

# Nuvolve Engineered Polysaccharides as Performance-Enhancing Additives for Latex Wood Adhesives

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## Abstract

The work presented here focuses on the incorporation of an engineered polysaccharide polymer,  $\alpha$ -1,3-glucan, derived from the enzymatic polymerization of sucrose, as a performance-enhancing additive for commercial, latex-based wood adhesives used in wood bonding applications. Adhesive performance was measured on hard maple (*Acer saccharum*) using ASTM Standard Method D-905. Dynamic mechanical analysis and solid-state nuclear magnetic resonance spectroscopy were the characterization techniques used to assess the properties of room-temperature-cured adhesive films. Significant increases in shear stress were observed for these formulated latex adhesives containing the polysaccharide polymer.

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Commercial latex-based wood adhesives, used in a variety of commercial and do-it-yourself wood-bonding applications, typically utilize polyvinyl acetate or polyacrylate polymers. A typical latex adhesive originates from the production process of emulsion polymerization. Depending on the desired product attributes, it can be a homopolymer-based system such as polyvinyl acetate at various degrees of hydrolysis to polyvinyl alcohols or also incorporate other monomers such as poly(vinyl acetate-co-ethylene). Cross-linking agents can be added to further increase the adhesion properties. The adhesive system can also contain a catalyst (e.g., aluminum chloride), which may be added separately or may be included in the formulation. Typical commercial uses for this family of adhesives are for finger-joining applications for lumber, moldings, and plywood seaming and patching. They may also be used in furniture assembly, furniture veneer laminating applications, wall systems in manufactured housing, and do-it-yourself home and woodshop applications. The ease of use (e.g., relatively quick setting, optional cold curing, hot or radio-frequency curing, water cleanup) and the good strength of latex adhesives in wood applications are key reasons for their extensive use. However, latex systems based on these types of polymer chemistries are considered inherently not biodegradable. As awareness continues to develop for this dimension of environmental impact, new alternative formulations will be required that support various end-of-life

options (recycle, reuse, or efficient biodegradation in addition to traditional landfills).

A key performance metric is the overall adhesive strength holding the wood-based structures together. Improvements in the overall adhesive strength will allow for a more efficient use of the adhesive, potentially reducing the overall adhesive resin load while maintaining the same performance. Also, the potential use of lower-quality wood components to meet the required structural performance may be possible with an improved adhesive technology.

Polysaccharides are biological materials obtained from a wide variety of plant sources. In general, woody biomass (from the forest processing industry) represents the largest source of industrially developed and utilized polysaccharide, cellulose. In general, polysaccharides are often highly aggregated materials, nonmelting, hydrophilic polymers that show extensive hydrogen bonding throughout the polyhy-

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droxy network. However, because of this, polysaccharides are often not soluble in water despite their hydrophilic nature. Solubility depends on the type of glycosidic linkages ( $\alpha$  or  $\beta$ ), polymer chain branching, and the resulting hydrogen bonding networks (Stumpf and Conn 1980, Yalpani 1988). A typical example that highlights these differences is a comparison between water-swallowable or -soluble amylose ( $\alpha$ -1,4-glucan), a typical component in many starches, and the water-insoluble cellulose ( $\beta$ -1,4-glucan), a typical highly aggregated component in wood biomass or cotton, as seen in Figure 1. The strong adhesive interaction between polysaccharides is the underlying reason for the broad use of starch-based materials in wood and paper adhesive applications. For example, starch is commonly added to some latex-based paper adhesives for the purpose of cost reduction, and they can also enhance tack.

DuPont BioMaterials has developed a new family of engineered polysaccharides from the enzymatic polymerization of sucrose that allows access to a range of materials with glycosidic linkage control, with designed-in molecular weights and molecular weight distribution, and with the capability to control the inherent material morphology from the molecular to the nano- and micrometer scale.

One specific example of such an engineered polysaccharide is an  $\alpha$ -1,3-polyglucose (glucan; PS) that is prepared with greater than 99 percent linkage selectivity as a linear, semicrystalline, water-insoluble structural polysaccharide. This polysaccharide is typically found in nature as part of the cell wall in mushrooms. It is now commercially available and produced by DuPont BioMaterials in a new bioprocess from sucrose using a glucosyltransferase enzyme as catalyst.

Typically, the PS may have a degree of polymerization of 800 glucose repeat units with a polydispersity in the range of 1.7 to 2.0, as controlled by the polymerization process conditions. Usually, polysaccharide materials show a significant degree of inter- and intramolecular hydrogen bonding, which leads to a highly aggregated material morphology. In the specific case of PS as isolated from this water-based bioprocess, high-surface-area spherical particle structures are observed with a high degree of bound water content (the isolated wet cake of PS contains 40% solids in a free-flowing wet powder), which, upon removal of water, can be further isolated as dry powder with an equilibrium solid content of 88 weight percent (wt%). The material utilized for the work described here was obtained as a dry powder having an average particle size of 9  $\mu\text{m}$  and as the above-described wet cake having a solids content of 40 percent. The objective of the work reported in this article is to assess the usefulness of incorporating the new, engineered PS into typical commercial latex systems and

determine if any performance advantage can be observed in these wood adhesives containing this glucan polymer.

## Experimental Methods and Materials

The adhesive samples used in this study were chosen because of their current use in commercial wood-bonding applications. TiteBond-II (TB-2) wood adhesive was purchased from the Home Depot. This adhesive is manufactured by Franklin Adhesives and is reported to be based on polyvinyl acetate and proprietary polymers that are not defined by Franklin Adhesives in their literature. Vinnapas-323 (Vin-323) and Vinnapas-EP-6300 (EP-6300) samples were obtained from Wacker Chemical Company. Vin-323 is reported to be a polyvinyl alcohol-stabilized vinyl acetate-ethylene (VAE) copolymer dispersion having a glass transition temperature ( $T_g$ ) of 23°C. EP-6300 is reported to be a carboxylated, high-solids VAE copolymer dispersion having a  $T_g$  of 0°C. The solids content of the latex adhesives was reported by the supplier and verified by gravimetric analysis by drying the samples in an oven at 100°C for 2 hours. The corresponding solids content for the Vin-323, EP-6300, and TB-2 are 55, 63, and 48 percent, respectively.

