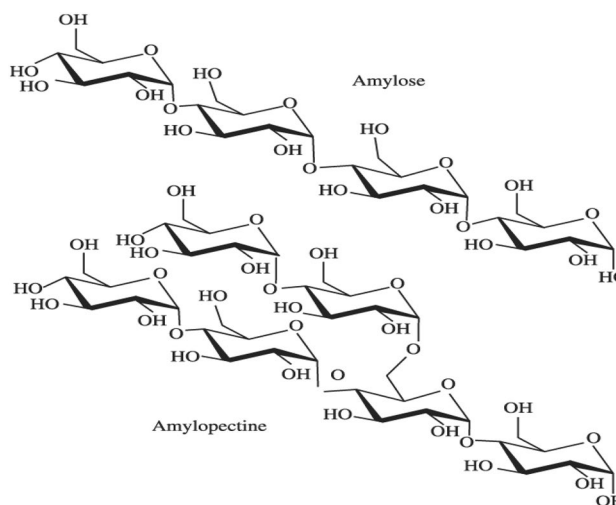
Polyvinyl alcohol and starch are biodegradable polymers. Also pulp is a source of biodegradable cellulose fiber. The chemical properties of cellulose are more important than its physical properties [8]. Chemical property of cellulose causes to undergo appreciable chemical change after aging. The roles of cellulose in composites are important from several points of view because it can be degraded under a variety of circumstances and these degradations happen in several ways [9]. Biodegradable packing materials are compostable, derived from nature, environment friendly, corrosion preventive and have a lot of varieties. For these properties, biodegradable composites can be used for production of alternative packing and packaging material to reduce global warming and to keep environment green.

Amid a large number of natural polymers, starch is one of the most enthusiastic and interesting natural bio-polymer. Plants produce this polymer by means of photosynthesis from CO_2 and H_2O [10]. Due to its entire biodegradability [11], renewability, little cost, and availability [12], starch is taken as an important and congenial successor for developing as well as improving long lasting sustainable materials [13]. Since 1970s, this natural polymer has been attracted growing interest and attention by the modern civilization [14, 15].

The king interest or objective of our current study is to construct polyvinyl alcohol–starch composites with accompanying pulp fibers as boosting materials. Fahma et al. [16] studied thermoplastic starch–PVA composite films using cellulose nano-fibers and glycerol as reinforcing and plasticizer agents respectively where nano-fibers decreased the elongation at break which was opposite in case of glycerol. Cassava starch–PVA based composite preparation by using bamboo nanofibrils was performed by Jr et al. [17] and they obtained better mechanical properties where bamboo nanofibrils performed as a good reinforcing agent. Guo et al. [18] reported that PVA–thermoplastic starch (TPS) using PVA microspheres composites provided dynamic mechanical properties in glass-transition temperatures and thermal stability also increased. To the best of our knowledge, PVA–starch composite with considering nanofibers/different nano-cellulose or micro-crystalline cellulose [8] has been done; therefore, utilizing pulp from paper mills sludge have never been investigated. This PVA–starch composite, reinforced by pulp has great a novelty about producing various types of bio-degradable composite materials (such as packaging



Scheme 1 Polyvinyl alcohol



Scheme 2 Starch (amylose and amylopectin)

materials, plastics, consumer materials, agriculture materials, biomedical materials etc.) [19, 20], especially recycling the paper mills waste (sludge). In many countries, a huge amount of pulp containing waste sludge is exposing in environment without recycling and therefore, this pulp containing sludge can be recycled, composite materials preparation. The Scheme 1 [21] and Scheme 2 (amylose and amylopectin) [22] represents the structure of polyvinyl alcohol and starch respectively. Different types of physical, mechanical, thermal methods were employed as well as achieved properties were scrutinized thoroughly.

2 Experimental

2.1 Materials and equipment

The chemicals utilized in this current study were of analytical grade and employed without subsequent purification. Polyvinyl alcohol (purity 99%, CAS Registration No: 9002-89-5) was pursued from Merck, Germany.

Starch (purity 99%, CAS Registration No: 9005-84-9) and pulp (Whatman filter paper, England) were used in this study. Distilled water was utilized throughout the whole research work for solution/sample preparation. Different equipment such as UTM machine 10 KN (HOUNSFIELD, H10KS), TG/DTA/DTG machine (6300, SEIKO, INCO, Japan), electric balance (Precisa XB 220A), magnetic stirrer (Lab Tech LNS-1003), electric drying oven (202-1, China), heating mantle (Electromantle, UK), and blender (Gallen-hamp, England) were utilized for various measurement.

