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Cross-linking of polyvinyl alcohol/starch blends by glutaraldehyde sodium bisulfite for improvement in thermal and mechanical properties

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Abstract

Crosslinking approach is evaluated for enhancing properties of polyvinyl alcohol (PVA) and starch (S) blend, for this a novel crosslinker glutaraldehyde sodium bisulfite (G) is introduced. The hydroxyl groups of PVA and starch reacts with glutaraldehyde sodium bisulfate via formation of acetal bonds, thus crosslinking could take place. Various analytical methods were carried to observe the effect of crosslinking of glutaraldehyde sodium bisulfite such as differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), and contact angle measurement. Reduction in hydrogen bonding of PVA and starch were observed at higher dosages of glutaraldehyde sodium bisulfite. As the amount of crosslinker increased, blend showed better cohesion and was evidenced by the increase in glass transition temperature (Tg) and storage modulus. Compared with the non-crosslinked sample, cross-linked blends showed better thermal and mechanical properties.

1. Introduction

Limited availability of petrochemical resources, with its negative impact on the environment made researchers investigate for alternatives. The introduction of biopolymers and biomaterials opened up new possibilities in every filed. Among various biopolymers, extensive research have been reported on on polysaccharides such as cellulose and starch [1]. These biopolymers have the advantage of abundance, renewability, and opportunity for modification; hence can be tailor-made for specific applications [2]. Starch (S) being a polysaccharide biopolymer is obtained from plant sources, finds huge application due to the inexpensive and easy availability [3, 4]. The reduced mechanical and thermal properties of starch limits its usage [5]. For enhancing the properties of biopolymers, chemical modification have found to be a good option [6]. The presence of hydroxyl groups allows the easy blending of starch with other polymers, which includes, polyvinyl alcohol [7], tannin [8], and isocyanates [9] and crosslinking the system have received much attention.

Polyvinyl alcohol (PVA) is a biodegradable polymer having good strength and mechanical properties with durability and high crystalline structure [10], which have free hydroxyl groups. The high cost of PVA hinders its application, to reduce the cost and enhance biodegradability, PVA and starch are blended [11]. Since PVA and starch are polar polymers, the blend of the two polymers (PVA/S) found to have synergistic interaction with physical bonds [12]. The degree of hydrolysis and synthesis controls the physical and chemical properties of PVA [13]. Crosslinking is a common approach to improve the properties of PVA, and many research works have reported on various crosslinkers for PVA, including boric acid, glyoxal, formaldehyde, and glutaraldehyde [14–16].

The work presented here investigates the effect of crosslinking on thermo- mechanical properties of PVA/S blend. A novel crosslinker, glutaraldehyde sodium bisulfite, is introduced for this purpose. It is expected that hydroxyl groups from PVA and starch react with glutaraldehyde sodium bisulfite via the formation of acetal bonds [17, 18]. Glutaraldehyde sodium bisulfite cross-links PVA/S by reacting with the hydroxyl groups and introduces intermolecular bridges between the polysaccharide chains and PVA. The crosslinked blend is expected to have enhanced thermo- mechanical properties and can be a potential candidate for bio-based adhesive applications.

2. Material and Methods

2.1. Materials

Polyvinyl alcohol (PVA) (with 87- 89 % degree of hydrolysis) were purchased from Kuraray cooperative limited, India. Maize starch (amylose content of 25-30 %) was purchased from Sanstar limited. The crosslinker, Glutaraldehyde sodium bisulfite (G) was procured from Sigma-Aldrich. Care was taken to avoid moisture absorption for all the chemicals.

2.2. Method of preparation

The blends of PVA and starch were prepared by mixing in water and transferred into a sealed kettle. The mixing sample is heated to 60° C under stirring at 175 rpm. Crosslinker glutaraldehyde sodium bisulfite (G) was added at concentrations of 0.5%, and 1% to the system, and the amount of PVA, starch, and water are shown in Table 1. For comparison, a blank sample was also prepared. After the addition of crosslinker, the reaction temperature was increased to 90-95° C, with continual stirring for 2.5 hrs. The prepared samples were then brought to room temperature and labeled as PVA/S-G 0.5 for the blend with 0.5% glutaraldehyde sodium bisulfite, similarly PVA/S-G 1 for 1% crosslinker and PVA/S for blank sample for analysis and characterization.

