

Combined effect of boric acid and citric acid on thermal and mechanical properties of starch-polyvinyl alcohol-based wood adhesive

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Abstract

Polyvinyl alcohol stabilized polyvinyl acetate emulsions are used as wood adhesives. To improve the properties of adhesive while considering the cost, incorporation of starch in polyvinyl alcohol stabilized polyvinyl acetate based wood adhesives were synthesized. Starch, being a biopolymer, has poor mechanical and aging properties. Commercially citric acid is being used as crosslinker to improve rheology and aging properties. Boric acid is used as crosslinker to enhance performance properties like tensile shear strength and wet tack. The work compares the effect on various properties of polyvinyl alcohol and starch blend-based wood adhesive by chemically crosslinking in the presence of citric acid and boric acid in an aqueous medium with conventional polyvinyl alcohol and starch blend wood adhesive. The combination of cross-linkers in the adhesive systems has been tested against the canarium wood substrate for tensile strength.

The crosslinked adhesives were analyzed by Fourier-transform infrared spectroscopy, dynamic mechanical analysis, conducted rheological study at varying shear rates and accelerated stability test. The crosslinking due to combination of citric acid and boric acid resulted in the enhancement of performance properties like wet tack and tensile shear strength without affecting the stability of wood adhesive after aging. From the results, it can be concluded that optimum level for the performance and stability of wood adhesive is attained at 0.3weight percentage of citric acid and 0.2 weight percentage of boric acid of the total composition of adhesive.

Keywords: Citric acid, Boric acid, Starch, Polyvinyl alcohol, Polyvinyl acetate, Wood adhesive

Introduction

Polyvinyl alcohol (PVA) stabilized polyvinyl acetate (PVAc) dispersion based adhesive is commonly used in bonding many porous substrates such as woods, papers, cardboards and textile materials¹. PVAc emulsion polymers are prepared by free radical polymerizing vinyl acetate monomers in the presence of PVA as a protective colloid and are used as wood adhesives^{2,3}. The synthetic product based

on petroleum-based raw materials for wood adhesives is being replaced by biopolymers such as lignin, soybean protein, tannin, cellulose⁴ and starch⁵. Starch is a renewable, biodegradable, inexpensive and readily available polymer extensively used as adhesive⁶⁻⁸, but starch is not used in wood bonding because of its water and thermal sensitivity.

The tensile strength and water resistance of starch-based adhesive improved when PVA aqueous solution was added⁹. Other effective methods commonly used to enhance the performance of PVA/starch composites in order to improve their mechanical and water resistance properties include chemically modifying PVA and starch by esterification, oxidation, etherification, cross-linking and methylation¹⁰ and chemically modifying the starch PVA blends by cross-linking reactions, grafting¹¹.

Cross-linking is a common way to enhance the performance of biopolymers based wood adhesives¹². It is reported that citric acid interaction with starch can form strong hydrogen bonds that improve its thermal and water stability and inhibit retro degradation¹³. However, incorporating citric acid substantially reduced the tensile stress of the products developed under the conditions used¹⁴. Citric acid is also used as an additive to starch-PVA films due to the antibacterial effects¹⁵ and can serve as a cross-linking agent¹⁵. Cross-linking of a blend reinforces the intermolecular binding by introducing covalent bonds that supplement natural intermolecular hydrogen bonds to improve the mechanical properties and water resistibility.

The residual-free citric acid in the PVA/starch blends may act as a plasticizer. Citric acid is also a naturally occurring organic acid with three carboxylic groups and is generally classified as a safe food additive. PVA is a well-known polymer with a wide range of applications. Its properties can be extensively modified by adding different additives and act as a wood adhesive. In particular, a complex of PVA with (ortho-) boric acid $B(OH)_3$ had been widely investigated¹⁶. Moreover, the polyvinyl alcohol polymer can react with borate ions to form a polymeric gel. Also, the formation of complexes between polyvinyl alcohol and borate ion has a significant effect on the viscosity behavior of polyvinyl alcohol aqueous^{16,17}.

Based on the above properties, this study investigates the combined effect of boric acid and citric acid on PVA/starch blend stabilized polyvinyl acetate wood adhesive and compared with the non-crosslinked conventional PVA/starch in polyvinyl acetate wood adhesive. By the

addition of these acids, the corresponding changes in wet tack, tensile strength and aging properties of wood adhesives were evaluated.

The combined effects of addition of boric acid and citric acid have been characterized by analytical methods such as Fourier-transform infrared spectroscopy (FTIR) and dynamic mechanical analysis (DMA). Therefore, the aim of this study is to increase the wet tack and tensile strength by the combined influence of boric and citric acid without compromising the stability of PVA/ starch in PVAc wood adhesive.

Material and Methods

Materials: PVA (physical state: solid, degree of hydrolysis of 86.5 to 89%, molecular weight: 99000 to 105000) was obtained from Kuraray Co. Ltd., India. Starch (Corn starch amylose content 25-30 %) was obtained from Sanstar Bio-polymer Ltd. To avoid absorption of moisture from the environment, these raw materials were kept in a dry environment from environment. Polyvinyl acetate (PVAc) (PVA stabilized, Solid %-50% and pH-4.7), butyl carbitol acetate (BCA), formaldehyde, boric acid and citric acid were obtained from Sigma-Aldrich.

Preparation method: Corn starch and PVA were first put into a round bottom reactor vessel. The water was added to them and the mixture was kept for continuous stirring at 175 rpm. The temperature was slowly raised up to 60°C after which the acids (citric acid and boric acid) were added and the final temperature was kept at 95-97°C. The reaction was

carried out for 2.5 hrs. Then the cross-linked solution was cooled down to 25°C. The cross-linking mechanism of PVA/S with boric acid is given below in fig. 1 and 2.

Now the remaining components containing PVAc, BCA and formaldehyde were added to the solution as per the composition shown in table 1. The formaldehyde was chosen for its better anti-bacterial and preservative properties at lower concentrations. The new formulated solution was kept for continuous stirring at 175 rpm for 1.5 hours. This final product was then stored in plastic containers and labelled as per table 1.