2.2 Preparation of solution, film and sample

At first, filter paper was taken in a beaker containing distilled water to disperse the pulp. Wet pulp was blended to prepare a homogeneous mixture of pulp and water. The solutions of PVA of different amounts (20 g, 15 g, and 10 g) (Table 1) were prepared by using distilled water. Then the prepared solution of PVA was inserted into the different measured amount of starch solution (5 g and 10 g) (Table 1); therefore the PVA–starch solution was taken into the homogeneous mixture of (pulp + water). The total mixture was heated at 70–80 °C for 1 h with continuous stirring and after heating, it was allowed for cooling at room temperature (RT). After cooling the prepared solution, it was dispersed on a Teflon sheet for natural drying.

For sample preparation, a molding device was used. The prepared mixture was poured in the cavity of the mold and thickness was controlled. Stamping on the mold was required for sufficient composition. Different types of mechanical (stress–strain curve, ultimate tensile strength, young's modulus, and thermal properties) and physical properties (bulk density and water uptake) were evaluated by applying different corresponding methods. In case of physical properties evaluation (bulk density), mass of particular composite batch/system of sample was taken and then it divided by corresponding volume. Values of water uptake were measured by water uptake tester (Prolific Engineers).

Table 1 Batch number and amount of different compositions of different contents

Batch no.	PVA (g)	Starch (g)	Pulp (g)
1	0.0	20	0.0
2	15	5.0	0.0
3	10	10	0.0
4	10	10	0.5
5	10	10	1.0

3 Results and discussion

After preparation of sample, different physical and chemical properties of the sample were determined. To use the composite in practical purposes, one should know about the properties of the composite. For a definite use of composite, it demands to pose some specific characteristic. So, one needs a clear knowledge about the properties of the composite. A discussion is presented here on the obtained test results of the prepared composite samples.

3.1 Physical properties

(a) Bulk density

Bulk density of a material depends upon the characteristics of the components materials. The effect of addition of pulp/fiber on bulk density of PVA–starch–pulp composite is given in the bar chart below. The obtained results demonstrated that bulk density of the present composite material changes with addition of pulp (Fig. 1). Figure 1 discloses that the density of the composite decreases with the accretion of pulp/fiber in PVA–starch matrix.

When fiber is inserted into the matrix, strong hydrogen bonds are formed between the primary alcoholic group of fiber and phenolic –OH group of matrix and thus fiber and matrix come into intimate contact. So, there should be increased in density but as fiber has very low density that is why the net density of composite is decreased.

(b) Water uptake

Water uptake determines swelling behavior of the blended films. The effect of immersion time on water uptake of composite is shown in Fig. 2.

Figure 2 exhibiting that the initial rate of water up-taking is faster for few minutes then it becomes slow; therefore almost all samples reached in the maximum level within 5 min. It is perceived from Fig. 2 that water uptake clearly depends on amount of fiber and immersion time. Water uptake increases with addition of increased amount of starch and pulp because water absorption capacity of those is high in comparison to that of PVA. It is known that PVA has hydroxyl group (–OH) in its structure which leads swelling of water or increasing its solubility. In our case, the addition of PVA declined the water uptake because of constructing crosslinking

