Cross-linking of Polyvinyl Alcohol/Starch Blends by Epoxy Silane for Improvement in Thermal and Mechanical Properties

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Effects of cross-linking were examined for polyvinyl alcohol, starch, and their blends. The blends were prepared using various compositions of pure starch, pure polyvinyl alcohol (PVOH), and a combination of both starch and polyvinyl alcohol. The cross-linker used for this study was epoxy silane. The blends were tested against the canarium wood substrate for tensile strength. Further properties, such as viscosity and wet tack, were also evaluated. Analytical tests such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) demonstrated the phenomenon of cross-linking, having shown an increase in glass transition temperature (*T*g) and area under the curve of tan delta. The efficient and novel cross-linking of hydroxyl groups present in the starch and PVOH contributed to better adhesion on the wood substrate and also better cohesion between the chains.

Keywords: Starch; Polyvinyl alcohol; Epoxy silane; Citric acid; Cross-linking

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INTRODUCTION

Polyvinyl alcohol (PVOH) has a high degree of orientation and consequently, high crystallinity in its structure (Klenina *et al.* 1970; Nambu 1984; Stauffer and Peppas 1992; Othman *et al.* 2011; Gadhave *et al.* 2018a,b). PVOH has various uses in the paper, textile, and adhesive industries (Sanjiv *et al.* 2017; Prosanov *et al.* 2018). Starch is another polymer that is highly similar to PVOH in structure and naturally sourced with minimum cost for processing (Immelman *et al.* 1993).

Starch is one of the most abundant biomass materials in nature (Chen *et al.* 2017). It has many advantages, such as being environmental friendly and having low cost, renewability, abundant supply, and availability. It is widely used in the food, paper-making, fine chemicals, and packing material industries, *etc.* (Wu *et al.* 2006). Chemically modified starches have even more uses because they exhibit excellent physicochemical properties that are markedly altered from those of their parent starches.

The bonding capacity of native starch is insufficient for gluing wood; starch-based wood adhesives lack high bonding strength and water resistance. By adding cross-linkers such as isocyanates, formaldehyde based resin, which exhibits water resistance, extremely low formaldehyde emission, and comparable performance properties, can be achieved. In another study, it was stated that different cross-linkers, such as glutaraldehyde and glyoxal can be used in starch-based wood adhesives (Gao *et al.* 2011). Cellulose nanofiber (CNF) also has been used as a reinforcement in a thermoplastic starch (TPS) matrix to improve performance properties (Fazeli *et al.* 2018).

The bonding strength and thermal properties of the adhesive can be improved significantly by adding a silane coupling agent and olefin monomer (Zhang *et al.* 2015). Silanes are recognized as effective coupling agents extensively used in adhesives formulations. Various silanes functionalized with methyl, epoxy, amine, and phenyl groups were also incorporated to adjust the hydrophobicity and mechanical flexibility. Silane coupling agent is commonly used to improve the interfacial interaction between starch hydroxyl groups (Kim *et al.* 2010; Nakatani *et al.* 2010). The acyloxy group in KH570 was used to improve the compatibility and bonding strength of starch based wood adhesive. For the adhesive, organo-silanes can combine with starch to form a very thin coat, and the C-Si-O- connects with the hydrogen bonding on the surface of wood (Heo and Park 2012; Gadhave *et al.* 2017; Gadhave *et al.* 2018c).