Table1: Composition of blends with and without addition Glutaraldehyde sodium bisulfite

	Blends	**PVA (g)**	**Starch (g)**	**Glutaraldehyde sodium bisulfite(g)**	**Water (g)**
Formulation	**PVA/S**	10	8	0	82
	PVA/S-G 0.5	10	8	0.5	82
	PVA/S-G 1	10	8	1.0	82

2.3. Viscosity analysis

Viscosity analysis of the samples was carried out with the aid of a Brookfield DV1 viscometer. The samples were conditioned at 30° C prior to the measurement.

2.4. Fourier Transform Infra-Red Spectroscopy (FTIR) analysis

A PerkinElmer FTIR spectrum 100 instrument was employed for obtaining spectra of prepared blend samples. Using an applicator, thin films of crosslinked blends and blank sample were casted before analysis.

2.5 Differential Scanning Calorimetry (DSC)

To study the thermal properties and the glass transition temperature (Tg) of the samples, DSC is done. For this, a Perkin Elmer instrument Q100 was employed.

2.6 Dynamic mechanical analysis (DMA)

DMA was performed using a thermal analytical instrument, DMA Q-800 of TA instruments. A 200-micron thin films of samples were prepared by applying it on a poly tetra fluoro ethylene (PTFE) sheet using an applicator. The films were then kept at room temperature for 30 hrs. and dry films were produced. With the help of a sample cutter, the dried films were cut in a specific dimension and loaded in the DMA sample holder. The viscoelastic nature of polymers can be studied by DMA analysis. By varying the temperature or frequency of stress applied in the specimen, the corresponding strain is measured, which correlates with the glass transition temperature (Tg) and the presence of crosslinking in the sample.

2.7 Contact angle measurement

The contact angle of water on the surface of samples were evaluated to study the hydrophobic or hydrophilic nature of the sample. Rame-Hart Goniometer instrument was used for the contact angle test.

2.8 Rheology measurement

Rheology was studied with DHA-2 Rheometer from TA Instruments, Pidilite R & D center, Mumbai, India. From the prepared samples, three to four drops were placed between the metallic discs of the rheometer and the analysis performed. The shear rate was gradually increased from 0 to 100 sec^{-1} and the values were noted. The viscosity at each point was recorded and the graph of viscosity vs. shear rate was plotted. Change in viscosity at increasing and decreasing shear rates were investigated. The final graph produced showed the relationship between the initial zero shear rate viscosity of the prepared samples with its final zero shear rate viscosity.

3. Results and discussion

The results obtained in various characterizations are shown in Table 2. The crosslinking is by the acetal reaction mechanism [19]. The presence of free hydroxyl units in starch (S) and PVA make the crosslinking reaction feasible. Acidic condition provided by dissolving PVA and starch in the water catalyzes the reaction. The hydroxyl groups of G get protonated in the acidic condition. As the protonated group leaves as water, an electrophilic center is formed, which is then attacked by the nucleophilic hydroxyls of the PVA/S blend. Simultaneously same mechanism happens on the other part of G by the excess of PVA/S in the reaction. Hence crosslinked structure is formed by acetal bonding, which connects two polymer chains, and a crosslinked structure is formed. The mechanism is shown in Fig.1. For the stabilization, water and SO_2 are eliminated in the last step, which is evidenced by the characteristic pungent odor of SO_2.

Table 2: Test results obtained after various characterizations.