Characterization and testing

Fourier Transform Infra-Red Spectroscopy (FTIR): Perkin Elmer FTIR spectrometer was used to record 100 spectra. The sample films of about 200 microns were analyzed by the reflectance process. The background spectra were run first and then eliminated from the obtained results of each sample.

Viscosity: The viscosities were measured by Brookfield DV1 Viscometer at 28°C temperature and 20 rpm.

Tensile strength: Tensile strength was checked with the help of UTM Tinus Olsen H25KT, Mumbai, India. The adhesives were applied onto 25 mm× 25 mm area of one end of the canarium (can) wood pieces (Fig. 3) in such a way that it properly wets the surface. The adhesive applied on wood pieces were bonded in such a way that the wood grains of two pieces were oriented in parallel.

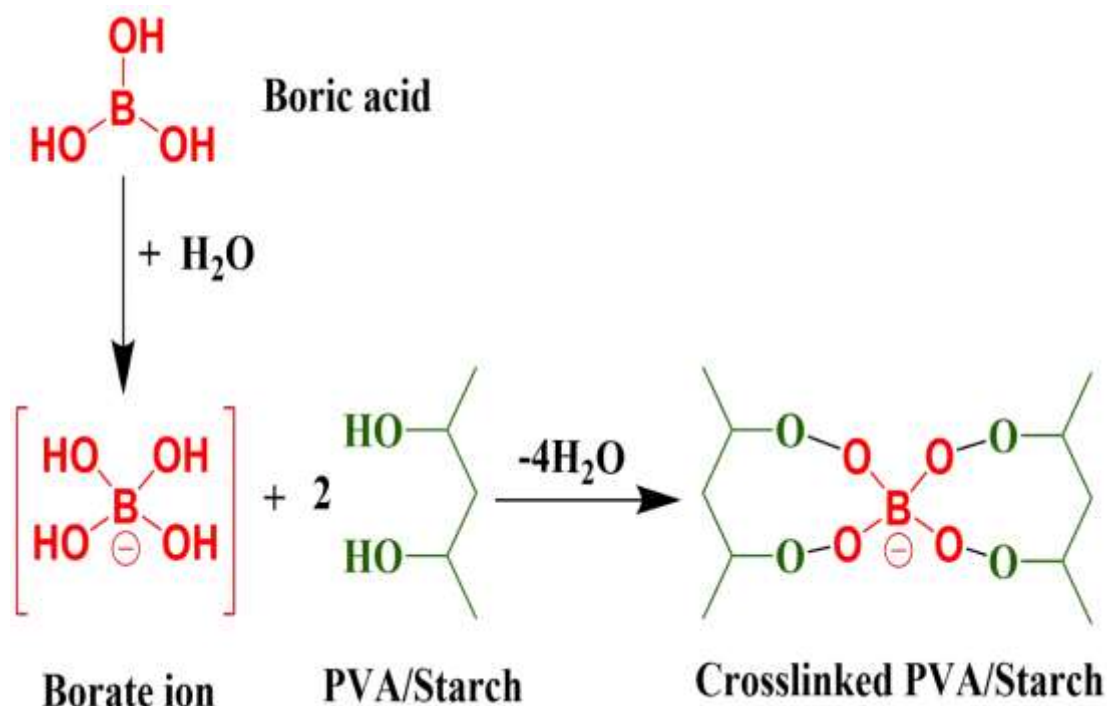


Fig. 1: Crosslinking mechanism of PVA/S with boric acid

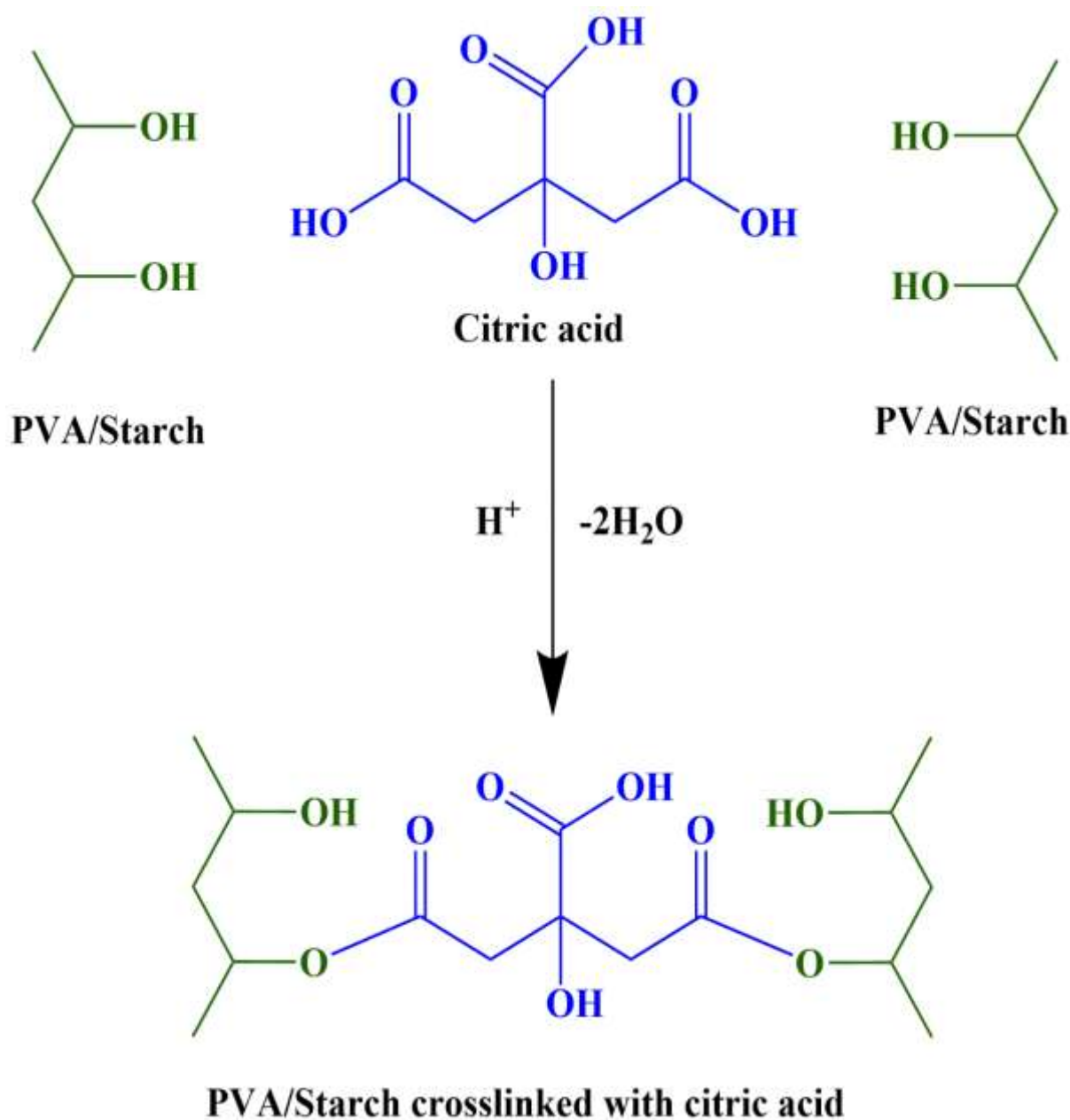


Fig. 2: Crosslinking mechanism of PVA/starch with citric acid

Table 1
Composition of Formulation 2 (F2) series with and without the addition of boric and citric acid

| Ingredients | F2- Std | F2-01 | F2-02 | F2-03 | F2-04 |
|--------------|---------|-------|-------|-------|-------|
| | Wt. % | | | | |
| Water | 36.45 | 36.45 | 36.45 | 36.45 | 36.45 |
| Starch | 5.66 | 5.66 | 5.66 | 5.66 | 5.66 |
| PVA | 4.68 | 4.68 | 4.68 | 4.68 | 4.68 |
| Citric Acid | - | 0.3 | 0.3 | 0.5 | 0.5 |
| Boric Acid | - | 0.1 | 0.2 | 0.1 | 0.2 |
| PVAc | 50.55 | 50.55 | 50.55 | 50.55 | 50.55 |
| Formaldehyde | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| BCA | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 |

Each end of the bonded sample was held by grips (total load - 5 kg cylinder + 2.5 kg arm) and pulled apart at a controlled rate (5 mm/min) and tensile strength for bonded wood pieces was recorded (temperature 28-30°C, %relative humidity 65-70). To study the tensile strength development over time, the values were calculated at various time intervals of 4hr. and 24 hrs. For each composition, 5 samples were tested and standard deviation was reported.

Rheology: Rheology was checked with the help of DHA-2 Rheometer from TA Instruments, Mumbai, India. A small amount of adhesive was placed between the metallic discs of the Rheometer. The discs were then closed and the shear rate was increased from 0 to 100 sec^{-1} . The viscosity at each point was recorded and the graph of viscosity vs shear rate was plotted. After reaching 100 sec^{-1} shear rate it was again reduced to 0 sec^{-1} . The graph shows the relationship between the initial zero shear rate viscosity and the final zero shear rate viscosity. Three samples were analyzed for each adhesive composition and the best graph was reported.