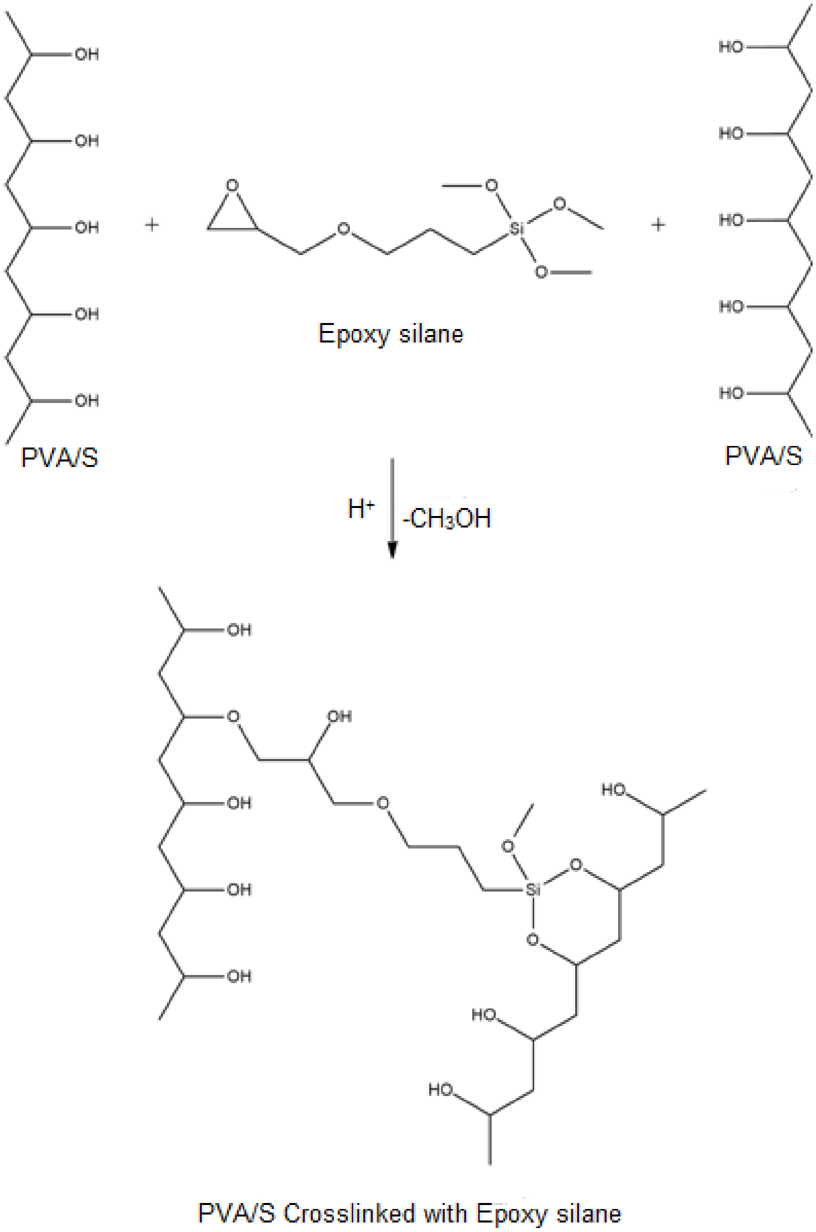

Fig. 1. Cross-linking mechanism of PVOH/S with epoxy silane

Alkoxy silanes react directly with –Si-OH groups of silica, forming –Si-O-Si- bonds without pre-hydrolysis (Salon *et al.* 2008). However, silanes do not undergo the same reaction with the hydroxyl groups of starch/PVOH, even at high temperature. This has been attributed to the lower acidity of starch/PVOH hydroxyl groups compared with silanol. In addition, starch/PVOH is generally un-reactive to many chemicals, and the OH groups have very low accessibility (Hill *et al.* 2004). Thus, an optional strategy is to activate the alkoxy silane by hydrolyzing the alkoxy groups, thereby forming the more reactive silanol groups (Donath *et al.* 2006). As a result, silanol may react with the hydroxyl groups of fibers or condense themselves on the surfaces of fibers and/or in the cell walls, forming the macromolecular network shown in Fig. 1 (Abdelmouleh *et al.* 2002).

Here the epoxy-functional silane is used as a coupling agent or cross-linker for starch and PVOH. Since both the epoxy and the silanol group are chemically reactive, it is possible that there is interaction between starch and PVOH with epoxy silane. This paper reports on the study of crosslinking of epoxy silane with PVOH and starch in aqueous solution and investigated the bonding strength and thermal properties of a starch-based wood adhesive prepared by the addition of the epoxy silane as crosslinking agent.

EXPERIMENTAL

Materials

PVOH (degree of hydrolysis of 86.5 to 89%) was obtained from Kuraray Co., Ltd., Mumbai, India. Normal corn starch [moisture content 10 to12%; amylose content 25 to 30 % (w/w, dry basis); purity>99%] was obtained from Sanstar Bio-polymer Ltd. (Gujarat, India). Citric acid was obtained from Sigma-Aldrich (Mumbai, India). These raw materials were kept in a dry environment to avoid absorption of moisture from the surroundings. Epoxy silane was obtained from Momentive, Bangalore, India.