Fig. 1 Effect of fiber addition on bulk density of PVA–starch–pulp composite

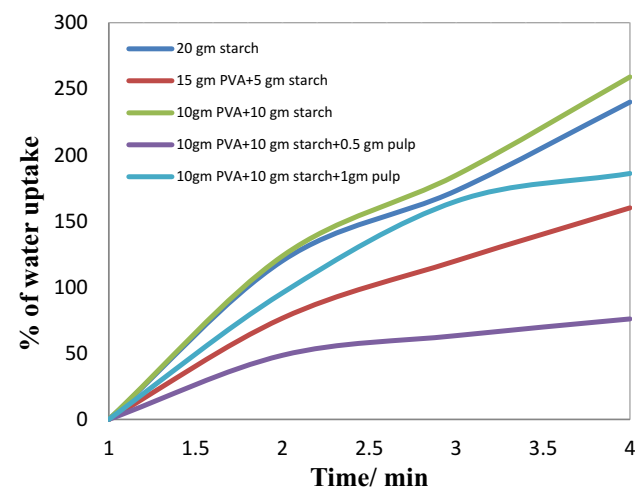
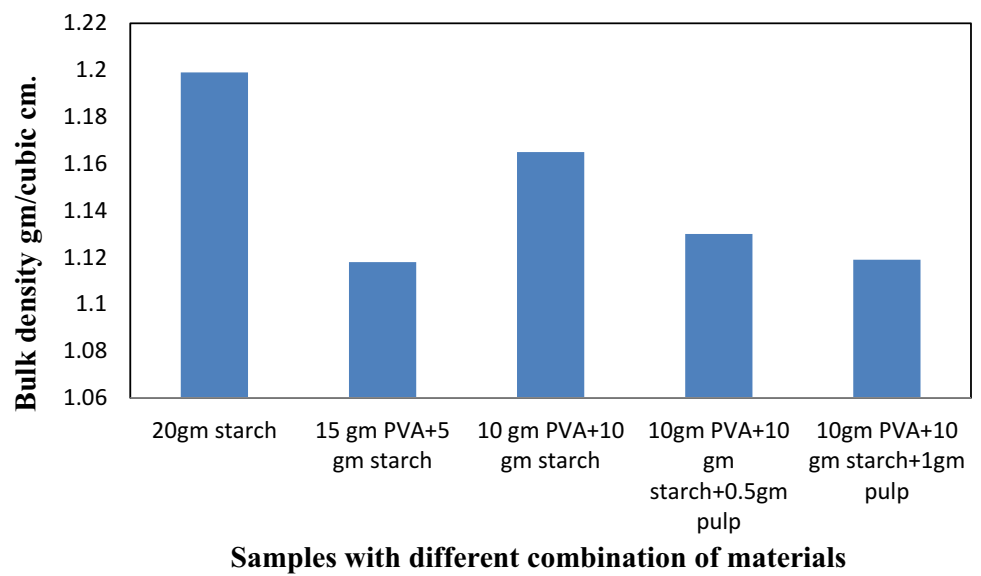


Fig. 2 Effect of immersion time on water uptake of composite with varying composition of PVA, starch, and pulp

between the studied components. As a result, from figure it is observed that composite with higher amount of starch and pulp has shown higher water uptake than that of with lower amount of starch and pulp content.

3.2 Mechanical properties

Mechanical properties of the composite are very much important from practical point of view because the product prepared by composite should be mechanically viable.

(a) Stress–strain curve

The tensile properties or stress–strain curves of the samples are given in the Figs. 3, 4, 5, 6 and 7.