Dynamic mechanical analysis (DMA): DMA was performed using DMA Q800 from TA Instruments, Mumbai, India. A thin film of 200 micron was first prepared by applying it on a polytetrafluoroethylene (PTFE) sheet. The film was kept for physical solidification at room temperature for 24 hrs. The film was peeled off from the PTFE sheet and kept in the DMA sample holder. The temperature range was from -30°C to 150 °C with ramp rate of 5°C/min, frequency 1Hz and strain 0.1%. Three samples were analyzed for each adhesive composition.

Wet tack: Wet tack was calculated using Probe tack analyzer from Rohit Instruments, Mumbai, India. Few grams

of the adhesive were first placed on the metal surface of the machine. It was taken care that the sample was still in liquid form and no surface drying took place. A metal probe then approached the sample downward at the speed of 5 mm/min. By the subsequent movement, the adhesive is squeezed between the cylinder and the metal surface. The cylinder touches the metal surface and again lifts at the speed of 5 mm/min. The adhesive resists the upward movement of cylinder and thus the force of resistance was calculated and termed as wet tack.

Stability Test: Viscosities were measured by Brookfield DV1 Viscometer after keeping the samples in an incubator for 3 hrs. at 30°C. Changes in viscosity after keeping the samples at 50°C for 15 days and 30 days were recorded to study the viscosity stability.

Results and Discussion

FTIR: The FTIR curves show the peaks at 3340 cm^{-1} of OH stretching. A sharp carbonyl peak due to PVAc is observed at 1730 cm^{-1} . Since the components responsible for changes in properties of the F2-01 and F2-03 are similar, the tests conducted for just one of F2 are enough for establishing the desired results.

The characteristic peaks of -OH bonds present in both PVA and starch are observed at 3340 cm^{-1} (Fig. 4). A strong sharp peak is observed at 1730 cm^{-1} due to the presence of carbonyl (C=O) group of PVAc (Fig. 4). In the case of boric acid, there is considerable overlapping of curves due to the tertiary alcohols of boric acid and secondary alcohols of PVA/starch.