Blended sample	Viscosity (centipoise)	pH	Tg (° C)
PVA/S	550	5.43	69.23
PVA/S-G0.5	650	5.77	70.7
PVA/S-G 1	750	5.88	72.28

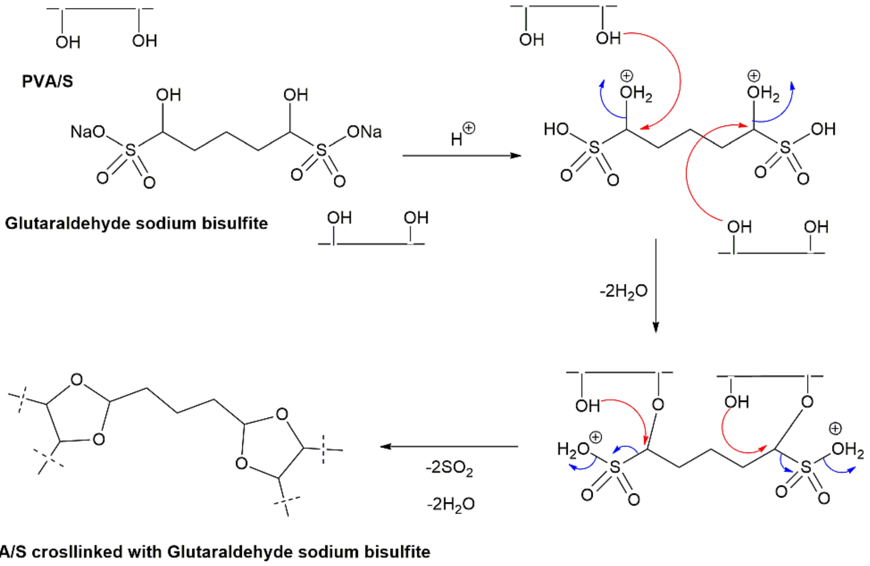

Figure 1: The mechanism showing crosslinking between PVA/S blend and G.

3.1 Viscosity analysis

The glutaraldehyde sodium bisulfite acts as a cross-linker for PVA/S blend, which made changes in the viscosity, as shown in Fig. 2.

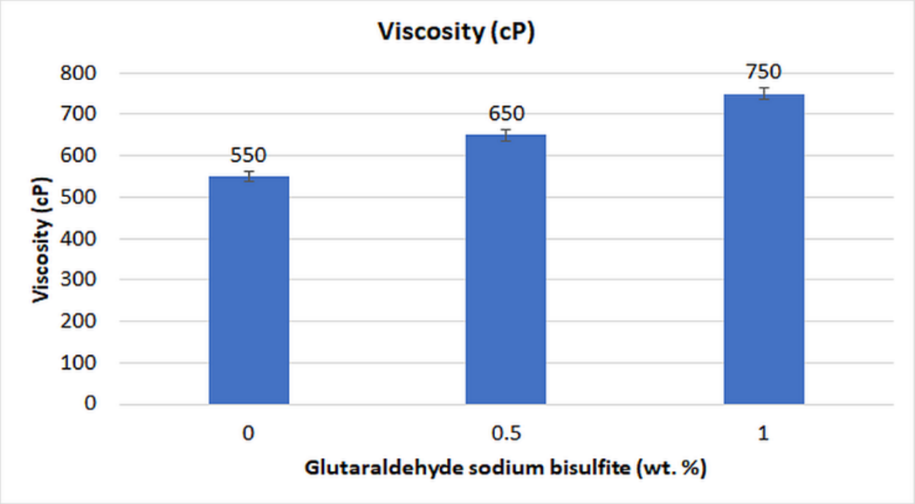

Figure 2: Effect of concentration of glutaraldehyde sodium bisulfite vs. viscosity of blend.

Incorporation of glutaraldehyde sodium bisulfite to the blend caused the viscosity to rise. The crosslinker has reacted with the hydroxyl groups of the blend, and thus forming a cross-linked structure. Cross-linking between PVA/S and glutaraldehyde sodium bisulfite makes a compact network structure that restricts the chain movements. The cross-linking causes an increase in the chain length of PVA and starch. As the longer chains are formed, chances of entanglement also increase; this makes a substantial rise in viscosity. The proportional increment in viscosity with the concentration of glutaraldehyde sodium bisulfite confirms the extent of crosslinking reaction.