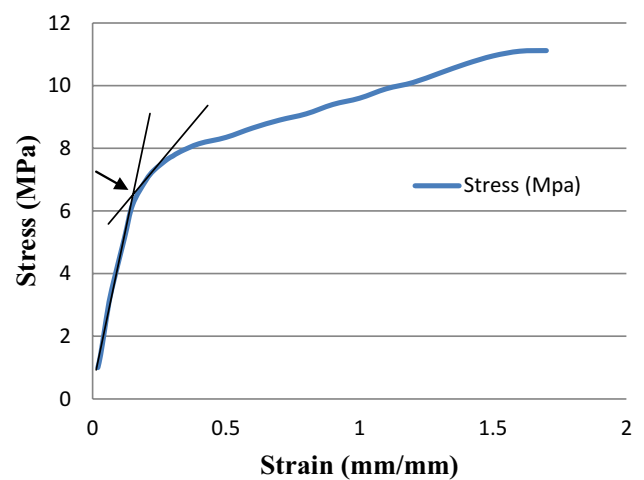


Fig. 3 Stress–strain curve for pure PVA (20 g PVA) film

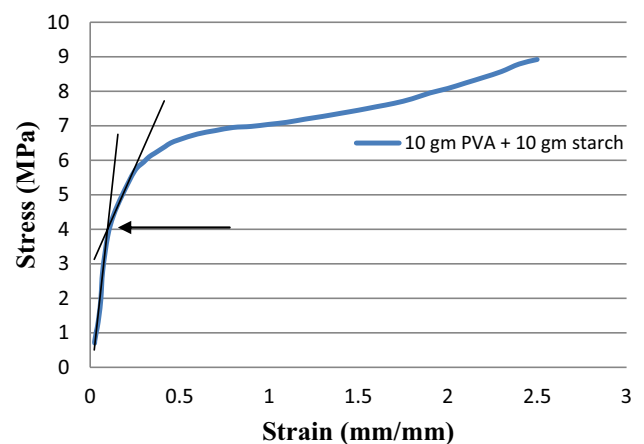


Fig. 4 Stress–strain curve for 15 g PVA film + 5 g starch film

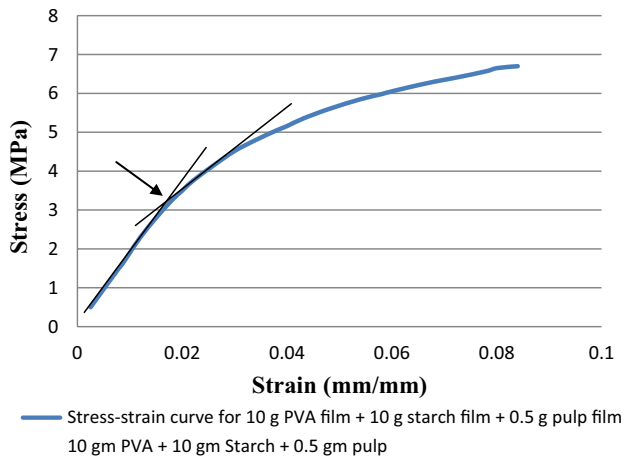


Fig. 5 Stress–strain curve for 10 g PVA film + 10 g starch film

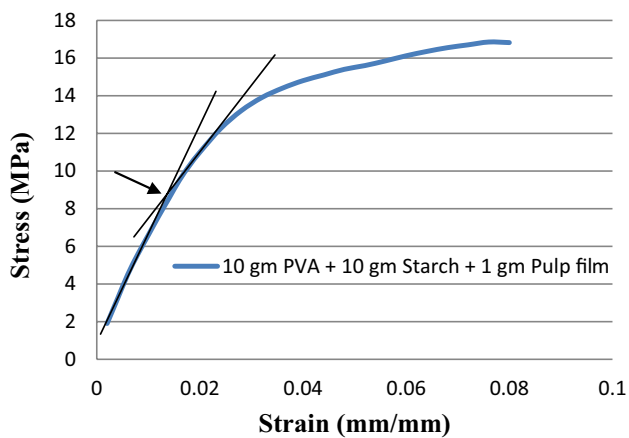


Fig. 6 Stress–strain curve for 10 g PVA film + 10 g starch film + 0.5 g pulp film

From figures (Figs. 3, 4, 5, 6, 7) it is observed that stress increases with increase of strain and attained maximum value and then fall down. The curves have two regions—one is the elastic region and another is plastic region i.e. composites deform elastically first and then plastic deformation starts. The first straight line among all the figures signifies the elastic region (stress 8.3 MPa) which is higher in case of those mixtures of components which contains 0.5 g pulp and showed the following pattern:

$$8.3 \text{ MPa (10 g PVA film + 10 g starch film + 0.5 g pulp film)} > 6.3 \text{ MPa (20 g PVA) film} \\ > 4.4 \text{ MPa (10 g PVA film + 10 g starch film + 1 g pulp film)} > 4.0 \text{ MPa (15 g PVA film} \\ &+ 5 \text{ g starch film)} > 3.2 \text{ MPa (15 g PVA film + 10 g starch film)}$$

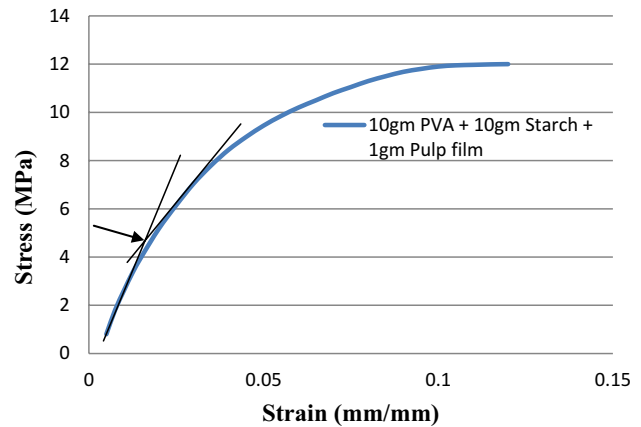


Fig. 7 Stress–strain curve for 10 g PVA film + 10 g starch film + 1 g pulp film

This style revealed that the attendance of 0.5 g Pulp in composite materials booster the elasticity. On the other hand, the plastic region in case of all figures is noticeably higher which indicates the increased plasticity of the composite materials.