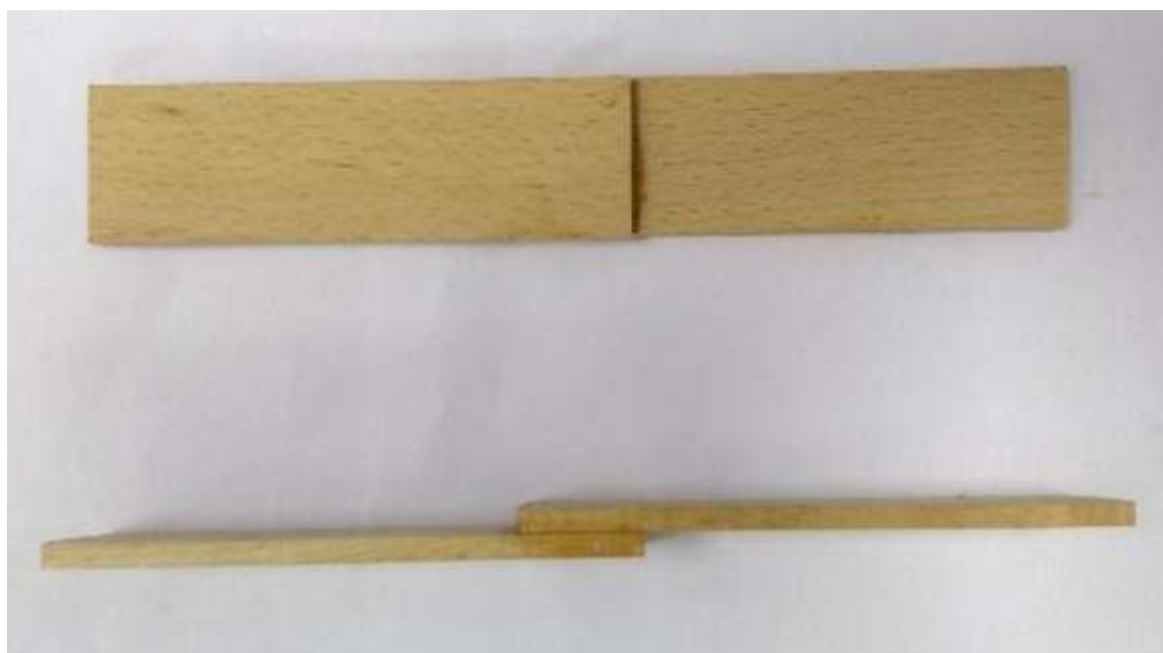


Fig. 3: Can to can assembly

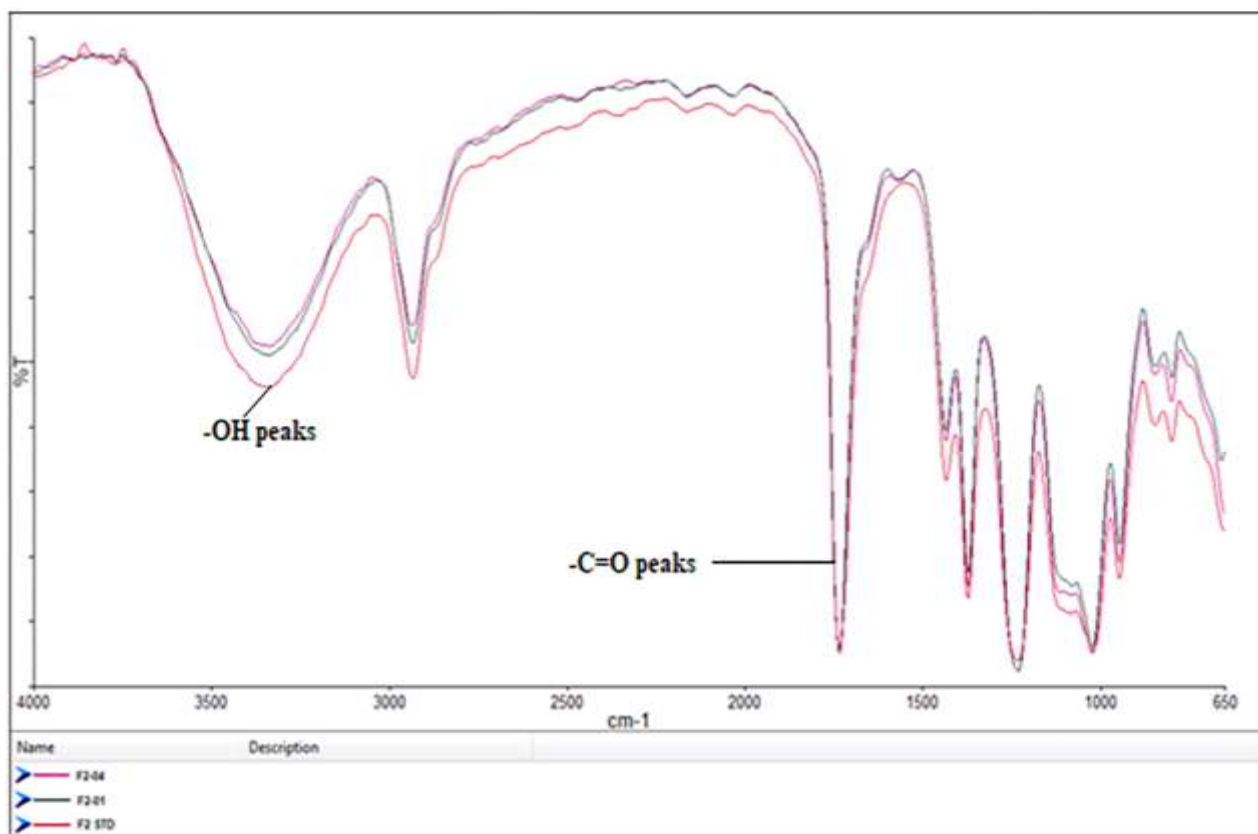


Fig. 4: FTIR curves of citric acid + boric acid crosslinked with PVA/Starch

Viscosity (RT): Due to the addition of boric acid and citric acid, it was expected that the formation of a coordination complex and ester linkage would happen respectively. But the findings were interesting, as the citric acid content increased a decrease in viscosity which was observed at all compositions (Fig. 5). This was attributed to the functioning of citric acid as the plasticizer. The citric acid forms ester linkages at temperatures well above the 95-97°C¹⁸. Usually citric acid is a crosslinker for PVA starch wood adhesive. In this study, the citric acid acts as a plasticizer by acting as a spacer between the chains and making them move easily. Gelatinization effect in starch by citric acid at acidic condition decreases the viscosity which relates to the decrease in viscosity as the amount of citric acid is increased.¹⁹

At the same time, the crosslinking reaction between F2-01 with boric acid caused an increase in the viscosity of the adhesive. F2-03 showed the lowest viscosity value is less than F2-std, this can be due to 0.5 % addition of citric acid nullifies crosslinking of 0.1% boric acid and net resultant of decreased viscosity is observed (Fig. 5). The boric acid reacts with the PVA and forms a coordination complex²⁰. The cross-links make it harder for chains to move which cause the viscosity to increase. The close packing of chains due to cross-linking has led to greater stiffness and chain entanglement is one of the reasons for increase in modulus which proves the gradual increase of viscosity. A decrease in viscosity for sample F2-03 was observed (Fig. 5). This decrement accounts for the fact that the increase in citric acid

concentration favors plasticizing of starch. The influence of citric acid with starch affects the morphology of starch globules which in turn reduces the viscosity.

