HEAT RESISTANT SUSTAINABLE ADHESIVES BASED ON SOY

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Introduction

Some biobased polymers have limited softening and depolymerization at elevated temperatures, which should make them perform well for structural wood composites under fire conditions. Our goals in this study were to develop tests for understanding material properties of biobased adhesives and to apply these tests to help understand failure of bonded materials. We characterized thermal performance of soy protein isolate alone and combined with several common denaturants using dynamic mechanical analysis (DMA).

Fire resistant adhesives are certified by various international standards, but these tests are costly and time-consuming, do not provide much structural information beyond a pass-fail criteria (for example, load at failure), and so do not provide enough information for development work or for understanding adhesion and failure mechanisms. DMA is widely used to determine the mechanical and rheological properties of polymers and adhesives [1]. When used in vibrational mode, a varying stress or strain is applied to the sample in sinusoidal fashion and the sample stiffness and damping is measured. The offset between the load and the displacement is used to calculate the elastic portion, called the storage modulus and the viscous portion, called the loss modulus.

For wood adhesives, DMA has been particularly useful to describe bond strength development [2, 3] either in a veneer sandwich tested in bending or on a glass fiber support (either torsion or tension) [4, 5]. The veneer sandwich technique is well suited for adhesive layers whose stiffness is much less than the veneers. When used for cured bonds subjected to high temperatures, relaxations in the wood substrate are convoluted with those of the adhesive, though large changes in adhesive properties can still be distinguished [6]. Glass fiber support is suitable for adhesives that are fluid enough to penetrate into the structure of the mat, such as phenol-formaldehyde [4]. When using glass fiber support, the applied load is transferred from fiber to fiber only at the fiber intersections through the adhesive layer or through entanglements. This presumes that the adhesive loading is low enough for the polymer to aggregate at fiber intersections, as is seen in a dilute solution.

Experimental

Soy protein isolate (ProFam 974, Archer-Daniels Midland, Decatur, IL) was used to make 5%(w/w) solutions with and without modification. Modifications were chosen from the literature as having improved bonding properties compared to unmodified isolate. The modifiers used were sodium dodecyl sulfate (SDS) [7], urea and guanidine hydrochloride [8] (Sigma-Aldrich, Milwaukee, WI) or adjustment to pH 10. pH was adjusted with sodium carbonate, 50% NaOH, or 1M HCl. A 5% solution of casein protein polymer powder (BL330, American Casein Co., Burlington, NJ) was made, with pH adjusted to 7.

Table 1: Protein and modifers tested by DMA

Protein	Modifier	pH	Ratio g additive per g protein
Soy isolate	--	7	--
Soy isolate	NaOH	10	--
Soy isolate	Na bisulfite	7	0.19
Soy isolate	Guanidine hydro-chloride	7	1.66
Soy isolate	Urea	7	2.90
Soy isolate	SDS	7	0.08
Casein	--	7	--

Table 1 summarizes the solution compositions and the adjusted pH. All solutions were mixed with a high-shear stick blender for 1 minute, adjusted to the target pH with sodium carbonate or 1M HCl, and allowed to rest for at least 1 hour.

The substrate for all glass fiber supported DMA was Whatman GF/C glass fiber filter paper, cut into strips approximately 50 mm wide. Strips were dipped into protein or protein+additive solutions. Excess solution was removed by using a hand roller. Samples were either air-dried or autoclaved at 120°C for 30 minutes, then air-dried. All samples were suspended vertically until dry to allow uniform solution distribution throughout the fiber mat without collecting on the surface. The tested specimens were cut from the dry strips to 6.5mm wide and tested in a TA Instruments Q800 DMA using the film tension fixture at 0.005%strain, 1 Hz.

DMA of neat adhesive films provides unambiguous results not influenced by the mechanical properties of the support, and is preferred. We chose the glass fiber support method because neat protein films fractured during drying. Our sample preparation is based on a method used previously to study curing of PF adhesives [9]. The temperature profile follows the sequence 5 minutes at 35°, ramp from 35 to 230° at 5°C/min and hold 30 minutes at 230°. This profile resembles that used in ASTM D7247 for testing compressive shear.

Results and Discussion

Scanning electron micrographs of the sample unmodified isolate deposited on the glass fiber show uniform protein deposition through the depth of the glass fiber support, as indicated by the appearance of particulates and film formation on fibers (Figures 1 & 2).

In figure 3, glass fiber shows little change on heating, with storage modulus around 100 MPa. Proteins show initial storage modulus 500-900MPa. Soy isolate with heat treatment (120°, saturated steam environment), shows higher storage modulus than air-dried isolate throughout the ramp to 230°. Casein, not autoclaved, which is used in adhesive for fire-rated doors, shows much higher initial storage modulus declining on heating to near that of the soy protein. Note that the tested casein formulation lacked the high levels of calcium, base and other additives that are used in casein adhesive. Commercial formulations may differ in properties.