3.2 Fourier Transform Infra-Red Spectroscopy (FTIR) analysis

As the concentration of cross-linker is increased, a shift in the intensity of the percentage transmittance curve is seen. Reduction in intensity is due to the crosslinking reaction. This is because, the cross-linker, glutaraldehyde sodium bisulfite reduces the inter-chain distance by bridging between them, leading to a lowering of hydrogen bonding. The reaction proceeds at higher dosages leading to a decrease in residual hydroxyl groups with a subsequent increase in the amount of cross-linker. The effect of crosslinker on the blends can be seen in Figure 3, as the intensity gets reduced at a higher concentration of glutaraldehyde sodium bisulfite.

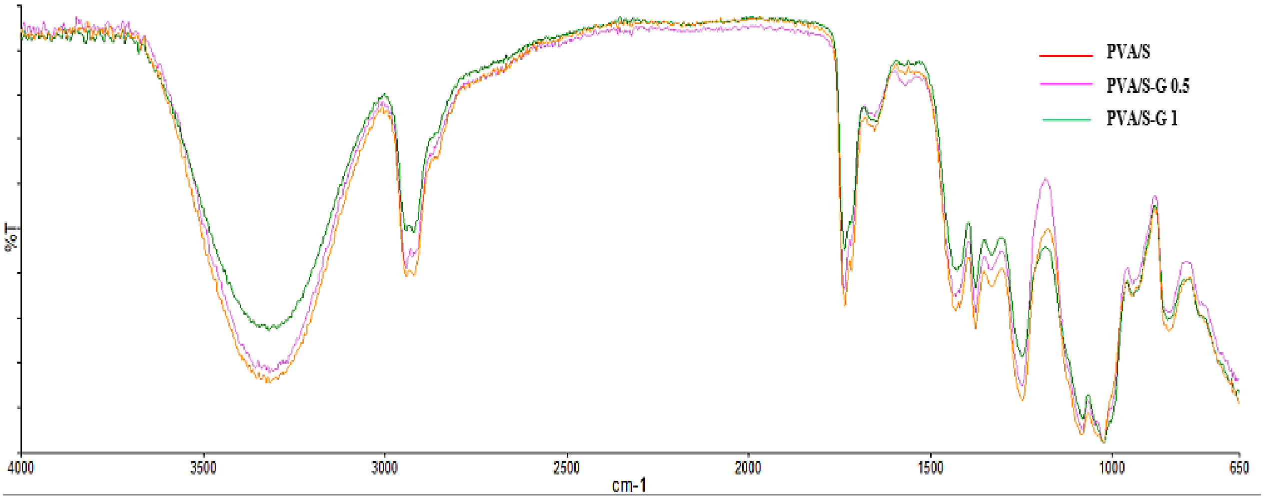

Figure 3: FTIR spectra of PVA/S blend, and the blends crosslinked with glutaraldehyde sodium bisulfite.

3.3 Differential Scanning Calorimetry (DSC)

The glutaraldehyde sodium bisulfite acted as a cross-linker for PVA/S blend, which has led to subsequent glass transition temperature (Tg), as shown in Fig.4.

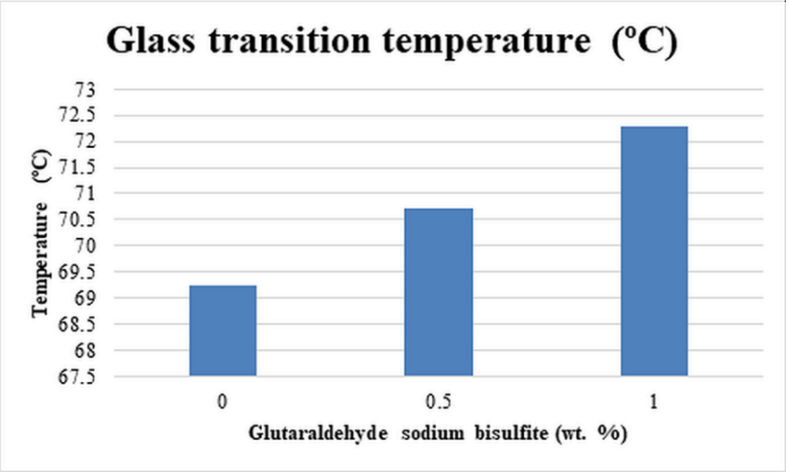

Figure 4: Dependency of increasing concentration of glutaraldehyde sodium bisulfite with (Tg).