Preparation method

Corn starch-PVOH blends (S:PVOH) were made as shown in Table 1 at a temperature of 95 to 97 °C for 2.5 h with continuous stirring using an overhead stirrer. Dissolution in water was performed in the presence of citric acid and epoxy silane, as shown in Table 1. The solution was cooled to 25 °C.

Table 1. Preparation of Various Adhesive Compositions with Epoxy Silane

Sample	SM- 01 (%)	SM- 02 (%)	SM- 03 (%)	SM- 04 (%)	SM- 05 (%)	SM- 06 (%)	SM- 07 (%)	SM- 08 (%)
Starch	18	0	10	18	10	18	0	10
PVOH	0	18	8	0	8	0	18	8
Citric Acid	0	0	0	0.5	0.5	0	0	0
Epoxy silane	0.5	0.5	0.5	0.5	0.5	0	0	0
Water	82	82	82	82	82	82	82	82

Characterization and Testing

Brookfield viscosity

Viscosities were measured using a Brookfield DV1 Viscometer at 20 rpm after keeping the samples in an incubator for 3 h at 30 °C.

Wet tack

Wet tack was calculated using Probe tack analyzer (Rohit Instruments, India). A few grams of sample adhesive were placed on the metal surface of the machine. It was assumed that the sample was still wet and no drying took place. A metal cylinder then approached the sample downward at a speed of 5 mm/min. The sample was squeezed between the cylinder and the metal surface. The cylinder touched the surface and again lifted up at a speed of 5 mm/min. The adhesive between the two resisted the upward movement of cylinder, thus the force of resistance was calculated in gram force (gmf) and termed as wet tack.

Tensile shear strength

Tensile strength was checked by a UTM Tinus Olsen H25KT (India). A constant amount of adhesive was applied on to a 20 mm × 10 mm area of one end of the steamed beech wood pieces (Fig. 2) in such a way that it properly wetted the surface. 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 held by vice grips and pulled apart at a controlled rate and tensile strength. Adhesive bond results were recorded.

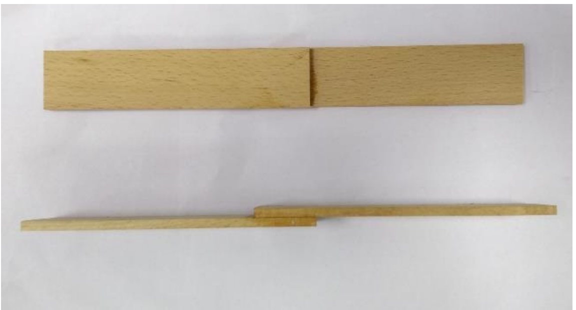

Fig. 2. Steamed beech wood to steamed beech wood assembly

Dynamic mechanical analysis (DMA)

DMA was performed using a DMA Q800 (India). A thin film of 200 μm was first prepared by applying it on a PTFE sheet. The film was cured at room temperature for 24 h. After curing, the film was peeled from the surface and kept in the DMA sample holder. A sinusoidal stress was applied, and the strain in the material was measured as the complex modulus. The temperature of the sample or the frequency of the stress are often varied, leading to variations in the modulus; this approach can be used to locate the glass transition temperature of the material, as well as to identify transitions corresponding to cross-linking between the molecules.

Differential scanning calorimetry (DSC)

The glass transition temperature (T_g) of cast films was evaluated by PerkinElmer DSC using TA instrument Q100 DSC (Mumbai, India). An oxygen- free nitrogen stream of 40 mL/min was maintained through the cell during the measurement. The scan was performed at a rate of 10 °C /min. A plot of heat flow against temperature was obtained in DSC, from which the T_g was determined.

RESULTS AND DISCUSSION

The batches SM – 01 and SM – 06 were of pure starch, and as a result, they achieved gelation after completion of the reaction. Therefore, the data for those two batches were unavailable.