The PS, trade named NuVolve, is a new engineered polysaccharide polymer product obtained from DuPont BioMaterials, Wilmington, Delaware and prepared as described in US Patent nos. 7,000,000, 9,080,195, and 8,642,757 (Fig. 2). The PS was obtained in two forms, a dry powder form (88 wt% solids) and the wet-cake form (40 wt% solids). The wet-cake material is chemically identical to the dried powder, and it is also a free-flowing high-surface-area material. In essence, the wet cake is an agglomerated version of the dry powder that can still flow freely. The dry powder and wet-cake samples were added to the latex samples and mixed using a Cowles blade mixer spinning at 1,600 revolutions per minute. Additional water was added to the samples containing glucan polymer, as needed, to keep the total percent solids the same as the neat latexes. Formulations containing 0, 10, and 20 wt% PS (relative to the initial composition of the latex) were selected for this study. Those higher than 20 percent were not considered since the NuVolve polysaccharide polymer is being used as an additive to the formulation and not an adhesive on its own.

The adhesive sample billets were prepared at the Advanced Composites Center at the University of Maine and tested using the ASTM Standard Method D-905 (ASTM International 2013).

## Billet preparation

Clear, straight-grained, thick hard maple (*Acer saccharum*) was purchased from a local lumber store. The boards

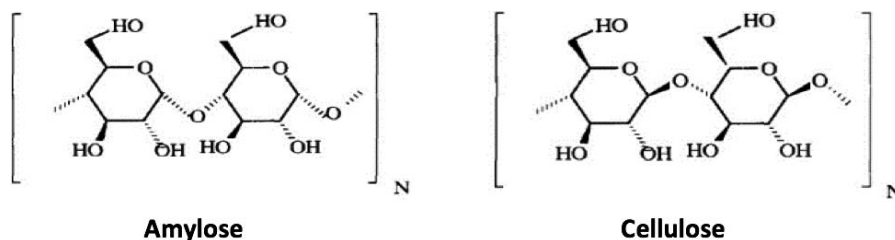


Figure 1.—Structures of  $\alpha$ -1,4-glucan, amylose and  $\beta$ -1,4-glucan, cellulose.

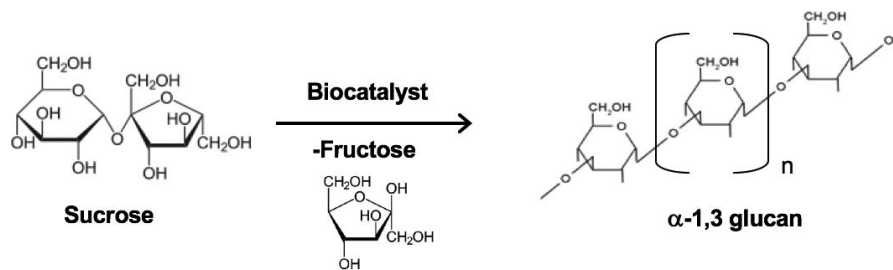


Figure 2.—Reaction scheme for preparing engineered polysaccharide  $\alpha$ -1,3-glucan.

were weighed and measured before purchase in an attempt to find boards of adequate surface quality and similar density. The purchased boards were ripped to 5.5 inches wide and cut into 32-inch lengths. The surfaces of the boards were planed to a thickness of  $\frac{3}{4}$  inch to ensure a fresh, smooth surface and uniform thickness of the boards. The boards were conditioned for 2 weeks targeting a moisture content of 8 to 9 percent. The board densities used for the billets were measured and in the range of 43 to 46 pounds per cubic foot.

Billets were manufactured by gluing together two  $\frac{3}{4}$ -inch-thick boards measuring 5.5 inches wide by 32 inches long. Adhesives were applied and spread by hand with a drywall knife. The amount of adhesive applied to each board was measured with a target adhesive amount of 60 g per billet. The billets were pressed in a 450-ton, 34 by 34-inches programmable logic controller–controlled Dieffenbacher hydraulic press. Four billets were pressed at a time, atop one another, for 90 minutes. The adhered billets were taken out of the press and conditioned at 70°F and 50 percent relative humidity for 7 days. Each of the billets was cut into 20-block shear specimens for ASTM D-905 (ASTM International 2013) testing, which also includes a D4 cycle of a pressure soak at 150°C followed by vacuum drying before shear testing. Testing was done on an Instron universal testing machine (Model 8801) using a 22-kPa load cell and a cross-head speed of 0.2 inches per minute.

### Polymer films

Polymer films of all the latex formulations were prepared by drying each of the formulations on polished ceramic plates at room temperature for 14 days, after which time they were gently peeled off the ceramic and allowed to further condition for a total drying time of 30 days. These polymer films were used for subsequent thermal analysis and solid-state nuclear magnetic resonance (SSNMR) studies for the purpose of trying to understand any performance differences observed in the D-905 studies.

### Thermal analysis

Differential scanning calorimetry (DSC) data were obtained using a TA Instruments Q2000 instrument operating in modulated DSC mode. The temperature ramp was 5°C per minute from  $-50^{\circ}\text{C}$  to  $+40^{\circ}\text{C}$ .

Dynamic mechanical analysis (DMA) data were obtained using a TA Instruments 850 DMA instrument with a thin film clamp configuration. The frequency of oscillation was 1 Hz. The temperature range was from  $-50^{\circ}\text{C}$  to  $+50^{\circ}\text{C}$  at a ramp rate of 3°C per minute.

### SSNMR spectroscopy

Solid-state  $^{13}\text{C}$  NMR spectra were obtained at 11.75 Tesla using a Varian Unity Inova instrument having a  $^1\text{H}$  frequency of 500 MHz. The solid latex samples were spun at 12,000 Hz with a Doty Scientific supersonic magic angle spinning (MAS) probe. The  $^{13}\text{C}$  NMR  $^1\text{H}$   $T_{1\rho}$  experiments were conducted using a variable  $^1\text{H}$  spin lock time with ramped cross-polarization. Spin lock array times ranged from 0 to 5,000 milliseconds. The  $^{13}\text{C}$   $T_{1\rho}$  experiments utilized spin lock array times in the range of 0 to  $1 \times 10^6$  milliseconds. For all experiments a cross-polarization contact time of 1 millisecond and a decoupling field strength of 62.5 kHz were used. Hexamethylbenzene was used as an external reference to correct  $^{13}\text{C}$  chemical shifts.