The glutaraldehyde sodium bisulfite has reacted with the hydroxyl groups of PVA/S blend, and thus forming a cross-linked structure. The crosslinking creates a network structure, decreasing the chain movements. Therefore, the increase in glass transition temperature is observed, which contributed to the enhancement of the thermal property. As evident from the FTIR curves, there is a decrease in residual hydroxyl groups with a subsequent increase in the amount of cross-linker. A similar trend is observed for Tg; hence it can be concluded that crosslinking increases Tg of the blends, with increasing Tg as the concentration of cross-linker increases.

3.4 Dynamic mechanical analysis (DMA)

Both the sample films exhibited major transitions above the glassy temperature region, close to 50° C (Tan delta peak, Fig. 5), this corresponds to the glass transition temperature (Tg) of PVA. The superimposed thermogram of storage modulus curves indicates a substantial increase in the storage modulus in the glassy region for PVA/S-G 1 compared to the blank, PVA/S. Rubbery plateau region of the storage modulus curve shows a substantial increase in the modulus values for PVA/S-G 1 sample compared to PVA/S. This confirms the crosslinking of glutaraldehyde sodium bisulfite with PVA/S.

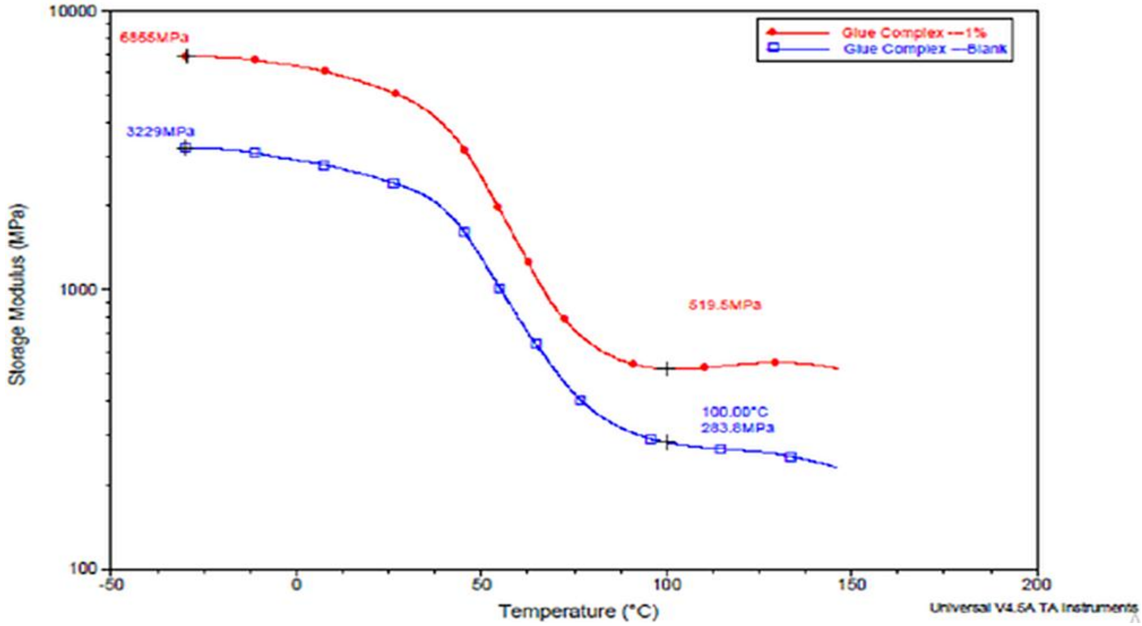

Figure 5: Superimposed thermogram for storage modulus (E') of samples PVA/S-G 1 and PVA/S

In reference to the blank, the superimposed thermogram of the tan delta curve indicates the minor shift of tan delta peak temperature with broadening of the peak for PVA/S-G 1 (Fig. 6). Similarly, a substantial increase in the loss modulus peak value with a shift to higher temperature is observed in the PVA/S-G 1 sample due to the crosslinking. From both storage modulus and tan delta curves, the crosslinked blend shows better mechano-thermal properties compared with the non-crosslinked sample.