(b) Ultimate tensile strength (UTS)

The Fig. 8 exhibited the impact of fiber addition on ultimate tensile strength of the studied composites.

From Fig. 8, it is observed that UTS of the composite decreases with addition of starch and after adding pulp it starts increasing. For some of the samples, UTS is higher than pure PVA sheet. This increase of UTS can be explained as, when pulp is incorporated into polymer matrix, interfacial bonds between the pulp fibers and polymer takes place. In this situation fiber orientation and loading plays an important role and fibers can take additional load. Sadhu et al. [23] reported that PVA have higher numbers of –OH groups which incurs greater strength along with better mechanical properties. Though, on the other hand, starch has a lot of hydroxyl groups, during acetylation many of them fails to increase the strength in starch. In our case, mixture of PVA and starch causes a bit modification of –OH groups which leads the lessening of strength of starch and therefore; addition of pulp increases the strength.

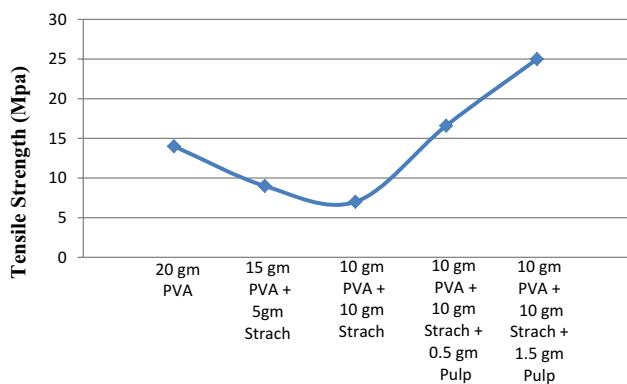


Fig. 8 Impact of fiber accession on ultimate tensile strength of the composite

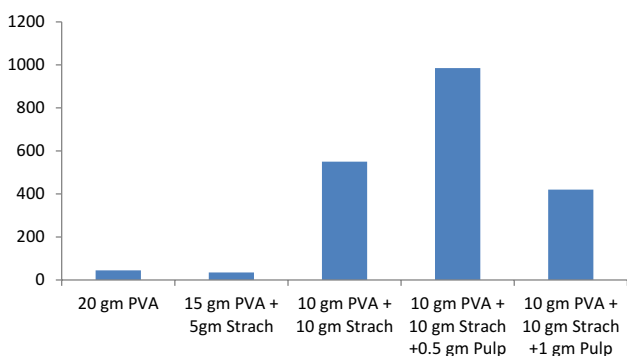


Fig. 9 Impact of fiber insertion on Young's modulus of the studied composites

(c) Young's modulus

Young's modulus is a well-known mechanical tract which measures the stiffness of a composite/solid material and established the relationship between stress and strain. Figure 9 views Young's modulus of the studied composite.

From Fig. 9 it can be said that Young's modulus of the composite enhanced with the addition of starch and pulp and thus stiffness of the composite also increases. From Fig. 9 it is clear that due to addition of 5 g starch there have not noticeable change of Young's modulus compared to pure PVA. But after insertion of starch and pulp this value is increased and it is probably because of better crosslinking among the polymers which enhanced the rigidity.

3.3 Thermal properties

Thermal property of the composite material is a very important and governing property for its practical implementation. To use composite materials in different application fields one needs a clear conception about the thermal property of the composite. For thermal stability and behavior analysis at higher temperature, TG, DTA and DTG have been performed for all samples in the absence and presence of starch and pulp (Figs. 10, 11, 12, 13, 14). The pure PVA and PVA containing other composites undergo three steps degradation which is summarized in Table 2.