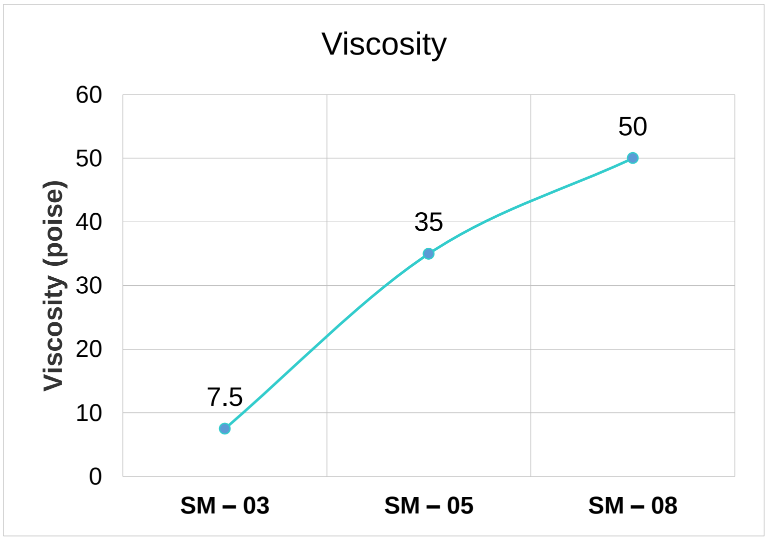

Fig. 3. Viscosity at increasing concentration with epoxy silane

Viscosity (RT)

The cross-linking reaction between PVOH/S with epoxy silane caused an increase in the viscosity of the glue, as shown in Fig. 2. The presence of citric acid while cross-linking with silane increased the viscosity (SM – 05), as the citric acid helped to open starch molecules and to form ester linkages at temperatures well above 95 to 97 °C (Yu *et al.* 2005). This allowed the silane to create a networked structure. Due to the absence of citric acid in SM – 03, the crosslinking did not occur as efficiently, which caused the subsequent decrease in viscosity. The viscosity of pure sample SM – 08 was greater (Table 2). The closer packing of the chains due to complex formation led to greater stiffness and modulus (as observed in DMA studies in the following section). Chain entanglement is one of the reasons for increase in modulus, which proves the gradual increase of viscosity.

The viscosity for pure PVOH solution (SM – 07) was comparable to the PVOH solution containing epoxy silane (SM – 02). The slight decrease was due to the plasticizing effect of epoxy silane. The pure starch solution had cross-linked forming the gel (SM - 06), while the presence of only epoxy silane yielded the same result (SM - 01). Only the sample containing both the epoxy silane and citric acid had a certain flowability due to gelatinization of starch by citric acid and the role of unreacted citric acid acting as plasticizer (SM - 04).

Table 2. Viscosity Data

Sample	Viscosity (poise)
SM – 02	2.5
SM – 03	7.5
SM – 04	1168
SM – 05	35
SM – 07	3.5
SM – 08	50

Wet Tack

Wet tack force data provides information about the internal cohesion in an adhesive. It shows a similar trend as observed in the case of viscosity. The crosslinking reaction between PVOH/S with epoxy silane caused an increase and then decrease in the wet tack force of the glue, as shown in Fig. 4. The series of starch and PVOH in 10:8 ratio, *i.e.* SM – 08, SM – 05, and SM – 03 had less wet tack values than the series with no starch, *i.e.* SM – 02and ST – 07. This effect was due to the better cohesion in PVOH chains as compared with starch. The complete starch solution having both epoxy silane and citric acid showed the least wet tack (SM – 04), which was due to the weak cohesion in starch compared with PVOH (Table 3).

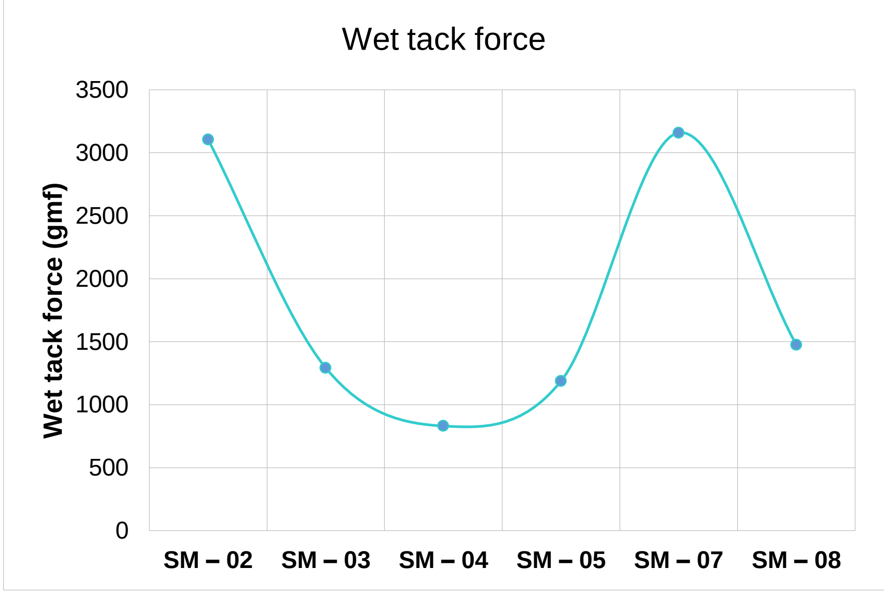

Fig. 4. Illustration of wet tack force for SM series

Table 3. Wet Tack Data

Sample	Wet Tack Force (gmf)
SM – 02	3105
SM – 03	1292
SM – 04	831
SM – 05	1388
SM – 07	3159
SM – 08	1475