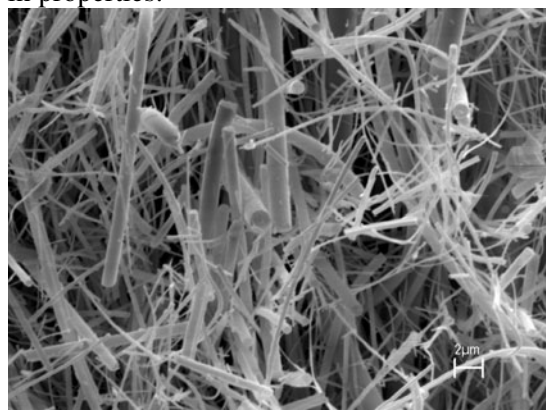

Figure 1: SEM of untreated glass fiber support

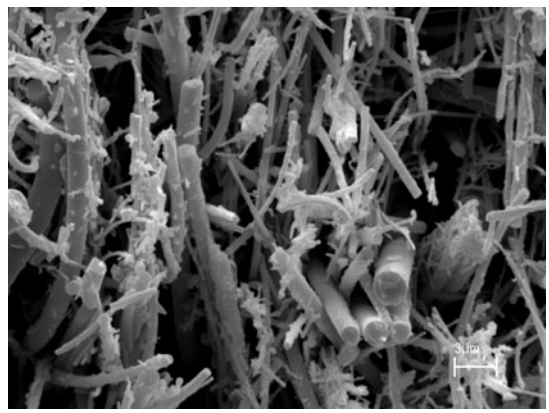

Figure 2: SEM of glass fiber support with treated with soy protein isolate and air dried.

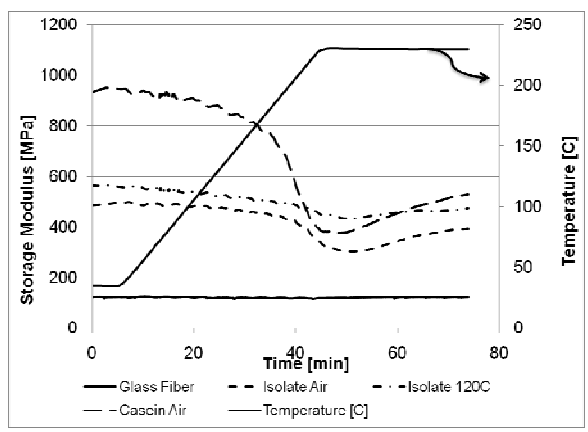

Figure 3: DMA of casein and soy protein isolate (air dried or autoclaved at 120°C) during the temperature profile shown

In figure 4, three of the modified soys (urea, guanidine HCL, SDS) had higher storage

modulus at room temperature, but showed dramatic declines in stiffness during heating. The urea-modified isolate shows the largest loss in storage modulus, followed by recovery to the level of the plain isolate. This may be explained by the physical properties of urea, which melts at 130°, vaporizes at 140-152° and decomposes at 152° [10]. Soy isolate modified with guanidine HCL showed greater darkening on heating than the other modifiers.

The procedure of ASTM D7247 measures compressive shear failure at two temperatures, ambient and after 230°, while structural composites can be expected to carry load through the temperature rise. The standard test would not reveal the loss of stiffness unless also paired with either a standard creep test or a full fire wall test.

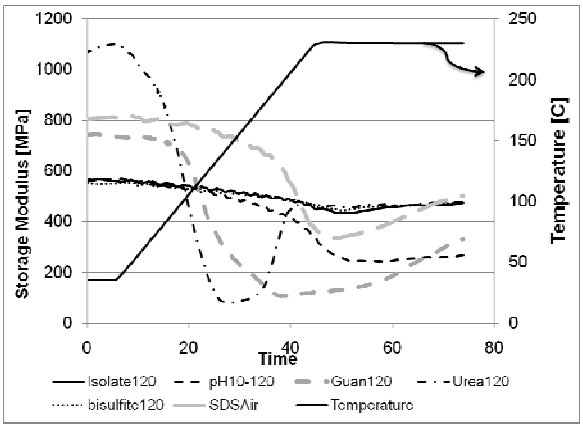

Figure 4: Effect of thermal exposure on soy isolate modified with sodium dodecyl sulfate (SDS), guanidine hydrochloride, urea, pH 10 and sodium bisulfite.

Though data presented here are for single samples for each treatment, we are encouraged by the reproducibility of the hot portion of the curve for several additives.

Conclusions

Our results suggest that the glass fiber support method can be extended to use with proteins. Specifically, we found it to be suitable for comparing the effect of additives on storage and loss modulus during thermal changes. This method provided indications of loss of stiffness due to elevated temperature, and revealed elevated temperature failure of modifiers that appeared promising at room temperature. Our results also indicated minimal changes in soy isolate denatured with bisulfite or exposed to steam environment.

Future work on the method should determine reproducibility of method and the effects of adhesive loading, and the effect of cure conditions.

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