

To study the effect of boric acid modification on starch–polyvinyl alcohol blend wood adhesive

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Abstract Starch–polyvinyl alcohol blends with enhanced properties are achieved with cross-linking it with boric acid. These blends are characterized by FTIR and DSC. A film of starch and PVA blends were prepared by casting on glass plate. The effects of various factors such as increasing starch content, increasing amount of boric acid, on the performance properties like tensile strength, pencil hardness and thermal properties like glass transition temperature were studied. The results showed that the starch–polyvinyl alcohol films prepared by boric acid cross-linking had excellent mechanical, thermal properties and hardness of the film.

Keywords Starch · PVA · Cross-linking · Adhesive · Boric acid

Introduction

Polyvinyl alcohol (PVA) is one of the most important commercial water-soluble polymers. It possesses high crystalline structure (Othman et al. 2011). It is prepared by partial or complete hydrolysis of polyvinyl acetate. Physical and chemical properties including water solubility of PVA depend on the synthesis conditions and degree of hydrolysis (Klenina et al. 1970; Stauffer and Peppas 1992; Peppas 1975; Nambu 1984; Gadhave et al. 2017a, b).

Starch (S) is an abundant, inexpensive, renewable and biodegradable polymer. It is the second most abundant

natural polymer after cellulose and can be obtained mainly from the roots, stalks and seed of staple crops such as rice, corn, wheat, tapioca and potato where it is found in the physical form of granules (Kennedy and Fischer 1983). Each granule of starch contains several million amylopectin molecules accompanied by a larger number of smaller amylose molecules. Generally, cornstarch consists of 20–30% amylose and 70–80% amylopectin (Wang et al. 2012). Same as lignin, it is readily available biopolymer and extensively used in binders, glues and pastes (Sanjiv Kasbe et al. 2017; Gadhave et al. 2018).

Cross-linking is a common approach to improve the performance of starch for various applications. Starch and starch products have been cross-linked with cross-linking agents, such as phosphorus oxychloride, sodium trimetaphosphate, sodium tripolyphosphate, epichlorohydrin and 1, 2, 3, 4-diepoxybutane. (Gadhave et al. 2017a, b; Kaewtatip and Tanrattanakul 2008; Kim and Kim 2006; Meshram et al. 2009; Reddy and Yang 2009). The cross-linking helps to improve the mechanical properties and water stability of starch products (Xie et al. 2006; Kaur et al. 2012; Baishya and Maji 2014). In addition to cross-linking, blending of starch with synthetic polymers has also been considered to improve the performance of starch-based products. Films have been developed from starch blended with PVA (Gu et al. 2014; Olsson 2013; Sridach et al. 2013). Polymer blending is a well-used technique whenever modification of properties is required because it has an easy and straightforward procedure, and additionally, it is a low-cost process (Sarwono et al. 2014; Huang 2006; Zhang and Wang 2013; Li et al. 2014; Shi 2014). PVA is well suited to be blend with natural polymers since it is highly polar and readily soluble in water solution. Boric acid is a commonly used cross-linker for PVA for various applications (Yin et al. 2005). Most of the times,

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PVA is blended with starch to reduce the overall cost of the blend.

In this study, starch–PVA blend is prepared in water solution coupled with boric acid as a cross-linking agent to observe the effect on physical, mechanical and thermal properties of blend adhesive.

Experimental

Materials

PVA (degree of hydrolysis of 86.5–89%) was obtained from Kuraray Co., Ltd., India. Starch (Cornstarch amylose content 25–30%) was obtained from Sanstar Bio-polymer Ltd. These raw materials were kept in dry environment to avoid absorption of moisture. Boric acid used for the study was obtained from Sigma-Aldrich.

Preparation method

Cornstarch/ PVA blends (S/PVA) were taken in round bottom flask with water. Initially, temperature was kept at 60 °C with continuous overhead stirring at 175 rpm. The given amount of boric acid was added after 30 min as per Table 1. The temperature of the solution was raised to 92–95 °C and kept under stirring for 2 h. Then, the solution was cooled down to 25 °C and discharged into empty bottles for further study.

Set 1

In this set, a S/PVA(25:5) blend was made in water namely S-PVA-01, S-PVA-03, S-PVA-04 and S-PVA-07 by varying the amount of boric acid from 3.3, 2.4, 1.5 and 0, respectively, as shown in Table 1.