Tensile Shear Strength (Can to Can)

The crosslinking reaction between PVOH/S with epoxy silane caused an increase the tensile strength of the glue, as shown in Fig. 5 and Table 4. SM – 04 had the least tensile strength of all samples, as it was the pure starch solution containing the epoxy silane and citric acid. Starch has much less strength than PVOH while bonding onto the wood substrate (Gadhave *et al.* 2018b).

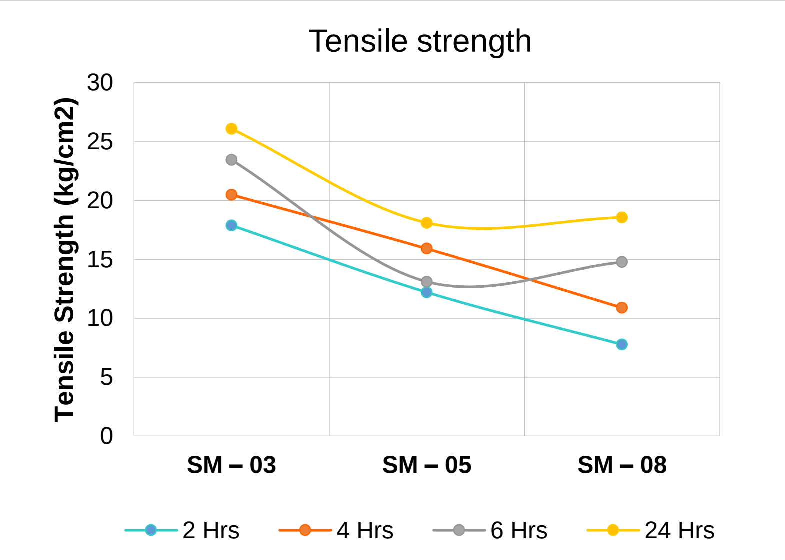

Fig. 5. Illustration of tensile strength for SM-03, SM-05, and SM-07

Table 4. Tensile Shear Strength Data

Tensile Shear Strength (kg/sq. cm)				
Sample	**2 h**	**4 h**	**6 h**	**24 h**
SM – 02	8.04	11.36	13.52	16
SM – 03	17.88	20.48	23.44	26.08
SM – 04	5.24	7.68	9.88	13.44
SM – 05	12.2	15.9	13.1	18.1
SM – 07	9.62	21.9	24.3	28.7
SM – 08	7.76	10.88	14.76	18.56

The highest tensile strength was observed for SM-03 having only epoxy silane, as opposed to the SM – 05, which had both epoxy silane and citric acid. This phenomenon indicated that the citric acid helped in the opening of starch, but the remaining unreacted citric acid molecules present in the system acted as plasticizer, hindering H-bonding. The result was lesser cohesion, and in turn, the tensile failure occurred early. The control sample SM – 08, which had no epoxy silane and citric acid, showed the least tensile strength.

The pure PVOH sample, SM – 07 had greater tensile strength than the PVOH with epoxy silane, SM – 02. This was due to the unsuccessful attempt of silane in cross-linking PVOH. The PVOH had very strong H-bonding, which kept its chains intact. Because the silane molecule could not penetrate between those chains, cross-linking did not happen. The epoxy silane remained in the system inhibiting the existent H-bonding and weakening it.

Dynamic mechanical analysis

The three samples showed major transition corresponding to polyvinyl alcohol at 90 °C. The storage modulus curve showed the highest value for SM-03 throughout the glassy and rubbery region. This result confirmed the cross-linking effect on the hydroxyl groups of starch and PVOH, which led to an increase in storage modulus. The SM-05 curve had less modulus than SM-08 initially at the glassy region, and following the transition temperature, it had higher modulus than SM-08. This change was mainly due to the presence of citric acid in SM-05; the citric acid helped to gelatinize starch, which increased its storage modulus in the rubbery region (Fig. 6).