### Results and Discussion

ASTM-D-905 (ASTM International 2013) block shear data are presented and compare adhesives both neat and with the addition of the PS either as a dry powder or as a wet-cake dispersion. Figure 3 shows the dry and D4 testing of the Vin-323 samples.

From the data presented in Figure 3 we observe that the addition of PS to the Vin-323 base formulation in general resulted in an increase in shear stress required for failure, which indicates that the engineered polysaccharide additives are able to improve the overall adhesion when compared with the standard latex system. In particular, the 10 percent addition of PS dry powder increased the mean maximum shear stress by 39 percent, representing a significant improvement over the baseline latex performance in dry testing. Vin-323 is not defined as a water resistant Type II adhesive in its product literature; however, the trend observed in the D4 water-soak samples also shows that the addition of dry PS enhanced D4 adhesion strength by 62 percent.

The sample containing 20 percent PS dry powder also increased the mean maximum shear stress performance but only by 21 percent. This suggests that there might be an optimum loading level between 10 and 20 percent PS dry powder for this particular system. The addition of PS wet cake also increased the dry maximum shear stress, but not by the same degree. We also observed that the wet-cake samples did provide enhancement in D4 shear testing. The differences in the enhancement of the shear-stress performance using the dry or the wet-cake form of the PS may be attributed to the processing and particle size differences within the samples. Additional work is underway to expand the processing conditions and formulation details to assess the impact of PS morphology on bond strength in this latex system. It is expected that morphology factors such as

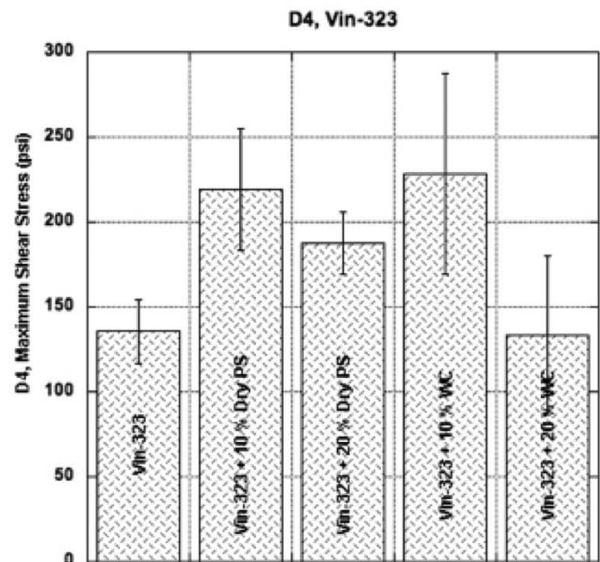
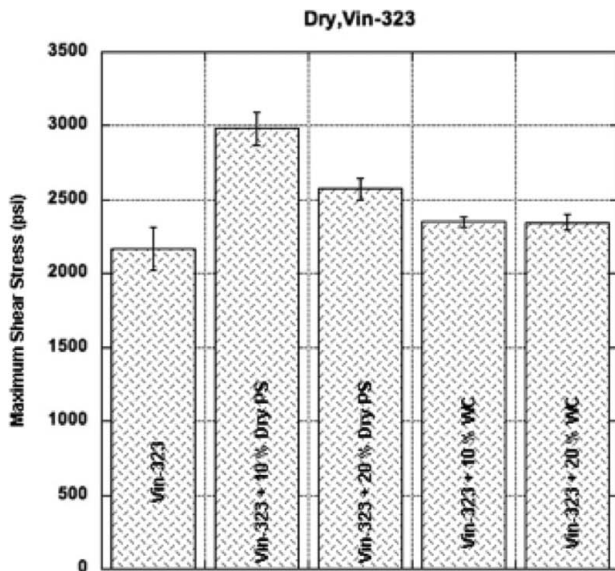


Figure 3.—Plot of the mean maximum shear stress of the Vinnapas-323 (Vin-323) samples as tested dry and after a D4 cycle. PS =  $\alpha$ -1,3-glucan; WC = wet-cake PS.

surface area or particle size should affect observed adhesive performance.

Figure 4 shows a comparison of another commercial latex, TB-2, which is defined as a moisture-resistant Type II adhesive. As with the Vin-323 sample, both dry and wet-cake PS were incorporated into the TB-2 latex as described earlier. In contrast to the Vin-323 samples, we observed no statistically significant difference between the neat TB-2 sample and the TB-2 sample with the addition of 10 percent dry PS. Furthermore, at higher loading levels of dry PS we observe a decrease in shear stress. In addition, incorporation of the wet-cake form of the PS shows a decrease in shear stress for the dry D-905 samples. Again, in contrast to the Vin-323 samples (seen in Fig. 3), the TB-2 samples

containing PS performed significantly worse than the neat TB-2 sample in D4 testing.

Vin-323 is a poly(vinyl alcohol)-stabilized VAE copolymer dispersion with a reported  $T_g$  of +23°C. This system is a fast-setting, high-heat-resistant dispersion with fully hydrolyzed poly(vinyl alcohol) compatibility. The presence of poly(vinyl alcohol) may be key to effective stabilization and synergistic activation of the engineered polysaccharide additive within this latex system. To further assess this hypothesis of a synergy with the latex system, a third, high-solids carboxylated VAE dispersion, EP-6300, was investigated. The potential interaction of the carboxyl functional group with the polyhydroxy surface of the engineered polysaccharide may result in the type of performance improvements observed for Vin-323.