Set 2

In this set, a S/PVA(25:5) blend was made in water namely S-PVA-02, S-PVA-05, S-PVA-06 and S-PVA-08 by varying the amount of boric acid from 3.3, 2.4, 1.5 and 0, respectively, as shown in Table 1.

Set 3

In this set, an S/PVA blend was made in water by variable amount of starch and PVA. Boric acid concentration was kept constant at 3.3% for all experiments as shown in Table 1.

Table 1 Composition of the ingredients for the preparation of S-PVA blends

Blends	PVA	Starch	Boric acid	Water
S-PVA-01	25	5	3.3	70
S-PVA-02	20	10	3.3	70
S-PVA-03	25	5	2.63	70
S-PVA-04	25	5	1.65	70
S-PVA-05	20	10	2.4	70
S-PVA-06	20	10	1.5	70
S-PVA-07	25	5	0	70
S-PVA-08	20	10	0	70
S-PVA(STD)	30	0	3.3	70

Film casting method

Each prepared solution was cast into film on clear glass plate using a bar coater of 1000 microns. The cast film was cured for 24 h at ambient conditions. The cured film was used for testing.

Characterization and testing

Brookfield viscosity

Viscosities were measured using *Brookfield DVI Viscometer*.

pH of samples

A pH meter was used to measure pH of solutions by using *pH meter CL54 + of Toshcon Industries, India*.

Fourier transform infrared spectroscopy (FTIR)

PerkinElmer FTIR spectrum 100 was used to record the interaction of IR radiation with a sample measuring the frequencies at which the sample absorbs the radiation and the intensities of these absorptions.

Differential scanning calorimetry (DSC)

Glass transition temperature (T_g) of cast films was evaluated by PerkinElmer DSC using TA instrument Q100 DSC.

Pencil hardness test

Pencil hardness was tested as per ASTM D 3363 testing method to test the pencil hardness of the cast film.

Ultimate stress of films

Ultimate stress and ultimate strain of films were determined by using UTM Tinius Olsen 5ST.

Tensile strength

Tensile strength was checked on wooden strips and tested with the help of UTM Tinius Olsen H25KT. A uniform thin layer of adhesive was applied on to 20 mm × 10 mm area of one end of the steamed beech wood pieces. The adhesive-coated steamed beech wood pieces were assembled in such a way that the grains of two pieces were oriented in parallel. Each end of the sample was tightly held together in a vice and kept at room temperature curing for 4 h, 24 h and 48 h. The adhesives were then pulled apart at a controlled rate, and tensile strength for adhesive bond was recorded.

Results and discussion

Boric acid can form a strong interaction between hydroxyl groups. The trivalent boron atom in boric acid has an empty p orbital that is very electrophilic in nature, which causes it to rapidly react with various nucleophiles to form complexes, because the PVA and starch are both rich in hydroxyl groups, boric acid can be expected to cross-link them and further improve the adhesion between the starch and PVA blends. The cross-linking mechanism of boric acid with alcohol functional groups is given Fig. 1. The boric acid first forms the borate ion in the presence of water and further reacts with alcohol groups which give the complex borate structure. The borate structure reacts with the nearby hydroxyl-containing chain which can be either of starch or PVA, and finally, we get a cross-linked structure as shown in Fig. 1.

Viscosity

The cross-linking reaction between starch and PVA with boric acid caused an increase in the viscosity of solution as shown in Fig. 2.

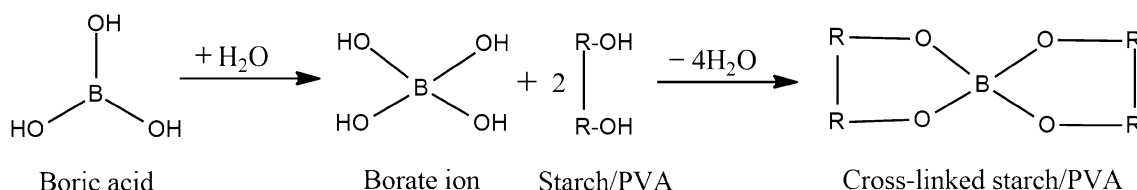


Fig. 1 Cross-linking mechanism of hydroxyl groups with boric acid

For set 1, as it is likely that two reactions occurred simultaneously: cross-linking between PVA and starch and hydrolysis of starch itself. Both these reactions may have led to an increase in viscosity. Viscosity is directly dependent on cross-linking reaction between starch and PVA with boric acid. For set 2, the viscosities on higher side as compared to set 1 because of high proportion of starch in blends. Nonetheless, the trend observed for set 2 is similar to set 1 due to decreasing order of concentration of boric acid. As for set 3, the boric acid concentration is constant but the increase in starch leads to increase in viscosity.