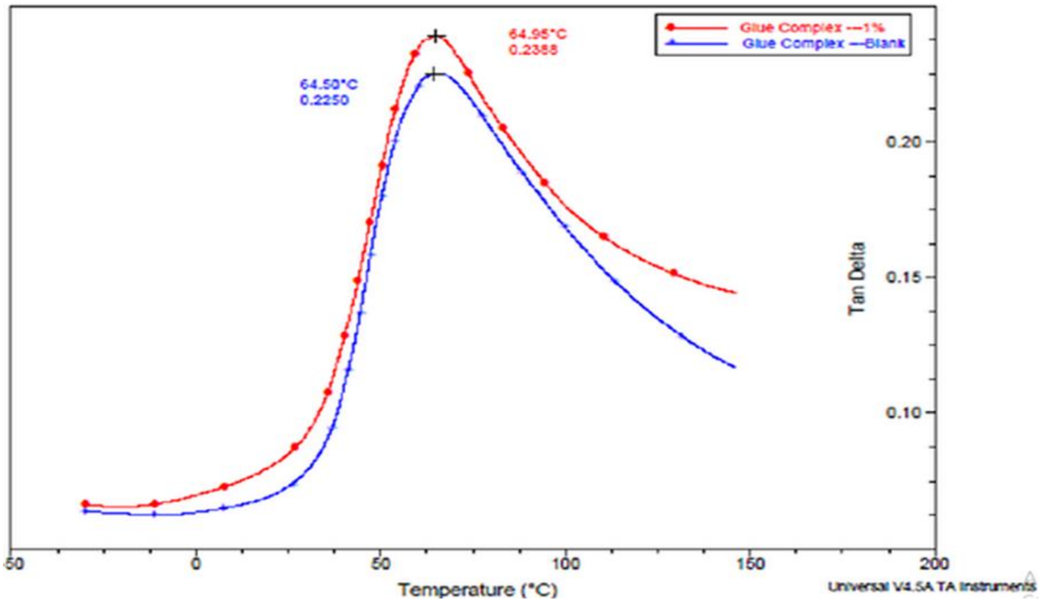

Figure 6: Superimposed thermogram for tan delta of samples PVA/S-G 1 and PVA/S

3.5 Contact angle measurement

The observation from the contact angle measurement shows an increase in contact angle as the amount of crosslinker increases showing the hydrophobic nature of crosslinked samples (Fig. 7 B and C) when compared to non-crosslinked sample (Fig. 7 A). Fig. 8 shows the values of contact angle as the concentration of crosslinker is increased. The surface hydroxyl groups in PVA/S are hydrophilic, which gets reduced, making the films hydrophobic as crosslinks are formed; hence this is in accordance with FTIR, DSC, and DMA analysis that as the concentration of glutaraldehyde sodium bisulfite increases crosslinking also increases.