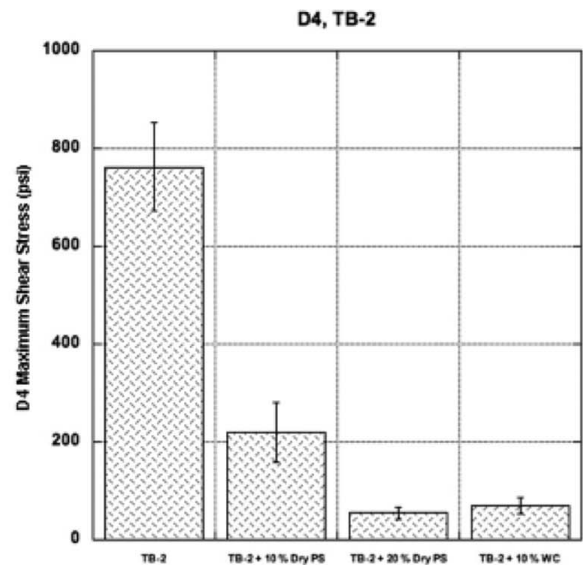
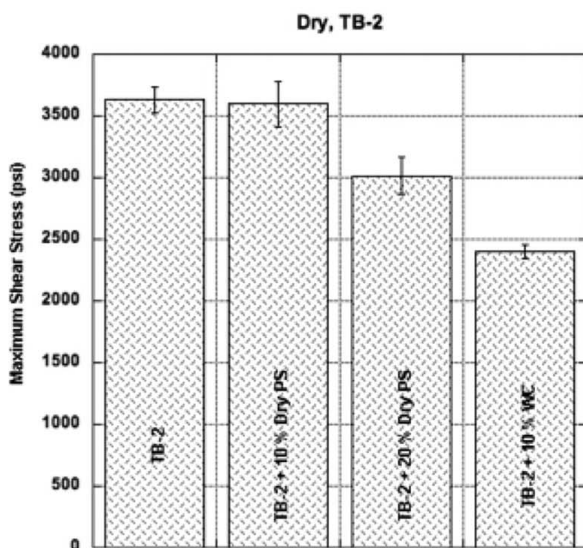


Figure 4.—Plot of the mean maximum shear stress of the TiteBond-II (TB-2) samples as tested dry and after a D4 cycle. PS =  $\alpha$ -1,3-glucan; WC = wet-cake PS.

The data for the EP-6300 samples do indeed show a similar trend when compared with the Vin-323 samples. Specifically, the presence of the dry PS powder enhanced the dry adhesive performance and the D4 adhesive performance, as can be seen in Figure 5. We did not test higher loadings of the dry PS or test the wet-cake PS in the EP-6300 latex.

From the data presented in Figure 5, we observe a 44 percent enhancement in dry adhesive strength with the addition of a 10 percent loading of dry PS and a 17 percent enhancement for the D4 testing. This suggests that the EP-6300 latex with the carboxylic acid functionality also positively interacts with the PS polymer and enhances adhesive performance under these experimental conditions. This is in contrast to the observations for the TB-2 samples, which showed a decrease in dry shear strength and D4 shear strength with the addition of PS in either form (dry or wet cake). Although the specific chemical composition of the TiteBond system is not fully described in the literature, it is apparent from this work that the adhesive performance of the engineered polysaccharide additive does strongly depend on the type of latex resin used in the formulation.

To assess the possibility of a general filler effect in the formulated Vinnapas samples, another series of billets was prepared that contained a 10 percent loading of corn starch and also a 10 percent loading of talc. Compared with the water-insoluble, linear, semicrystalline PS, the polysaccharide in corn starch is a mixture of water-soluble amylose ( $\alpha$ -1,4 glucan) and amylopectin ( $\alpha$ -1,4 glucan with various degrees of  $\alpha$ -1,6 glucan branching). The corn starch had an average particle size of 13  $\mu$ m and the talc had an average particle size of 10  $\mu$ m. The data can be seen in Figure 6.

As can be observed from the data in Figure 6, the presence of corn starch and talc does not enhance the adhesive properties of the Vin-323 system in the same way as the PS sample does. Therefore, we can say that the enhancements observed for the PS in the Vinnapas systems are not just filler effects.

## Wood failure measurements

In addition to adhesive strength, the actual performance of an adhesive system with regard to the type of failure observed during stress is of commercial relevance. Ideally, the adhesive-based interlayer should not provide the failure point for stress initiation or propagation resulting in macroscopic failure of the parts bonded through the adhesive. If a forced failure is observed in the wood structure (increase in wood failure), the performance of the adhesive and the interlayer bond formation is exceeding the inherent structural integrity of the bonded wood elements. This is usually the desired outcome.

An interesting additional finding from the D-905 block shear test shows that the presence of the PS in most latex samples, both as dry powder or as wet cake, will generally enhance the average percent wood failure measured for the formulations, the exception being the EP-6300 system. These data can be seen in Table 1, which shows the average percent wood failure.

The enhancement in wood failure could be due to molecular interactions between the latex and the engineered polysaccharide particles and the overall entanglement and secondary bonding interactions with the wood surface structure. This is reasonable considering the similarity of the PS structure and the structures of hemicellulose and cellulose in wood. Of course, only the amorphous domains of cellulose would be accessible for secondary bonding, but the possibility does exist.

## Thermal analysis

To further understand the differences in these adhesive formulations with and without the presence of the PS polymer, thermal analytical measurements were carried out on films of the adhesive samples to investigate the physical properties of the cured polymer (adhesive). Films of the neat adhesive and adhesive containing PS were prepared as described earlier.