pH of solution

As the boric acid concentration increased, pH of solutions was decreased as shown in Fig. 3. In the presence of boric acid, starch had undergone hydrolysis reaction. The hydrolysis reduces the concentration of hydroxyl groups which decreases the pH. Set 1 and set 2 show the similar decrease in pH trend but a slight difference between them is observed due to the variation of starch content. In case of set 3, the pH is almost constant due increase in starch content containing hydroxyl groups; therefore, the decrease in hydroxyl groups has been compensated by starch molecules.

Fourier transform infrared spectroscopy (FTIR)

The width and shape of the entire peak for cross-linked samples were similar to those of starch–PVA non-cross-linked sample. This confirmed that the structure of hydrogen bonding in the cross-linked blends was similar to that in non-cross-linked starch–PVA blend but at the same time, a new structure of hydrogen bonding appeared due cross-linking reaction. As the cross-linking increased, the peak of –OH for cross-linked starch–PVA blends therefore moved to a lower wave number as shown in Table 2 (for set 1 and set 2). The same shifting was observed for both the sets as shown in Figs. 4 and 5.

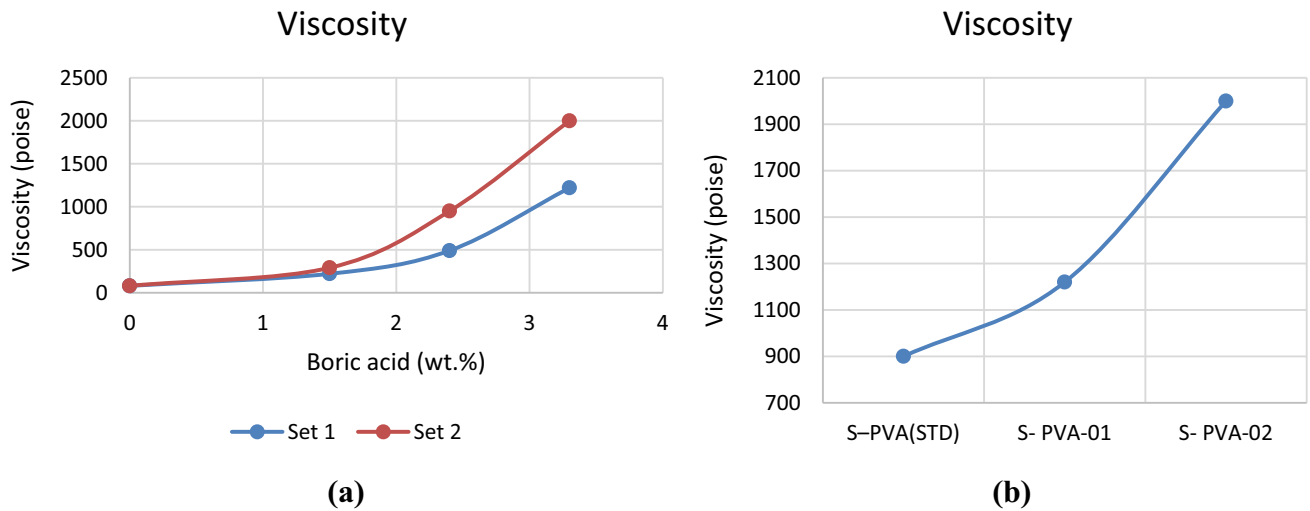


Fig. 2 Viscosity **a** at different concentration of boric acid given by set 1 and set 2 and **b** at different concentration of starch given by set 3