A slight increment in viscosity was observed in F2-04 compared to F2-03. An increase in the concentration of boric acid created crosslinks with PVA, hence viscosity slightly increases. But as citric acid concentration remained the same, viscosity of F2-04 compared to F2-02 is less. This again confirms that citric acid functions as a plasticizer.

Tensile strength (Can to Can): The additional can to can wood tensile strength study was done to observe the hardwood behavior of the adhesives. In this case both the wood surface bonded are of same hardwood (Canarium wood). For all the formulations, tensile strength of F2-Std was lower compared to all other samples for both 4 hr. and 24 hr. The trends of tensile strength of can to can are which decreases due to citric acid addition and increases due to boric acid addition.

A major difference is observed while comparing their values. The tensile strength of can to can for F2-02 was found to be highest (Fig. 6). The addition of boric acid increases the tensile strength at both 4 hr. and 24 hr. for F2-02 and F2-04 compared with other formulations in which boric acid concentration was low.

Even though amount of boric acid remained same (0.2%) for both F2-02 and F2-04. In F2-04, as concentration of citric

acid (0.5%) was higher, it acts against the crosslinking effect of boric acid. Hence the result is reduction in tensile strength compared with F2-02. Tensile strength F2-03 is compared to be lower as that of F2-01. Even though boric acid (0.1) is in same amount due to the plasticizing effect of citric acid at higher concentration (0.5%) in F2-03. This considerable difference is observed due to the difference in the wood substrate.

Rheology: The rheology measures the viscosity of a compound at the varying shear rate with the so-called zero shear viscosity as the viscosity extrapolated for zero shear rates. A sample is considered as stable if its change in viscosity at start and end of the shear rate cycle shows minimum variation.

In the case of F2-04, a difference in zero shear viscosity is large compared to F2-Std (Fig. 7 a). The minimum difference is shown by F2-01 sample. Thus, it can be concluded that least stable is F2-04 and F2-01 shows better viscosity stability at varying shear rate (Fig. 7 b and 7 c)

In the case of boric acid in F2-04, the stabilization effect is very low. The applied shear rate has damaged the existing H-bonding which developed upon complex formation. The chains move far apart beyond recovery as the shear rate is applied. Therefore, the significant drop in viscosity is observed (Fig. 7c).