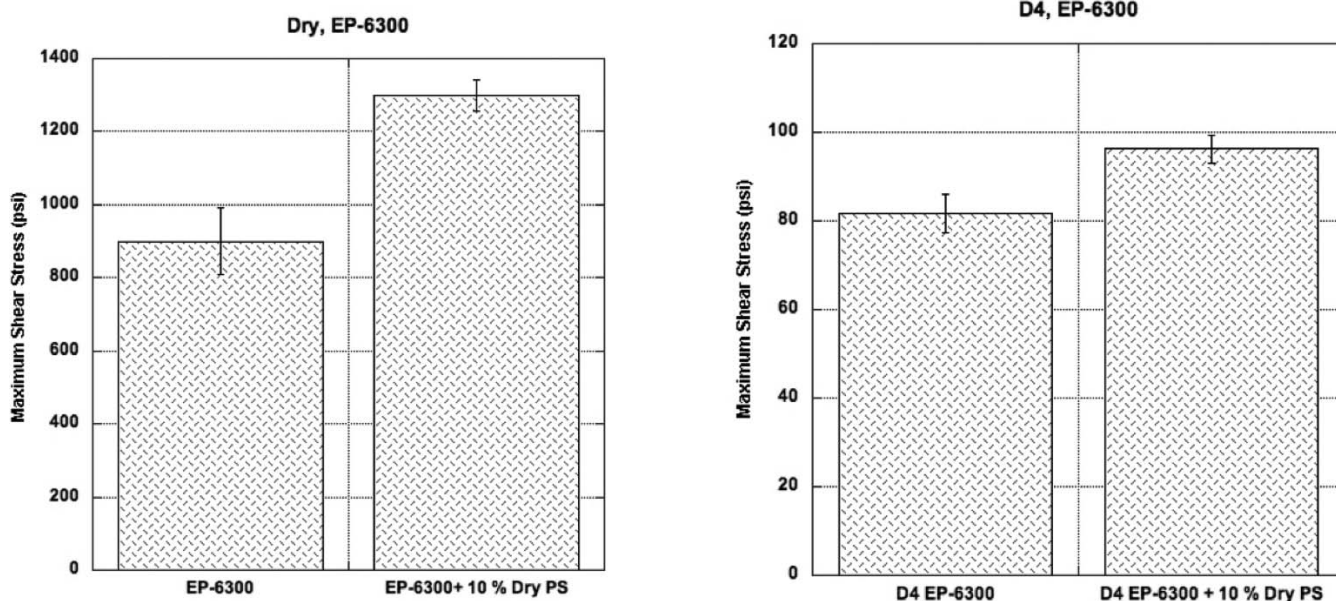


Figure 5.—Plot of the mean maximum shear stress of the Vinnapas EP-6300 (EP-6300) samples as tested dry and after a D4 cycle. PS =  $\alpha$ -1,3-glucan.

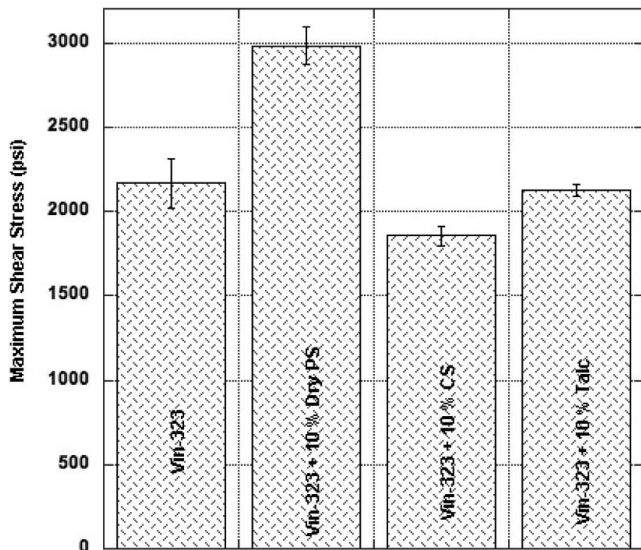


Figure 6.—Plot of the mean maximum shear stress of the Vinnapas-323 (Vin-323) samples comparing various fillers. CS = corn starch; PS =  $\alpha$ -1,3-glucan.

DSC measurements were taken on the adhesive films and there were no discernable differences observed between the samples. As such, DMA was used as an alternative method to assess morphological changes associated with the incorporation of the PS into the latex polymer formulations. DMA is known to have a relative signal sensitivity for  $T_g$  about 200 times that of DSC (Sepe 1997, Menard and Menard 2017). In Figure 7 we observe changes between the neat Vin-323 adhesive and the formulation containing a 10 percent loading of the dry PS.

As observed in Figure 7, the low-temperature modulus is increased for the sample containing the PS. This is expected for a material functioning as a reinforcing additive. However, the  $T_g$  of the PS-containing sample is lower as compared with the neat Vin-323. The  $T_g$  for the neat material, as measured by the loss modulus maxima, is 22°C, consistent with the Vin-323 literature. The  $T_g$  measured for the sample containing the PS is reduced to 15°C. This finding suggests that the PS must be intimately associated with the polyvinyl alcohol-stabilized VAE copolymer molecules in the latex dispersion. This intimate association

Table 1.—Average percent wood failure. The numbers are the average of 20 samples per formulation.

| Adhesive <sup>a</sup>           | Dry D-905 average % wood failure |
|---------------------------------|----------------------------------|
| Vinnapas-323                    | 0                                |
| Vinnapas-323 + 10% dry PS       | 2                                |
| Vinnapas-323 + 20% dry PS       | 6                                |
| Vinnapas-323 + 10% wet-cake PS  | 46                               |
| Vinnapas-323 + 20 % wet-cake PS | 46                               |
| Vinnapas-EP-6300                | 0                                |
| Vinnapas-EP-6300 + 10% dry PS   | 0                                |
| TiteBond-II                     | 65                               |
| TiteBond-II + 10% dry PS        | 75                               |
| TiteBond-II + 10% dry PS        | 80                               |
| TiteBond-II + 10% wet-cake PS   | 97                               |

<sup>a</sup> PS =  $\alpha$ -1,3-glucan.

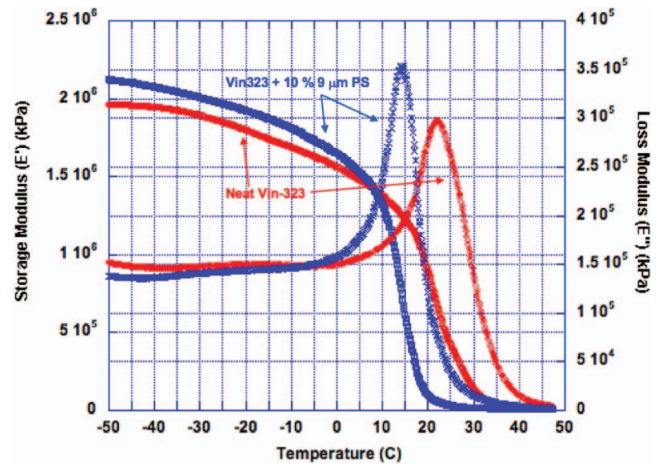


Figure 7.—Dynamic mechanical thermogram of neat Vinnapas-323 (Vin-323) compared with Vin-323 + 10 percent dry  $\alpha$ -1,3-glucan (PS).

may be changing the free volume and thus the radius of motion of the molecules within the solid polymer. If the polymer exhibits more mobility, the  $T_g$  is expected to be lower, as we observe in Figure 7. This increase in mobility and intimate association may account for the enhancement of block shear strength previously discussed. Further studies will be required to further support this hypothesis.