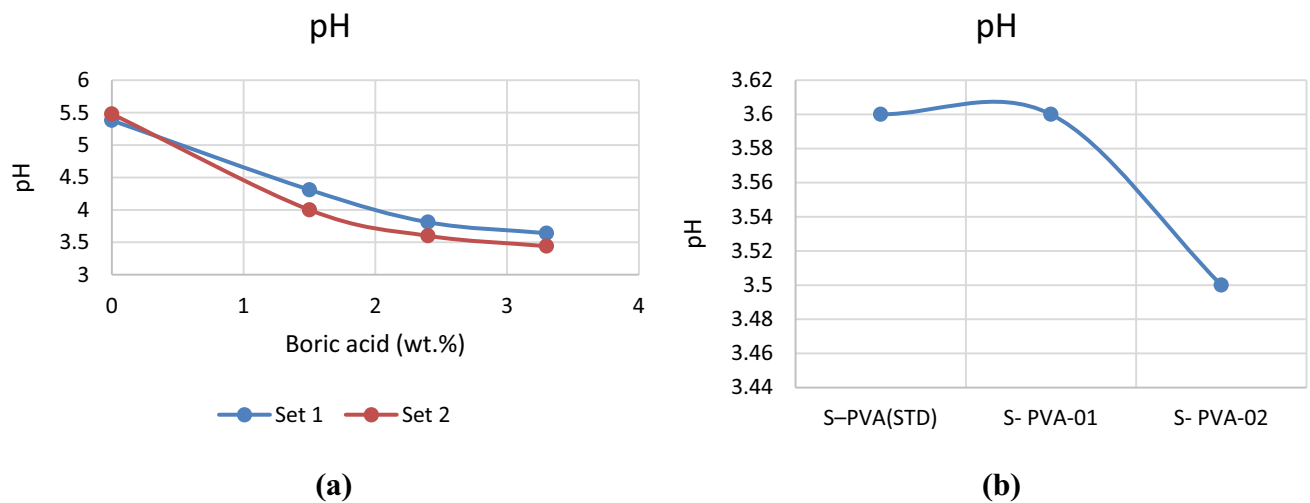


Fig. 3 pH **a** at different concentration of boric acid given by set 1 and set 2 and **b** at different concentration of starch given by set 3

Table 2 Position of hydroxyl peak in blends of set-1 and set-2 as observed in FTIR

Set-1		Set-2	
Blends	Wavenumber (cm ⁻¹)	Blends	Wavenumber (cm ⁻¹)
S-PVA-01	3300	S-PVA-02	3390
S-PVA-03	3340	S-PVA-05	3310
S-PVA-04	3400	S-PVA-06	3410
S-PVA-07	3411	S-PVA-08	3420