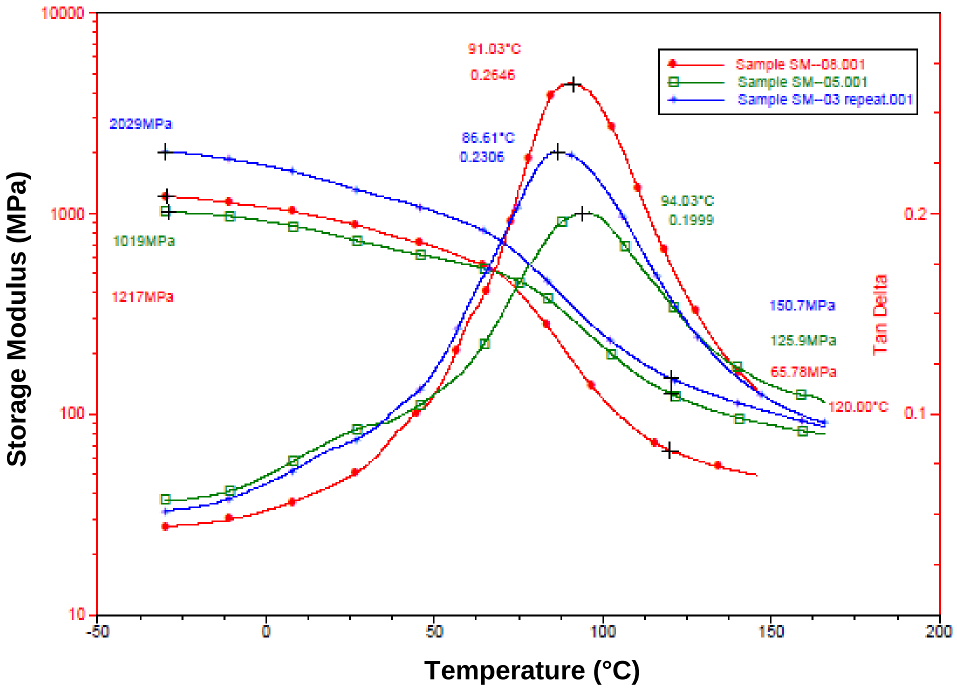

Fig. 6. Overlaid thermogram of storage modulus (*E*') and tan delta for all five samples is given

The cross-linking was shown by tan delta curve where there was an evident shift in the peak of the curve towards the higher temperature (from 91.0 to 94.0 °C).The shift represented the transition temperature change, which was caused by the cross-linking of silane (Fig. 6).

Differential scanning calorimetry

The crosslinking reaction between PVOH/S with epoxy silane caused an increase in the glass transition temperature of the glue, as shown in Table 5. Comparing the glass transition temperature for (Starch: PVOH = 10:8 series) SM-03, SM-05, and SM-08, it was the T_g for SM-03 was almost equivalent to SM-05. This result suggested that the presence of citric acid in the SM-05 had little effect on the glass transition temperature. Although the T_g change was notable while comparing both SM-03 and SM-05 with SM-08, the T_g for SM-08 was on lower side of other two compositions. From this, the role of silane in cross-linking of starch an PVOH was evident. While comparing the T_g of SM-02 and SM-07, it was evident that the cross-linked SM-02 had greater T_g than the non-cross-linked SM-07.

Table 5. Glass Transition Temperature Data

Sample	T_g (˚C)
SM – 02	71
SM – 03	72.5
SM – 04	-
SM – 05	73
SM – 07	66.7
SM – 08	70.4

CONCLUSIONS

1. Using epoxy silane acting as a cross-linker for PVOH and starch led to an increase in the thermal and mechanical properties.
2. The viscosity showed a major drop due to presence of epoxy silane only, but combining it with citric acid helped to stabilize the viscosity to a certain extent.
3. The wet tack values remained comparable for each PVOH/S composition.
4. Tensile strength showed a considerable increase in the properties of the blends due to better adhesion to the wood substrate.
5. An increase in area under the tan delta curve combined with greater storage modulus at 110 °C confirmed the cross-linking mechanism. The T_g values were shifted towards the higher temperature due to cross-linking.
6. PVOH/starch cross-linking can increase the performance properties of a blend without compromising its original properties.

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