### Impact of PS particle size

On the basis of the positive findings seen for the Vinnapas samples containing the PS, further experiments were conducted to assess the effect of the PS particle size on the physical properties of the formulation, the maximum shear stress, and the related DMA measurements. Vin-323 formulations were prepared with 10 percent additive loading of 9-, 15-, and 30- $\mu$ m dry PS powders. Figure 8 compares the effect of particle size, via DMA, on polymer films made of these adhesives.

As can be observed in Figure 8, increasing particle size has the effect of increasing low-temperature modulus. Specifically, as the particle size increases from 9 to 30  $\mu$ m, the storage modulus increases at low temperature. However, we also observe changes in the storage modulus associated with particle size in the glass transition region of the polymer. This is better observed via loss modulus thermograms, as seen in Figure 9. In the comparison of the loss moduli we observe that the  $E''$  maximum moves to a lower temperature in the series of neat latex, the latex formulated with the 9- $\mu$ m particle and to an even lower temperature with the 15- $\mu$ m particle additive. The incorporation of the 30- $\mu$ m particle results in the loss maxima moving toward higher temperatures, approximately intermediate between the position of the 9- and 15- $\mu$ m particle data but still lower than the neat latex sample.

### Shear adhesion assessment of PS with various particle sizes

Another series of block shear samples was prepared using Vin-323 adhesive, which incorporated different particle-size PS powders (5-, 9-, 15-, and 30- $\mu$ m dry powders). As previously reported, 20 D-905 test specimens were tested

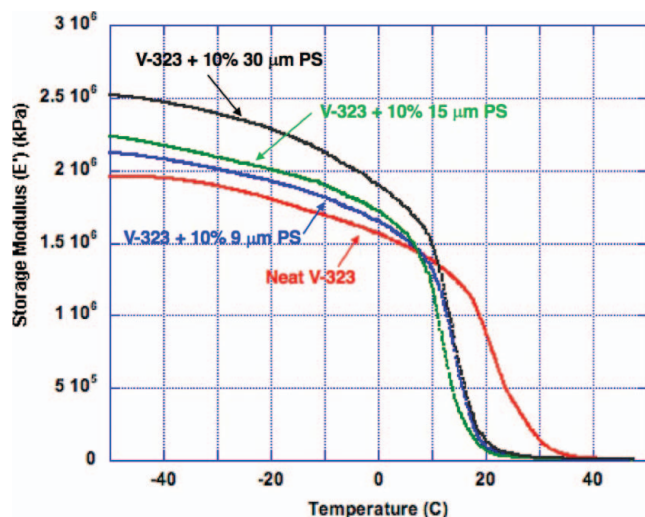


Figure 8.—Dynamic storage modulus ( $E'$ ) of a series of Vinnapas-323 (V-323) formulations having different polysaccharide particle sizes. PS =  $\alpha$ -1,3-glucan.

for each latex formulation and the data can be seen in Figure 10.

The combination of the DMA and the D-905 block shear data indicates that a PS particle size between 5 and 9  $\mu\text{m}$  might be optimal for strength and energy dissipation performances.

### SSNMR analysis of latex formulations

To gain further insight into the molecular dynamics occurring in the dried latex film samples, SSNMR spectroscopy studies were conducted. SSNMR is an effective technique for examining localized polymer morphology that can be seen as chemical shift differences, variation in peak shapes, and differences in relaxation behavior related to the efficiency of nuclear spin diffusion within the sample (Schaefer et al. 1977, Gerstein and Dybowski 1985, Komoroski 1986, Bovey and Mirau 1992).

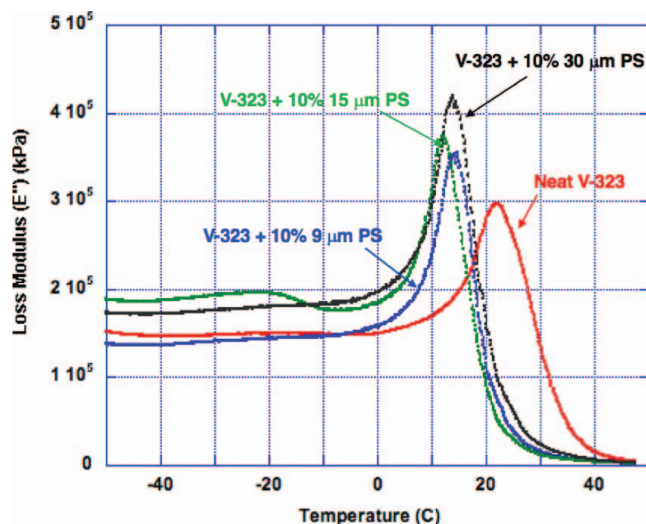


Figure 9.—Dynamic loss modulus ( $E''$ ) of a series of Vinnapas-323 (V-323) formulations having different  $\alpha$ -1,3-glucan (PS) particle sizes.