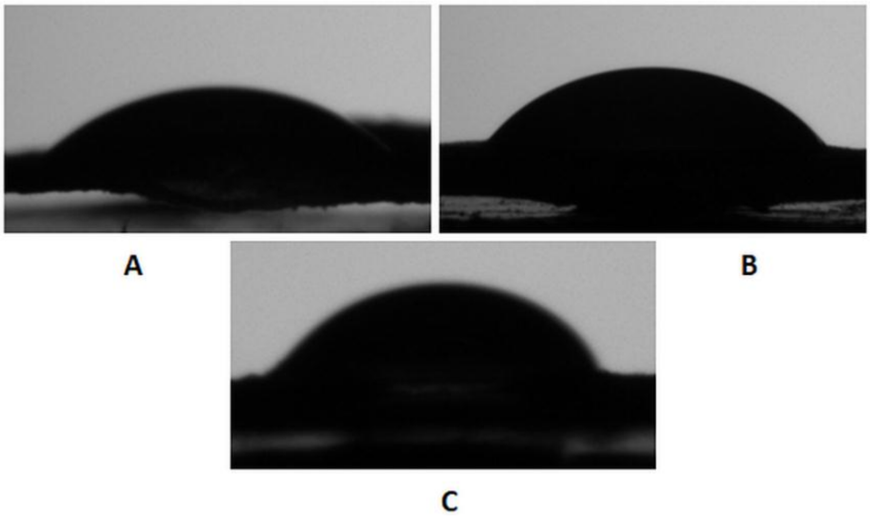

Figure 7: Contact angle images A) PVA/S B) PVA/S-G 0.5 C) PVA/S-G 1

3.6 Rheology

The rheology of any compound is measured by varying shear rate and finding its effects on viscosity. A zero shear viscosity is taken as the viscosity extrapolated for zero shear rates. A sample is considered as stable, if its change in viscosity at the start and end of the shear rate cycle shows minimum variation. All the samples in Fig. 9 show an initial drop in viscosity. After the initial drop sample shows a stable viscosity profile in both the increasing & decreasing shear ramp. None of the samples regains its original viscosity in decreasing shear ramp (i.e. when shear is decreased from high to low).

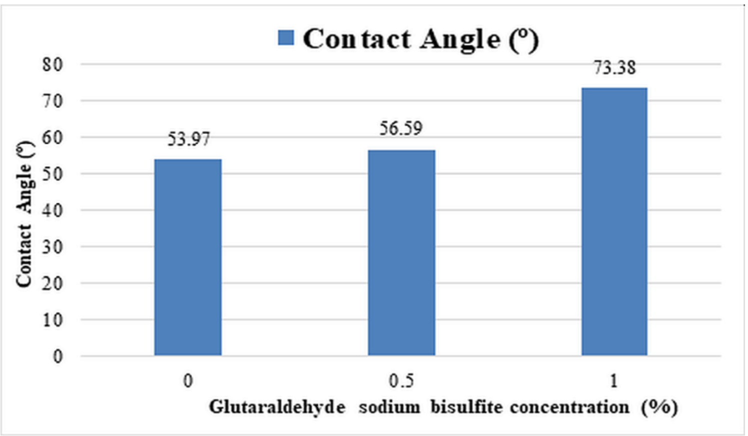

Figure 8: Contact angle data for samples at various concentrations of glutaraldehyde sodium bisulfite.