From Fig. 10 one can observe that TG curve shows 6.5% weight loss which is due to moisture content. Also onset temperature, 50% degradation temperature and maximum slops are at 291.6 °C, 335.4 °C and 349.3 °C. Total degradation loss is 84.8%. The 334.5 and 425.5 values

Fig. 10 TG, DTA and DTG curves for pure PVA

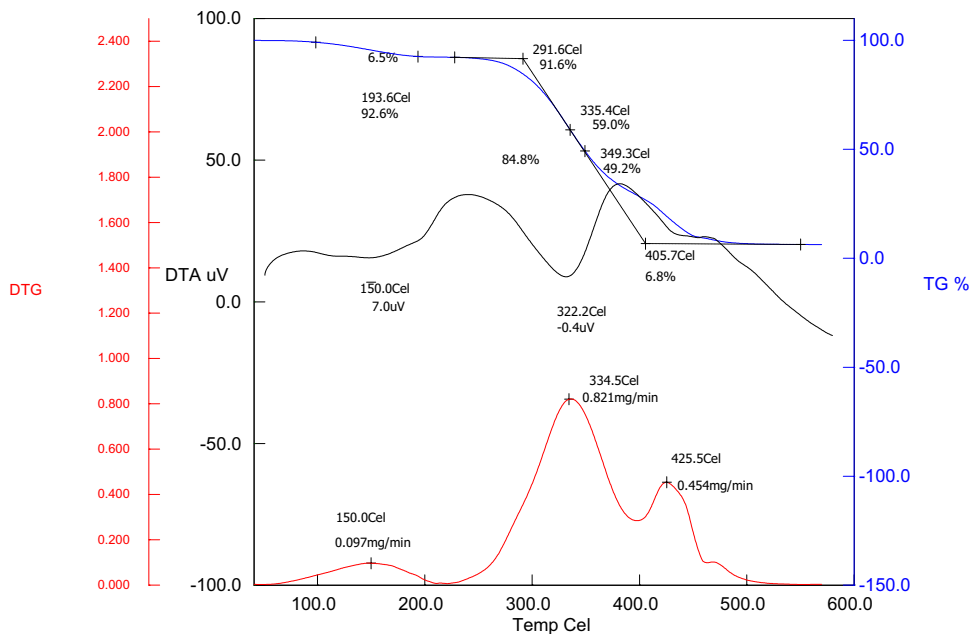


Fig. 11 TG, DTA and DTG curves for 15 g PVA + 5 g starch

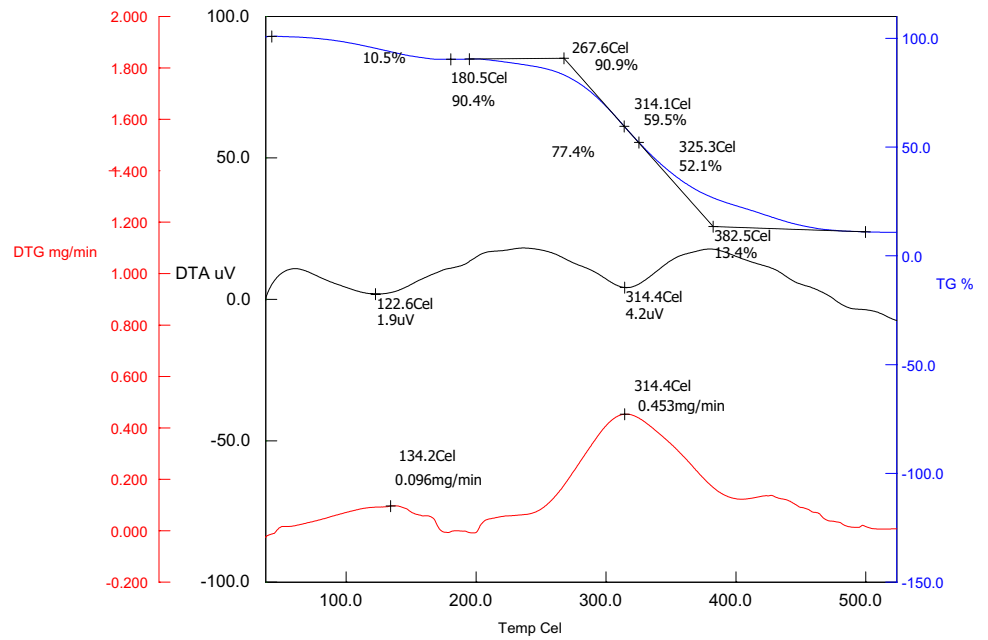
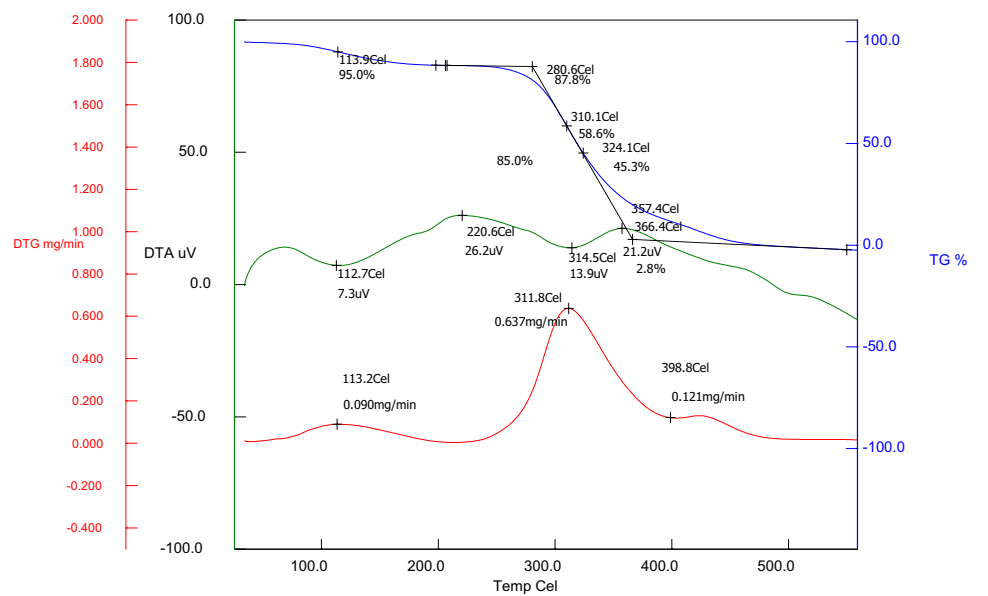