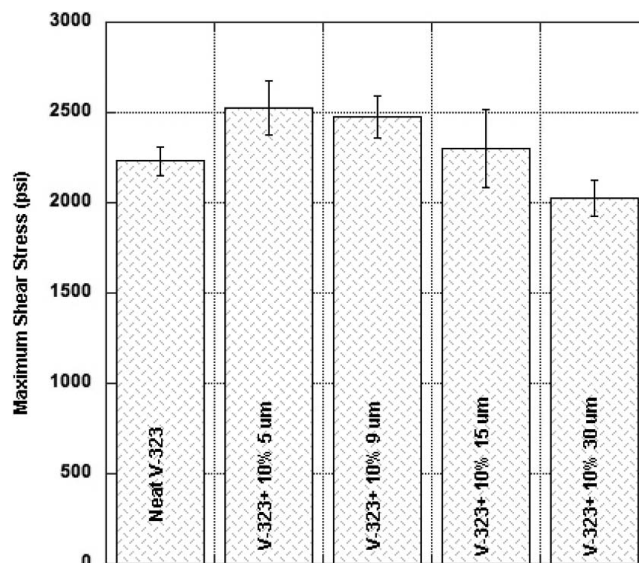


Figure 10.—Plot of the mean maximum shear stress of the Vinnapas-323 (V-323) samples containing varying  $\alpha$ -1,3-glucan particle sizes.

Using cross-polarization and magic angle spinning (CPMAS), we are able to easily resolve the unique carbon resonances of interest in the polymers (latex and PS).

For the initial SSNMR experiments, analyses of the proton rotating frame relaxation ( $^1\text{H } T_{1\rho}$ ) and the carbon rotating frame relaxation ( $^{13}\text{C } T_{1\rho}$ ) were selected. These experiments are sensitive to the influence of spin diffusion on equilibrium magnetization. The experiments are thus sensitive to the intimacy of spatial components within the polymer, as the modulation of spin diffusion by the components affects the motion of the polymer chains (Schaefer et al. 1977, Gerstein and Dybowski 1985, Komoroski 1986, Bovey and Mirau 1992). In these two experiments the proton magnetization decay is followed as a function of time in its rotating frame or the carbon magnetization decay as a function of time in its rotating frame.

Figure 11 shows a comparison of the CPMAS spectra for the Vin-323 samples with and without the dry PS. A spectrum of the neat PS is given for reference.

Vin-323 is a commercial material and the exact composition is not described in the literature or by Wacker Chemical. However, the peaks in the range of 10 to 80 parts per million (ppm) are likely associated with the methylene and methine carbons of polyvinyl alcohol. The peaks around 170 ppm are associated with the carbonyl carbon of the polyvinyl acetate. Comparing the spectra of neat Vinnapas and Vinnapas containing the dry PS, a slight downfield shift of the peaks in the sample containing PS is observed, supporting the hypothesis that the polysaccharide is hydrogen bonding to the latex system. Changes in the intensity and line shapes of the peaks associated with the Vinnapas sample in the presence of PS also support this hypothesis. These changes indicate that there is a difference in the efficiency of spin diffusion when comparing the neat Vinnapas sample with the sample containing PS. Tables 2A and 2B show the relaxation data associated with these samples.

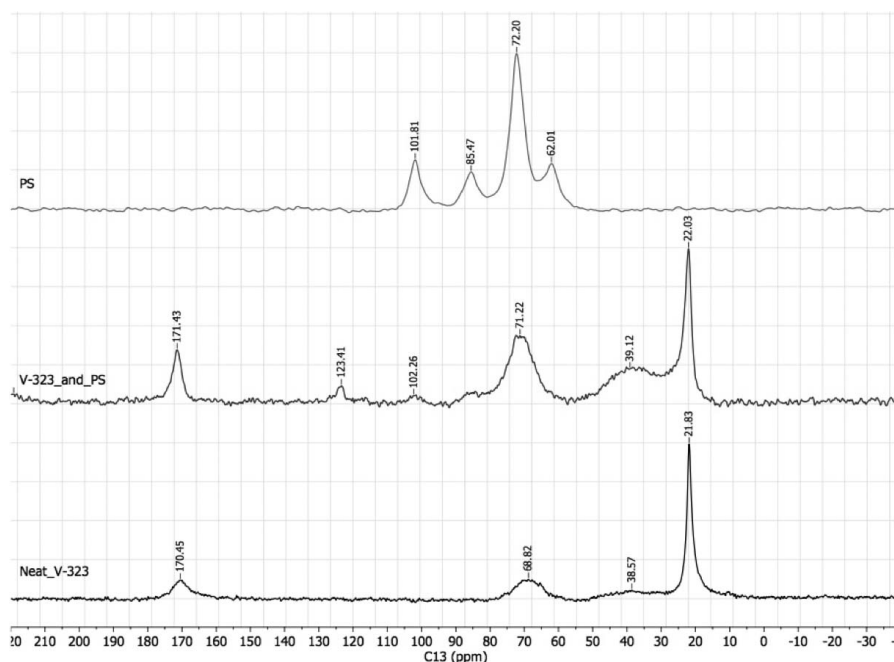


Figure 11.—Cross polarization and magic angle spinning spectra of neat Vinnapas-323 (V-323), V-323 containing 10 percent dry  $\alpha$ -1,3-glucan (PS), and the PS reference.

When comparing the relaxation rates for the defined peaks in Table 2, large changes in relaxation rates are observed for both  $^1\text{H}$   $T_{1\rho}$  and  $^{13}\text{C}$   $T_{1\rho}$ , indicating a large change in the efficiency of spin diffusion, most likely caused by changes in polymer chain motions. That is, higher motion will make the spin diffusion process less efficient and result in longer relaxation times under the conditions of the experiment. This finding in polymer chain mobility is consistent with the DMA data discussed earlier and shown in Figures 7, 8, and 9. In addition, since the relaxation rates are best defined by a single exponential fit (as opposed to a biexponential fit), we can conclude that the PS particles and the latex polymer must be intimately associated, forming a homogeneous system. If they were phase separated or existed in different domains, we would most likely observe a biexponential fit of the data.

Figure 12 shows a comparison of the CPMAS spectra for the TB-2 samples with and without the PS polymer. As with Figure 11, a spectrum of the neat PS is given for reference.