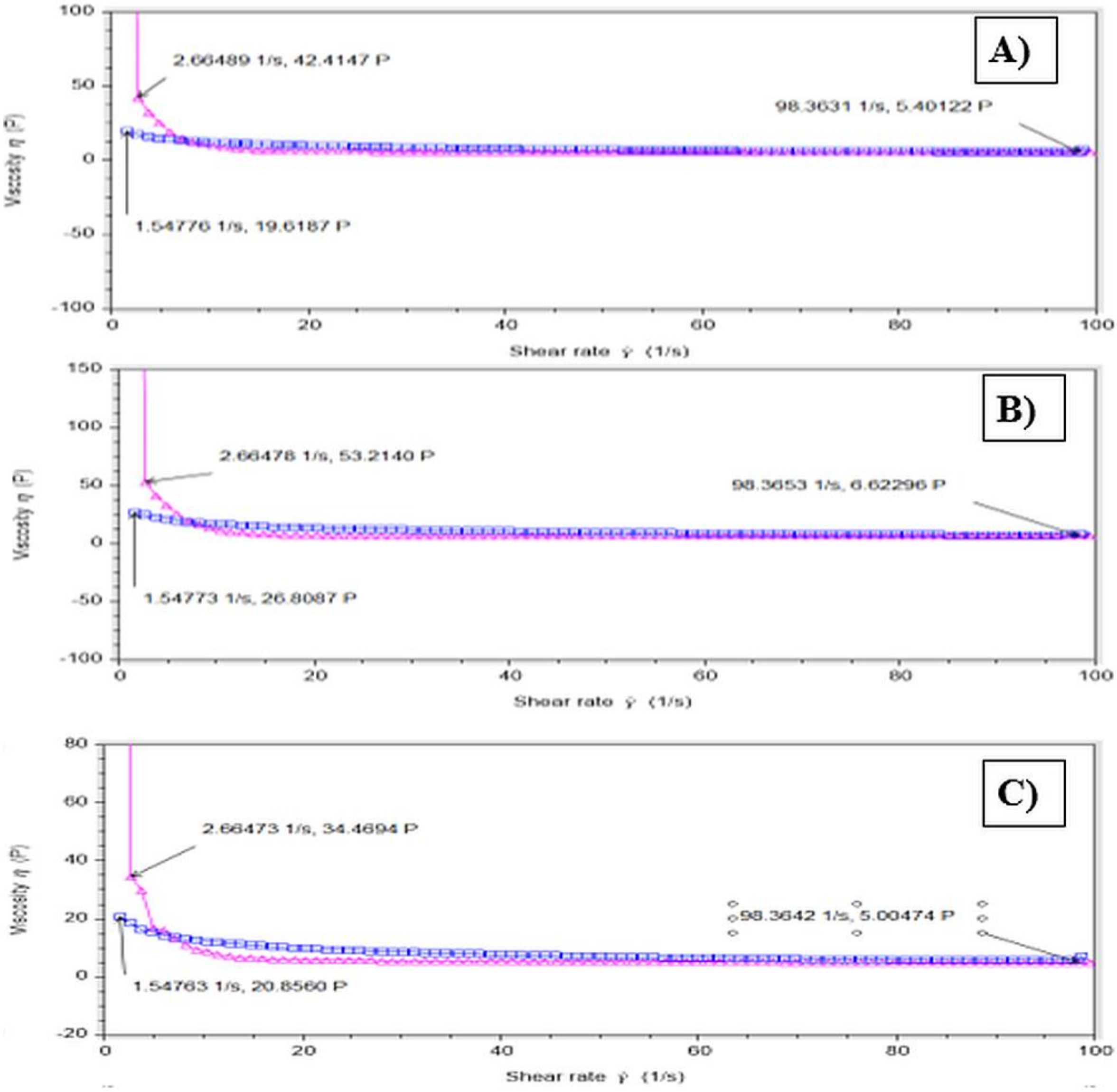

Figure 9: Rheology (viscosity vs. shear rate) curves of A) PVA/S B) PVA/S-G 0.5 C) PVA/S-G 1.

The viscosity at 100 shear rate is around 5 P. Initial viscosity for the sample is between 30-60 P. Samples PVA/S and PVA/S-G 0.5 (Fig. 9 A) and B)) samples show stable viscosity profile with increase and decrease in shear rates. For the sample PVA/S-G 1, the stabilization effect comparatively low. The applied shear rate has broken the existing H-bonding which was developed upon acetal formation. The movement of chins exeeded beyond the recovey state, as the shear rates are applied. Hence a major drop in the viscosity is shown by the graph (Fig. 9 C).

Conclusion

Glutaraldehyde sodium bisulfite act as a crosslinker for PVA/S blend. The acetal reaction mechanism effectively proceeded in the acidic condition. Crosslinking consolidates the chain and affects its mobility and is shown by the increment in viscosity of crosslinked samples. Reduction in the hydroxyl groups of PVA/S blend is observed as crosslinker concentration is increased, indicating the extent of crosslinks formed. The same is evidenced by an increase in hydrophobicity as the contact angle with water increases with increase in the cross-linker amount. DMA analysis proves the enhancement of mechano- thermal properties as storage modulus and tan delta values of crosslinked samples are higher. Rheological properties show that samples have a stable viscosity profile with increase and decrease in shear rates. Overall, with the incorporation of novel crosslinker, glutaraldehyde sodium bisulfite, PVA/S blend showed enhancement in thermo- mechanical properties compared to the non- crosslinked blend. Hence the crosslinked blend can be a potential material for development of bio-based adhesives.

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