Fig. 12 TG, DTA and DTG curves for 10 g PVA + 10 g starch



are the maximum peaks in which maximum weight loss occurred in the third step. The Fig. 10 also views the residual mass 6.8% at 405.7 °C. Maximum weight loss of PVA was also observed in the second step by other researcher [23]. When starch was added in PVA, the first and second peaks were noticeably decreased from pure PVA values (150.0 °C and 334.5 °C respectively) while the third value approximately remained same (425 °C) [23]. The presence of starch reduced the thermal stability while the attendance of pulp enhances the thermal stability.

DTA curve shows endothermic peaks at 150.0 °C and 322.2 °C which are due to moisture and thermal

degradation respectively. The DTG curve exhibits peaks at 150.0 °C, 334.5 °C and 425.5 °C. This signal shows two steps degradation which is corresponded to lighter material and heavier material respectively. As discussed on Fig. 10, the corresponding characteristics of the composite materials are shown in Figs. 11, 12, 13 and 14 which is given below. The others figure (Figs. 11, 12, 13, 14) demonstrate that the 0.5 g pulp containing sample shows lowest TG values (74.4%) while DTA values shows lower thermal degradation value at 310.4 °C. DTG figures show two steps signal among which the second signal of pulp samples is noticeably higher than others.

Fig. 13 TG, DTA and DTG curves for 10 g PVA + 10 g starch + 0.5 g pulp

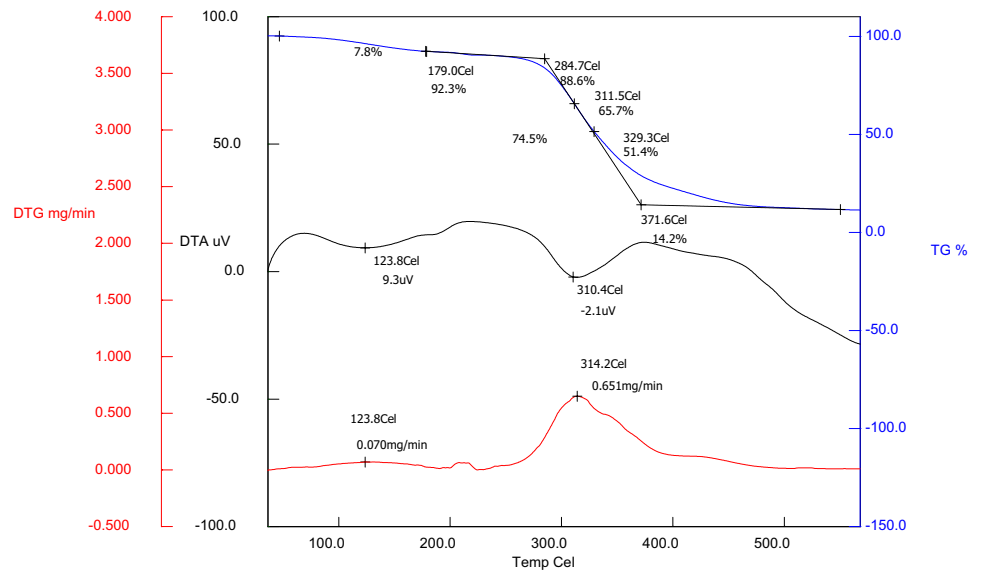


Fig. 14 TG, DTA and DTG curves for 10 g PVA + 10 g starch + 1.5 g pulp

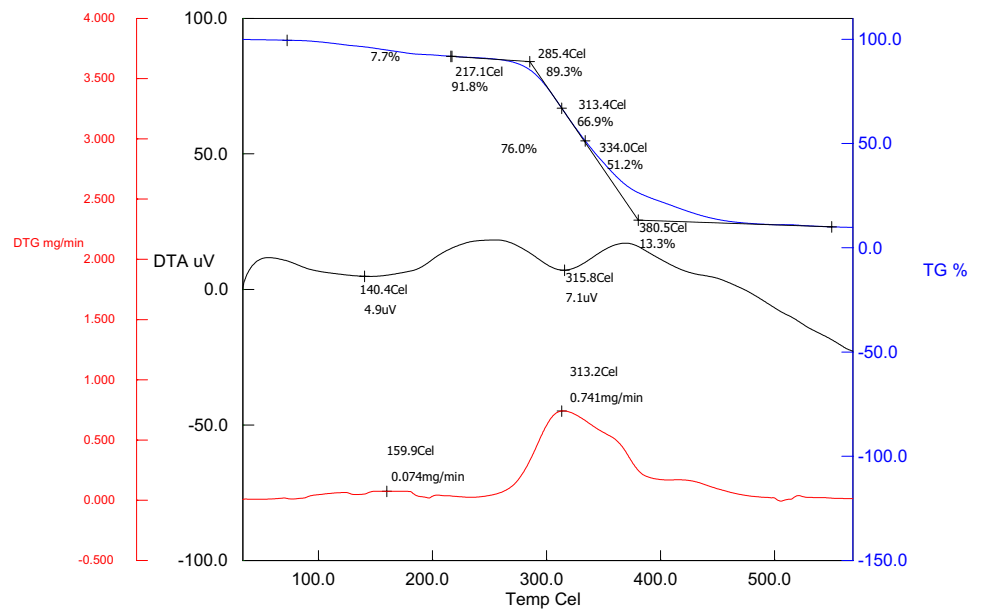


Table 2 TG and DTG results of PVA and PVS–starch composites