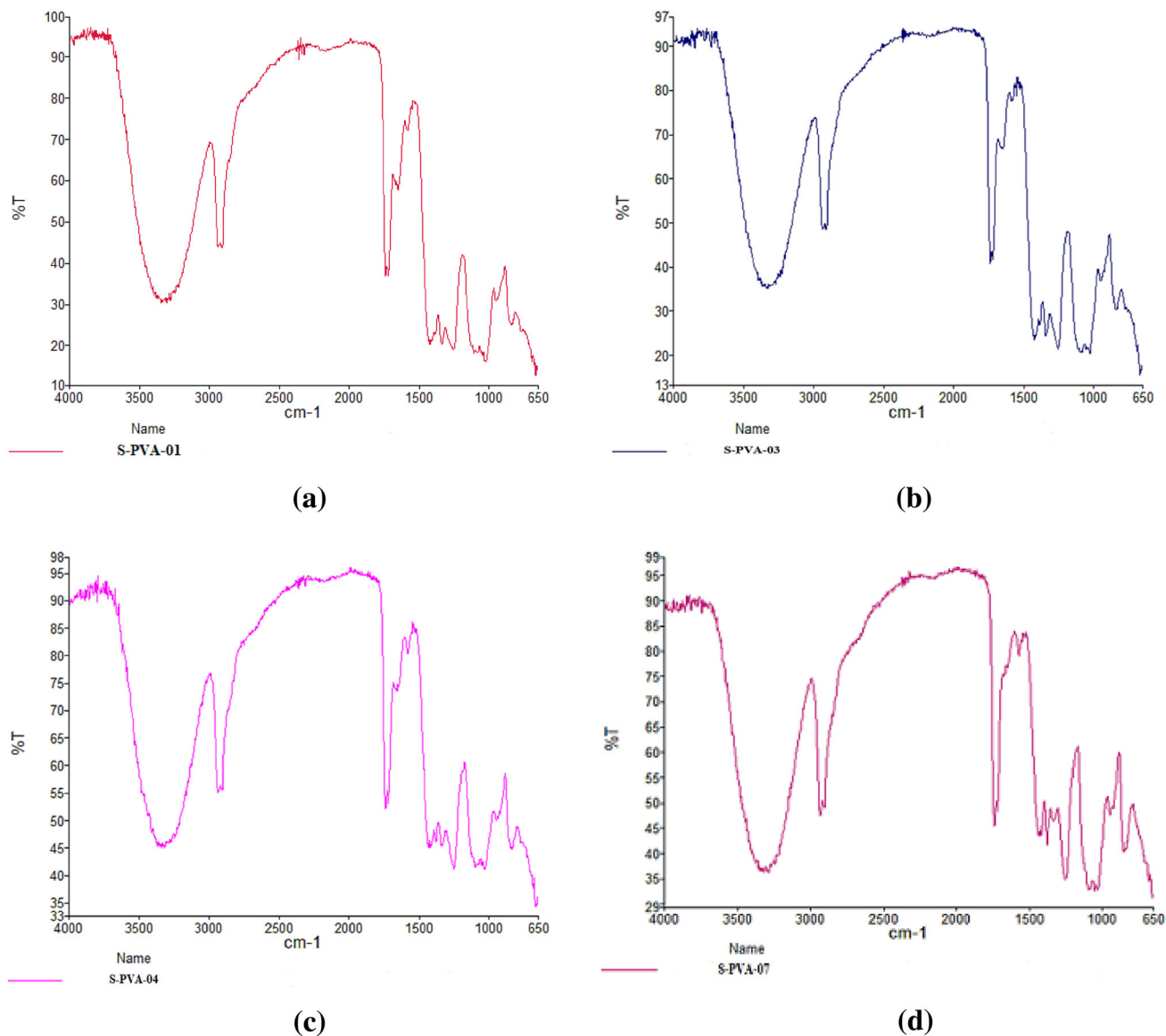


Fig. 4 FTIR curves of set 1 **a** S-PVA-01, **b** S-PVA-03, **c** S-PVA-04 and **d** S-PVA-07

Differential scanning calorimetry (DSC)

As the boric acid concentration increases, glass transition temperature of the polymer solutions was increased as shown in Fig. 6.

Reaction of boric acid with starch and PVA leads to cross-linking of two polymers. The cross-linking increases the molecular weight. This factor is responsible for increase in glass transition temperature of cross-linked films. The presence of more concentration of starch leads to more cross-linking due to high reactivity of starch hydroxyl groups as compared to PVA. The PVA hydroxyl groups are closely packed making it harder for cross-linker

to attack the site and for bond. The same trend is observed for set 3.

Pencil hardness of film

As the boric acid concentration increases, hardness of film was increased as shown in Tables 3 and 4. The PVA has flexible chains which can be easily bent as opposed to the starch which contains large rings in its chain. The rings impart stiffness to the final starch-based compounds. The similar trend is observed as the increase in boric acid leads to better cross-linking bringing the chains together forming a compact chain macromolecule. Due to cross-linking,