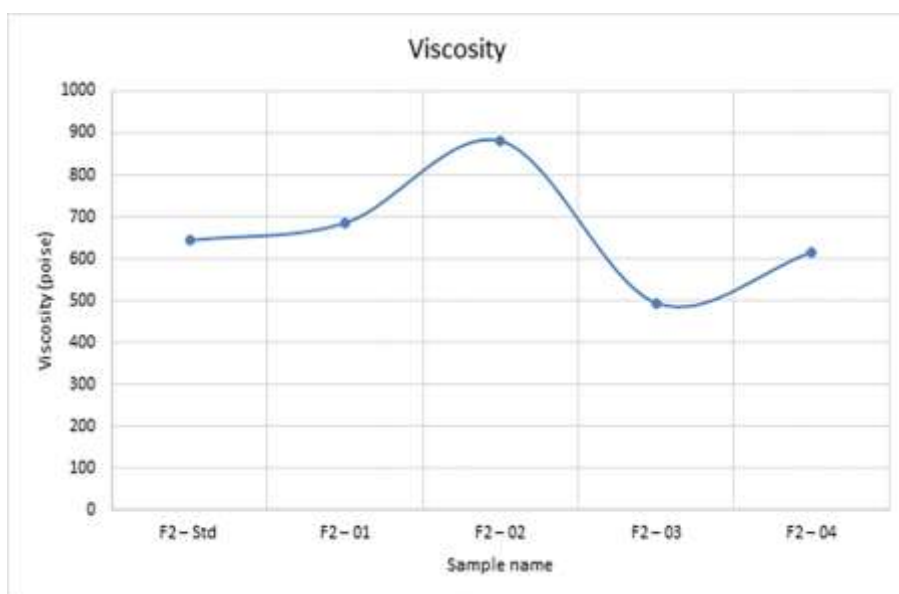


Fig. 5: Viscosity changes for F2 + Citric acid + Boric acid

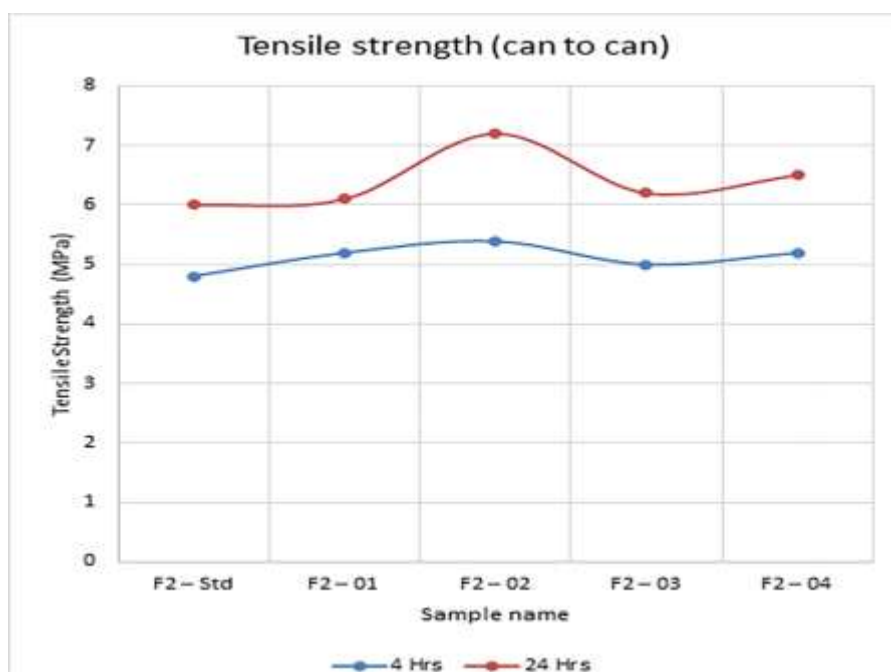


Fig. 6: Tensile strengths (Can to Can) for F2 + Citric acid +Boric acid

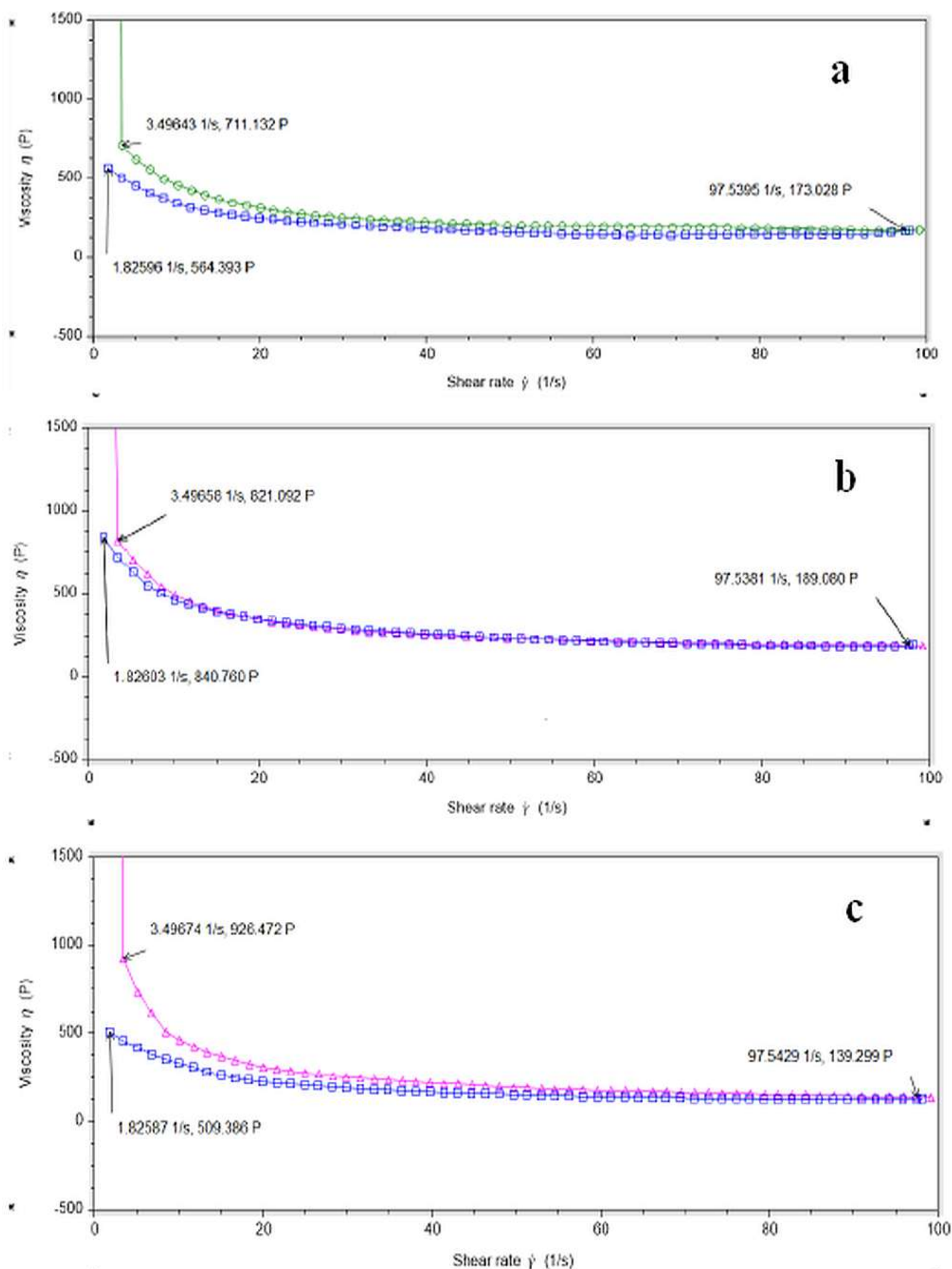


Fig. 7: Rheology (viscosity vs shear rate) curves of (a) F2-Std., (b) F2-01 and (c) F2-04

Dynamic mechanical analysis (DMA): Higher storage modulus value in rubbery region and shift of tan delta second peak to the higher temperature with decreased peak height and peak broadening indicate the formation of the cross-linked network in boric acid and citric acid incorporated systems (Fig. 8a).

The tan delta curves show two significant peaks in each series: one near 50°C (first tan delta peak) which corresponds to PVAc glass transition, the other near 90°C (second tan delta peak) associated with PVA glass transition (Fig. 8 b). The first tan delta peak is almost identical in each adhesive composition since the PVAc undergoes no such modification. The second tan delta peak shows a major change by increase in area under the curve in case of higher concentration of boric acid (0.2 %) and the peak temperature shift (Fig. 8 b). These changes confirm an increase in glass transition temperature of the boric acid-modified adhesive. The observations provide conclusive evidence to the increase in viscosity, tensile strength and wet tack.

Wet Tack: Wet tack force provides information about the internal cohesion in an adhesive. A similar trend was observed in the case of viscosity. The addition of citric acid has led to decrease in wet tack (Fig. 9). The presence of citric acid acting as plasticizer weakened the cohesion of the adhesive. In case of boric acid, the co-ordination complex helps in packing of chains together and thereby increasing the wet tack. Thus, combined effect on addition of boric acid and citric acid contributed to increase in wet tack (Fig. 9).