Sample	Peak-1	Slop (°C)	Peak-2	Slop (°C)	Peak-3	Slop (°C)	Residue left (%)
Pure PVA	150.0	291.6	334.5	335.4	425.5	349.3	6.80
15 g PVA + 5 g starch	134.2	267.6	314.4	314.1	425.0	327.3	13.4
10 g PVA + 10 g starch	113.2	280.6	311.8	310.1	425.0	324.1	2.80
10 g PVA + 10 g starch + 0.5 g pulp	123.8	284.7	314.2	311.5	425.0	329.3	14.2
10 g PVA + 10 g starch + 1.0 g pulp	159.9	285.4	313.2	313.4	425.0	334.0	13.3

4 Conclusions

In this current study the poly vinyl alcohol–starch composites reinforced with pulp samples were prepared, characterized, analyzed by means of various physical, mechanical and thermal mnemonics and discussed in detailed. Bulk density of the composite material decreased when it was reinforced by the addition of pulp in PVA–starch matrix. Water absorption of PVA–starch composite was increased with the increasing addition of pulp/fiber. UTS of the composite decreased with the insertion of starch and after adding pulp it started to increase. For some of the samples, UTS was higher than pure PVA sheet. Young's modulus of the composite rose with the addition of starch and pulp and thus stiffness of the composite also increases. Stress increased with the increase of strain and attained maximum value and then felled down. From the analysis of TG, DTG and DTA curves it is found that thermal stability of PVA is maximum, it decreased after the addition of starch and regain on addition of pulp in PVA–starch matrix. Therefore, due to better mechanical and physical properties, this composite can be utilized for manufacturing of various composite materials/products.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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