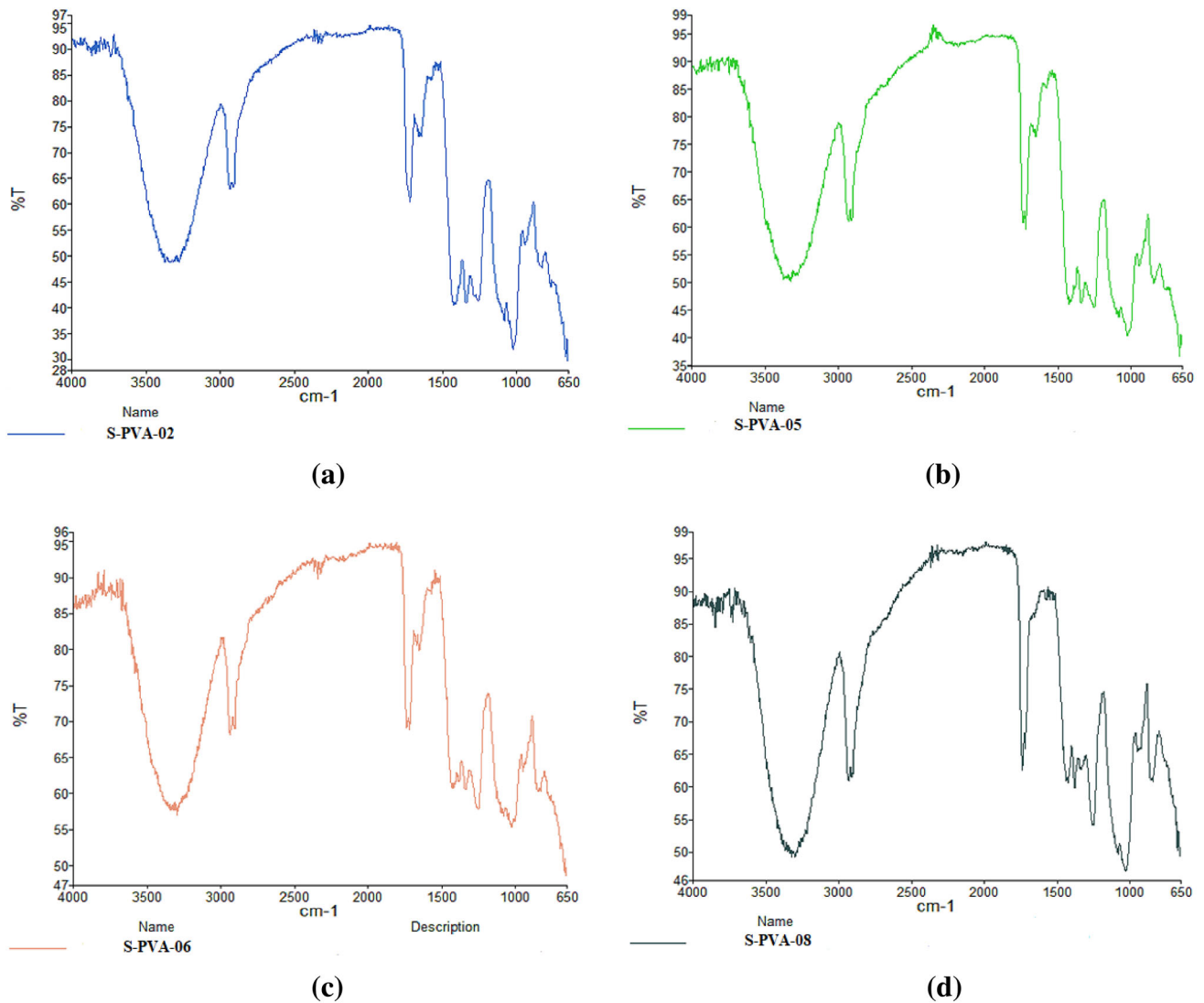


Fig. 5 FTIR curves of set 1 **a** S-PVA-02, **b** S-PVA-05, **c** S-PVA-06 and **d** S-PVA-08

friction from sharp pencil increased. As the starch concentration increases, hardness of film was increased as shown in Table 5. Due to cross-linking, the hardness has increased which is in proportion to the starch content.

Tensile shear strength

As the boric acid concentration increases, lap shear strength was increased as shown in Fig. 7.

Due to the cross-linking of PVA and starch molecule, the cohesion in the adhesive has increased. This cohesion imparts better interaction between chains, and closeness has led to reduction in the free volume thus there are more closely packed chains which interact with the wood surface. This has led to better interaction between wood surface and the adhesive which causes the increase in tensile

strength. Since the increase in boric acid increases the cross-linking so subsequently it can be inferred that the concentration of boric acid is directly proportional to tensile strength (as shown in Fig. 7a and b). The tensile strength development over time (from 4 to 48 h) is due to loss of water, which causes the adhesion.

In case of Fig. 7c, the increase in starch leads to better adhesion strength which is in line to the better interaction between the starch and cellulose derivatives present in the wood.