Table 2.—Carbon rotating frame relaxation rates ( $^{13}\text{C}$   $T_{1\rho}$ ) and proton rotating frame relaxation rates ( $^1\text{H}$   $T_{1\rho}$ ) given in milliseconds for neat Vinnapas and Vinnapas containing 10%  $\alpha$ -1,3-glucan (PS) polymer.

| Peak (parts per million)  | $^1\text{H}$ $T_{1\rho}$ (ms) | $^{13}\text{C}$ $T_{1\rho}$ (ms) |
|---------------------------|-------------------------------|----------------------------------|
| A: Neat Vinnapas-323      |                               |                                  |
| 170.45                    | 0.92                          | 1.93                             |
| 68.82                     | 0.52                          | 0.92                             |
| 38.57                     | 0.22                          | 0.24                             |
| 21.83                     | 1.27                          | 2.49                             |
| B: Neat Vinnapas-323 + PS |                               |                                  |
| 171.43                    | 5.26                          | 11.98                            |
| 71.22                     | 4.62                          | 5.19                             |
| 39.12                     | 3.55                          | 4.03                             |
| 22.03                     | 4.69                          | 8.01                             |

We do not observe the same degree of change in line shape or peak position for the TB-2 samples that we observed for the Vinnapas samples. If we also compare the  $^1\text{H}$   $T_{1\rho}$  and  $^{13}\text{C}$   $T_{1\rho}$  relaxation data in Table 3, we do not observe the dramatic changes in relaxation rates observed for the Vinnapas samples. The differences in relaxation rates are within experimental error of the measurements.

The DMA and the SSNMR results along with the results of the D-905 block shear studies suggest molecular-level intermolecular interactions between the polysaccharide and the latex polymer. It is hypothesized that the increase in performance that was observed for the Vinnapas samples may be due to the ability of the Vinnapas samples containing the PS to provide intimate hydrogen bonding-based interaction between the two components, hence increasing the effective surface area that is available for substrate adhesion. A similar enhancement in the D-905 data for the TiteBond samples that contained the PS was not

Table 3.—Carbon rotating frame relaxation rates ( $^{13}\text{C}$   $T_{1\rho}$ ) and proton rotating frame relaxation rates ( $^1\text{H}$   $T_{1\rho}$ ) given in milliseconds for neat TiteBond-II and TiteBond-II containing 10%  $\alpha$ -1,3-glucan (PS) polymer.

| Peak (parts per million) | $^1\text{H}$ $T_{1\rho}$ (ms) | $^{13}\text{C}$ $T_{1\rho}$ (ms) |
|--------------------------|-------------------------------|----------------------------------|
| A: TiteBond-II           |                               |                                  |
| 171.13                   | 2.41                          | 6.40                             |
| 68.0                     | 1.88                          | 3.23                             |
| 40.30                    | 2.18                          | 2.63                             |
| 21.86                    | 3.04                          | 5.84                             |
| B: TiteBond-II + PS      |                               |                                  |
| 171.19                   | 2.78                          | 5.49                             |
| 71.06                    | 2.06                          | 3.07                             |
| 40.06                    | 2.05                          | 1.87                             |
| 21.90                    | 2.76                          | 4.98                             |



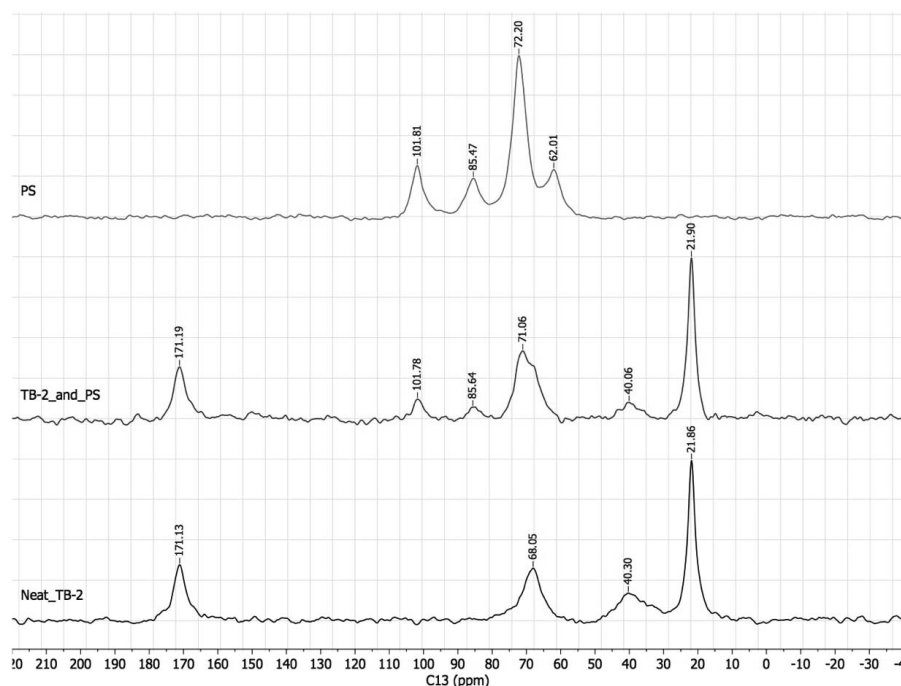


Figure 12.—Cross polarization and magic angle spinning spectra of neat TiteBond-II (TB-2), TB-2 containing 10 percent dry  $\alpha$ -1,3-glucan (PS), and the neat PS polymer.

observed and also supported by differences in molecular-level relaxation rates obtained from the SSNMR studies.

### Conclusions

The examples described here utilize a new engineered polysaccharide polymer, PS, incorporated into commercial latex-based wood adhesives. The addition of PS polymer to polyvinyl alcohol–stabilized VAE copolymer dispersion-based adhesives results in a significant performance increase of the adhesive as measured by ASTM-D-905 (ASTM International 2013) block shear testing. The mechanical properties and molecular dynamics as measured by DMA and SSNMR respectively confirm that the PS additive is intimately associated with the polyvinyl alcohol–stabilized VAE copolymer molecules and dramatically affects the molecular mobility of the latex polymers. An increase in molecular mobility, as was observed, may contribute to the ability of the adhesive to dissipate energy and stress more efficiently, resulting in enhanced adhesive bond strength and wood failure.

The unique morphology of the PS allows it to be easily formulated into various adhesive systems with excellent compatibility. The PS polymer described in this article has also been shown (but not in this article) to provide performance improvements in other wood adhesives as well; for example, in combination with soy flour adhesives, isocyanate-based adhesives, urea-formaldehyde formulations, and other low- $T_g$  polymeric systems, which will be published soon.

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