Stability: The incorporation of citric acid caused a decrease in the viscosity of the adhesive as shown in fig. 8. The viscosity build-up over time is observed in all the concentrations of citric acid, this is mainly due to the increase in secondary forces. Over time, the internal movement of chains causes the polar hydroxyl groups to achieve better orientation. This orientation has low energy state and thus the low energy configuration is achieved through increased H-bonding.

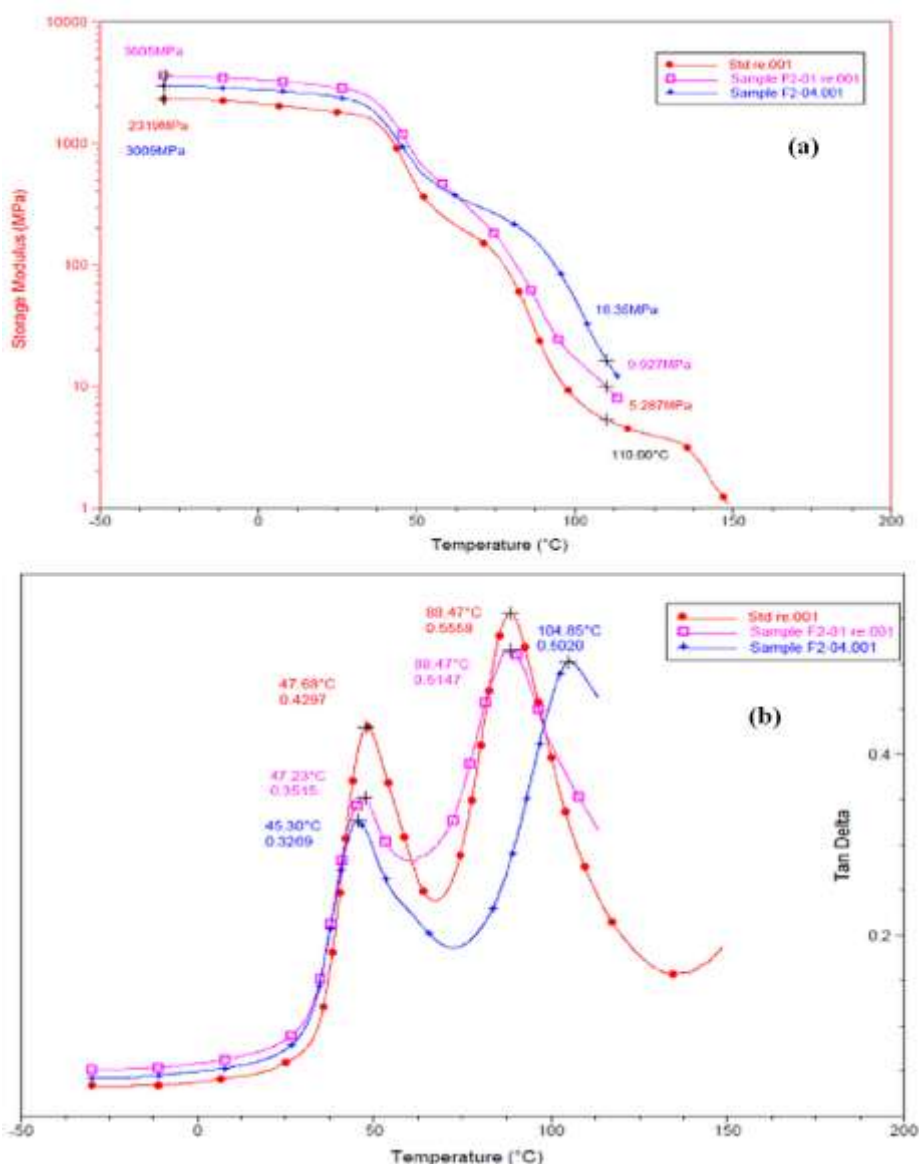


Fig. 8: Graph of (a) storage modulus and (b) tan delta, both in dependence of temperature