Ultimate stress of films

The boric acid cross-links the system consisting of PVA/S better than only PVA. The PVA hydroxyl groups are hard to react due to high intramolecular H bonding between

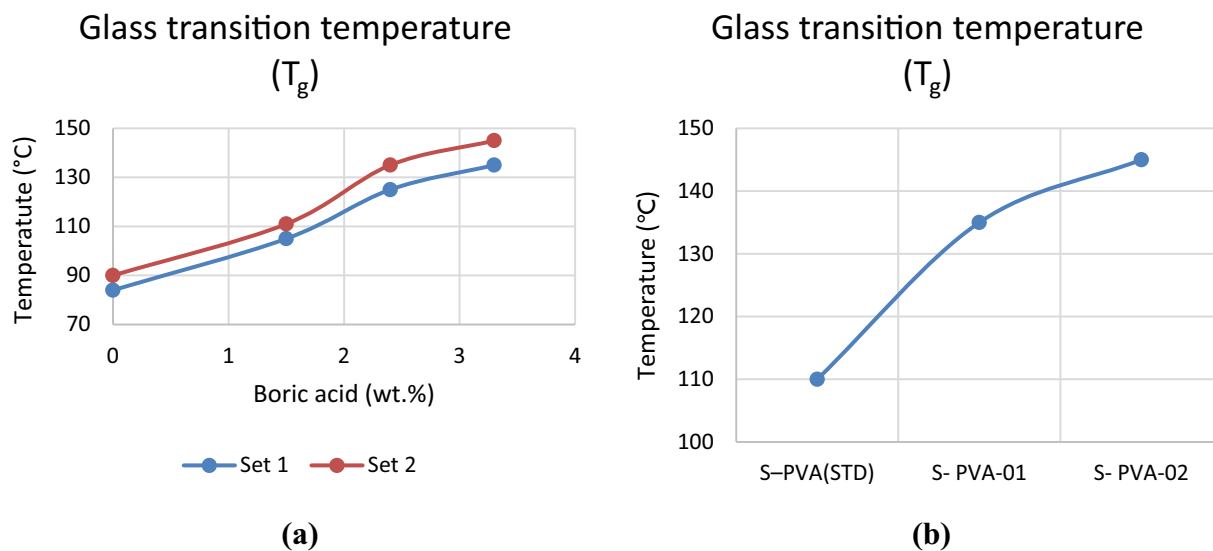


Fig. 6 Glass transition temperature (T_g) **a** at different concentration of boric acid given by set 1 and set 2 and **b** at different concentration of starch given by set 3

Table 3 List of tested parameters for set 1

Blends	Boric acid (wt%)	Viscosity (poise)	pH	T_g (°C)	Pencil hardness	Tensile shear strength (Kg/sq.in.)		
						4 h	24 h	48 h
S-PVA-01	3.3	1220	3.64	135	3H	295	410	465
S-PVA-03	2.63	490	3.81	125	3H	274	370	385
S-PVA-04	1.65	220	4.31	105	2H	202	310	310
S-PVA-07	0	80	5.38	84	HB	140	210	200

Table 4 List of tested parameters for set 2

Blends	Boric acid (wt%)	Viscosity (poise)	pH	T_g (°C)	Pencil hardness	Tensile shear strength (Kg/sq.in.)		
						4 h	24 h	48 h
S-PVA-02	3.3	2000	3.44	145	5H	310	450	490
S-PVA-05	2.4	950	3.6	135	5H	325	390	470
S-PVA-06	1.5	290	4	111	4H	205	340	340
S-PVA-08	0	80	5.48	90	H	175	195	205

Table 5 List of tested parameters for set 3

Blends	Viscosity (poise)	pH	T_g (°C)	Pencil hardness	Ultimate stress	Tensile shear strength (Kg/sq.in.)		
						4 h	24 h	48 h
S-PVA(STD)	900	3.6	110	H	44.4	250	380	435
S-PVA-01	1220	3.6	135	2H	38.3	295	410	465
S-PVA-02	2000	3.5	145	5H	35.9	310	450	490

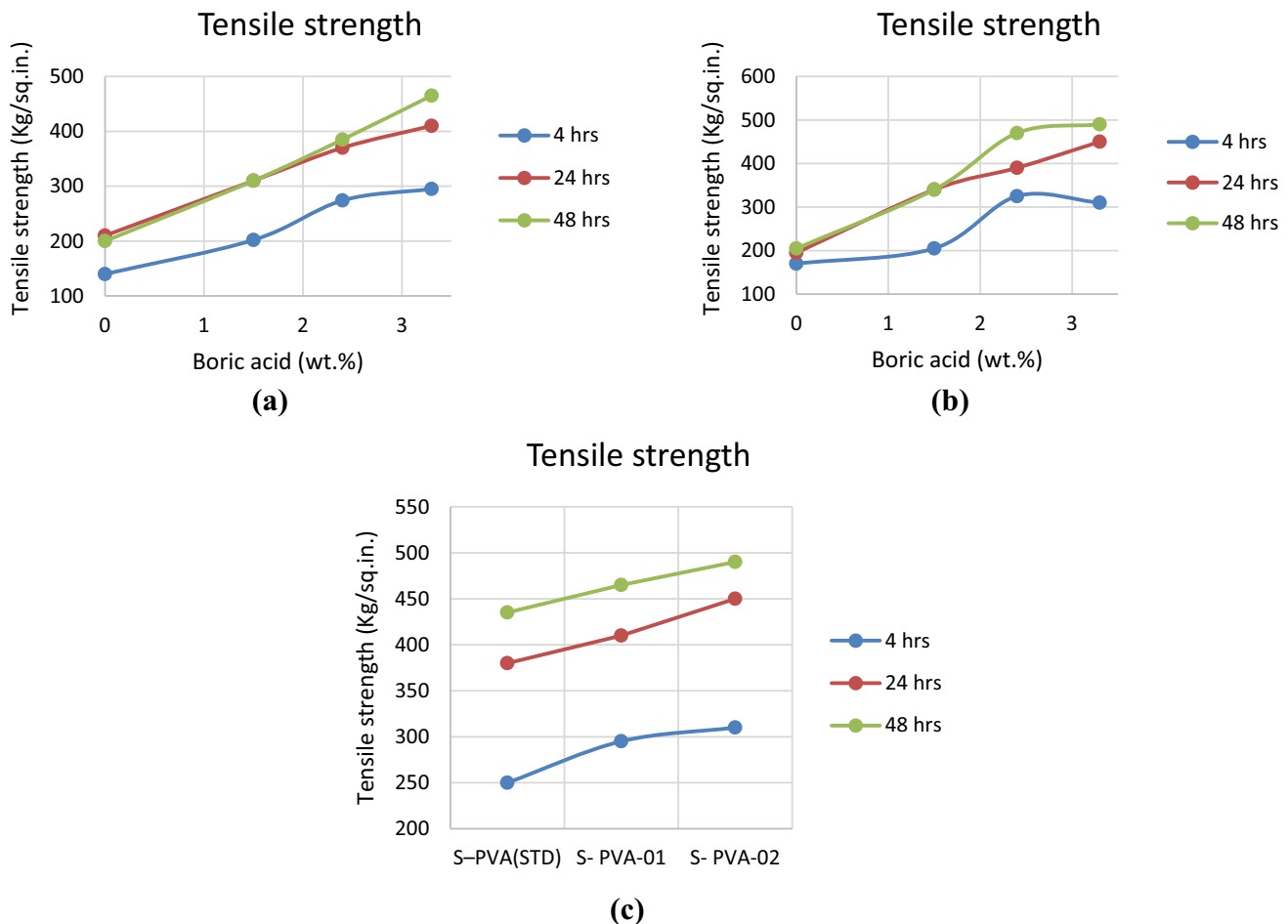


Fig. 7 Tensile shear strength values after 4 h, 24 h and 48 h of **a** set 1, **b** set 2 and **c** set (3)

them. In case of starch, they are not that closely packed which makes them easier to cross-link as compared to PVA chains. Subsequently, it is observed in Table 5 and the increase in starch has led to better ultimate stress in films.

Conclusions

Boric acid acts as cross-linking agent for starch–PVA blend, and this has led to enhancement in mechanical and thermal properties of the blend. In case of constant ratio of starch to PVA, cross-linking showed direct proportionality to the concentration of boric acid. Additionally, an increase in ratio of starch to PVA in a blend with constant concentration of boric acid resulted in increase in the mechanical and thermal properties. The analytical tests of FTIR and DSC supported the notion of cross-linking. The decrease in pH showed the reduction of hydroxyl groups due to cross-linking.

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