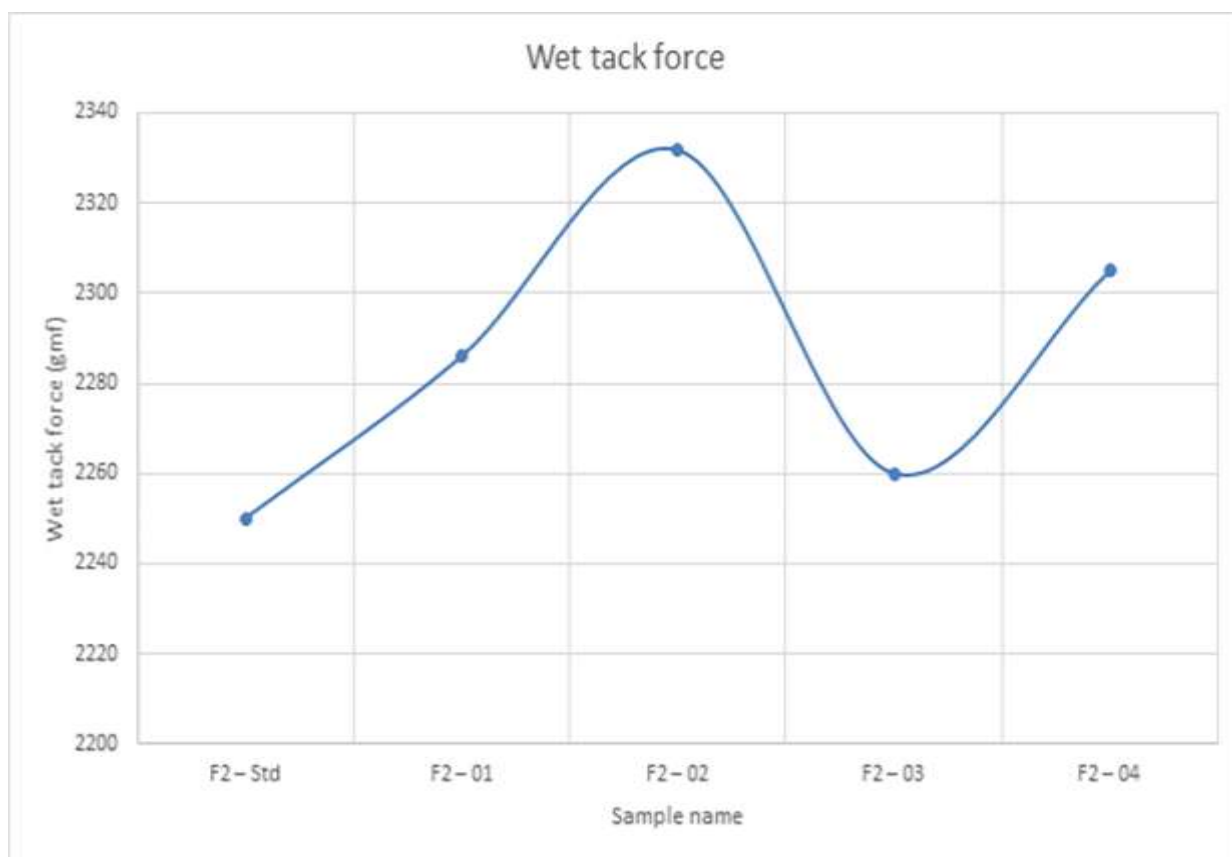


Fig. 9: Wet tack force for F2 + Citric acid + Boric acid

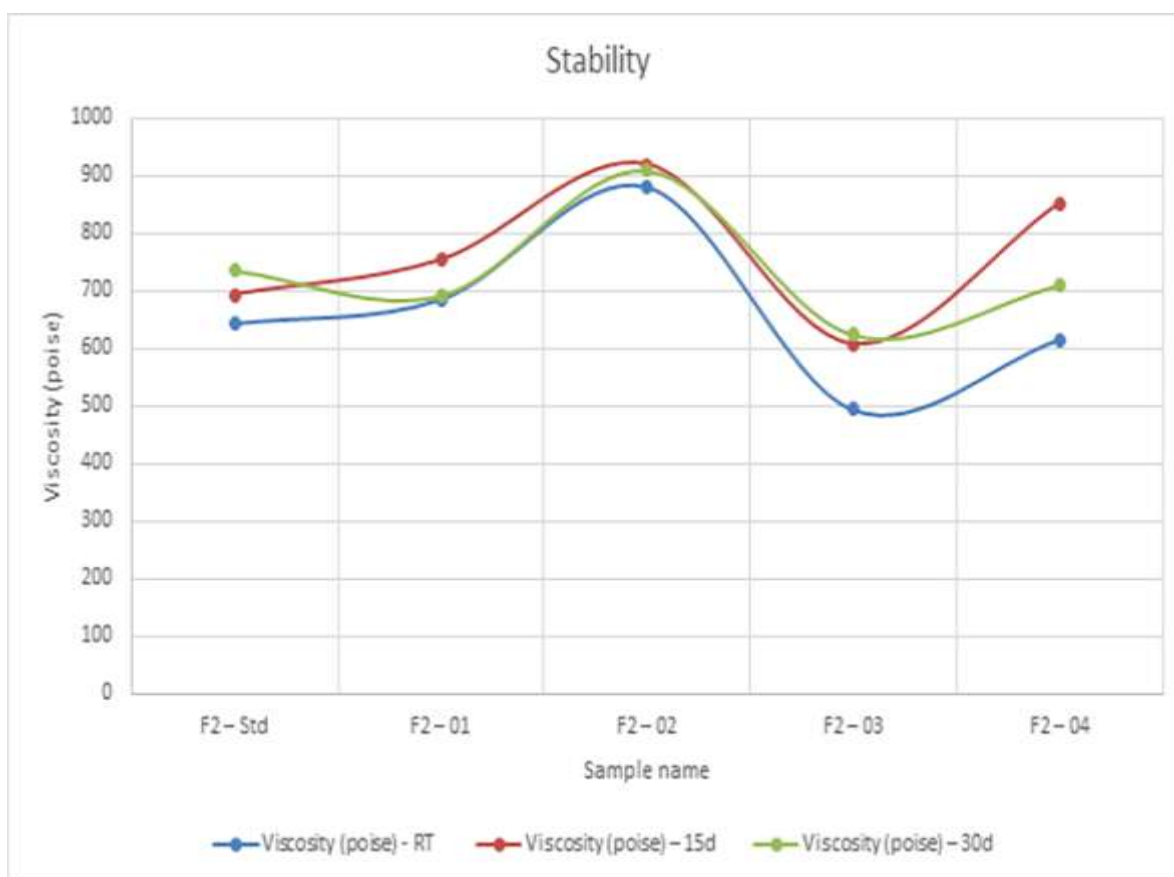


Fig. 10: Illustration of stability

The increase in H-bonding has led to a rise in viscosity over time. An important point to note is that due to the increase in cross-linking, the viscosity is decreased. So, addition of optimal amount of citric acid can help to overcome the problem of viscosity build up overtime. As seen from fig. 8, the viscosity curve is converging towards 0.2% boric acid and 0.3 % citric acid concentration.

The viscosity build-up over time is observed for the F2-04, this is mainly due to the increase in secondary forces over time. Due to the increase in cross-linker percentage, the viscosity build-up has increased. Although, at 0.2 % of boric acid and 0.3 % citric acid, there is least change in viscosity after 15 and 30 days for both the adhesives (Fig. 10).

Conclusion

This study aimed to achieve faster handling strength, high tack development and better-aged stability over the existing PVAc white glues. The approach employed to achieve the above properties was by the combined effect of addition of citric and boric acid into the PVA/starch system. By increasing the content of boric acid, it was found that the wet tack, tensile strength increased.

Similarly, the addition of citric acid imparted better viscosity stability and rheological properties. The maximum tensile strength and wet tack were observed at 0.3 wt.% of citric acid and 0.2 wt.% of boric acid. Here, the citric acid showed better stability; the better tensile strength and wet tack were achieved by boric acid. Hence by incorporating 0.2 wt.% boric acid and 0.3 wt.% of citric acid to PVA/ starch stabilized polyvinyl acetate emulsion, better properties are observed when compared with the standard PVA/starch stabilized polyvinyl acetate wood adhesive.

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