# Bond Strength of Biodegradable Gelatin-Based Wood Adhesives

D.N. Dorr, S.D. Frazier, K.M. Hess, L.S. Traeger and W.V. Srubar III\*

Department of Civil, Environmental and Architectural Engineering, University of Colorado Boulder, ECOT 441 UCB 428, Boulder, Colorado 80309-0428 USA

Received January 14, 2015; Accepted June 9, 2015

**ABSTRACT:** A study of the potential for gelatin-based derivatives to serve as biorenewable, biodegradable adhesives for wood and engineered wood products is presented in this article. The effect of gelatin-to-water weight percent on the mechanical, specifically ultimate breaking (bond) strength, and thermal properties was investigated using tensile testing and differential scanning calorimetry, respectively. The breaking strengths of the gelatin-based adhesives were characterized and compared to four commercially available wood adhesives. The effect of 1–5% tannin addition on the mechanical, thermal, and moisture absorption behavior of the gelatin-based adhesives was also investigated. Results show that the gelatin-based materials demonstrate 1) appropriate thermal behavior for wood adhesive applications, namely no phase transitions occur from 15–80°C after three days of curing, and 2) comparable mechanical properties to the commercial adhesives. Specifically, the data suggest that the melting peaks of a) gelatin and b) gelatin-tannin adhesives disappear after three and two days of ambient curing, respectively. Furthermore, the tannin modifications did not cause reductions in the initial strength of the gelatin adhesives. Results of moisture conditioning and mechanical tests indicate that the tannin modifications did improve the short-term moisture resistance of the gelatin-based adhesives.

**KEYWORDS:** Adhesive, gelatin, mechanical properties, differential scanning calorimetry

# **1** INTRODUCTION

Over the past few decades, increased environmental awareness has fueled the development of more renewable and sustainable building materials and components [1]. Given that popular green building rating programs, such as the Green Building Initiative's Green Globes and the United States Green Building Council's Leadership in Energy and Environmental Design rating schemes, advocate for the specification of greener building products, materials that possess low embodied energy, low embodied carbon, and low human health toxicity are in high demand.

Worldwide, wood and engineered wood, such as dimensional lumber, plywood, particleboard, and glue-laminated lumber, are among the most prevalent materials used in building and construction. A majority of engineered wood products are manufactured using adhesives that emit noxious volatile organic compounds (VOCs). VOCs are organic compounds that volatilize at room temperature, causing molecules to either evaporate or sublimate into the surrounding

\**Corresponding author:* wsrubar@colorado.edu

DOI:10.7569/JRM.2015.634108

J. Renew. Mater., Vol. 3, No. 3, August 2015

air from liquid or solid form [2]. Extensive research has shown that VOCs are toxic to humans and have the potential to cause adverse short- and long-term health effects [3–5], including elevated risks of cancer, liver and kidney disease, and damage to the central nervous system.

Recent materials research has focused on reducing the environmental impact of construction adhesives [6]. While starch-based wood adhesives have received much attention [6-8], chemical or physical modifications are required to enhance the adhesive properties of starch-based materials. These modifications have been achieved via graft polymerization [9], blending [8], and use of crosslinking agents [10]. Other authors have noted the promising adhesive properties of other natural polysaccharides and polypeptides such as soy, sericin, and gelatin [11–13]. Gelatin is derived from partial hydrolysis of collagen from animal skins, bones, and tendons in either highly alkaline or acidic pH solutions [14]. The worldwide production of gelatin in 2007 was approximately 326,000 tons, of which 46.0%, 29.4%, 23.1%, and 1.5% was derived from porcine skin, bovine skin, bones, and other parts, respectively [15]. While gelatin has been obtained from fish and other animals [15,16], economics currently limit

Sample Identification	Gelatin (g)	Water (g)	Tannin (g)
G5	5.0	100	0
G10	10.0	100	0
G20	20.0	100	0
G30	30.0	100	0
G40	40.0	100	0
G50	50.0	100	0
G10T1	9.9	100	0.1
G10T3	9.7	100	0.3
G10T5	9.5	100	0.5

**Table 1** GelatinandGelatin-Tanninadhesivesamplenomenclature.

the main sources of gelatin to porcine and bovine byproducts.

For adhesive applications, gelatin and other proteins have positive attributes, including their renewability, biodegradability, global availability, nontoxicity, and low cost [17,18]. Gelatin has the potential to be manipulated during processing to produce tailored material properties, which depend on the polydispersity and amino acid sequence, such as gel strength, viscosity, and setting behavior [17]. Gelatin films demonstrate high Young's modulus and tensile strength when compared to other biopolymers (e. g., methylhydroxyethyl cellulose, starch, acacia gum) [19]. Mammalian gelatins (e.g., bovine, porcine) demonstrate improved mechanical properties when compared to other gelatins (e.g., fish) [20].

Despite the positive attributes of gelatin, one prominent disadvantage is the natural interaction of gelatin and water during and after gelation. The mechanical properties of gelatin are dependent upon the regeneration of the triple helix structures as aqueous gelatin solutions are cooled below 40°C and transition to the gel phase. When in solution, water is needed to regenerate the triple helix. Therefore, water has an influence on the mechanical properties of the gelled film [21]. When dehydrated films are exposed to moisture, gelatins tend to swell and absorb water, which causes mechanical property degradation [21, 22]. Therefore, there is interest in ensuring sufficient water resistance of gelatin films for use in applications such as food packaging or wood adhesives, while not compromising their ability to biodegrade [22].

In related work, Gómez-Estaca *et al.* [23] looked at the effect of gelatin origin and chitosan addition on the rheological, mechanical, and thermal properties, water solubility, water permeability, and microbial resistance of gelatin films. The addition of chitosan increased the water resistance of bovine hide gelatin by 30% and tuna skin gelatin by 18%. The strength of bovine hide gelatin decreased by 11%, while the strength of tuna skin gelatin decreased by 68% [23]. Bigi et al. [24] investigated the mechanical, thermal, and swelling properties of gelatin crosslinked with glutaraldehyde. The addition of glutaraldehyde increased the Young's modulus of porcine skin gelatin films by a factor of 20. The melting temperature increased from approximately 40°C to 70°C. Swelling was observed to decrease by more than 50% [24]. Cao et al. [25] looked at the effect of gelatin crosslinked with ferulic and tannin acid on mechanical properties, water sensitivity (dissolvability), and water permeability. Ferulic and tannin acid increased the tensile strength, elongation to break, and elastic modulus, but the overall benefits highly depended on pH. While no change in water sensitivity or water vapor permeability was observed [25], Peña et al. [26] found that tannin modification reduced the water absorption of gelatin films by 50%.

To further explore the potential for protein-based materials, namely gelatin, to serve as a viable alternative to conventional wood adhesives, this study investigated the mechanical behavior, thermal properties, and water absorption behavior of gelatin-based wood adhesives. To assess the effect of gelatin concentration on mechanical properties, adhesives were prepared with gelatin-to-water (g/w) ratios of 5–50% by weight. The mechanical bond strength and thermal properties of the adhesives were characterized via mechanical testing and differential scanning calorimetry (DSC), respectively. The results were compared to five commercial construction adhesives. To address the undesirable hydrophilic nature of gelatin, the effect of 1-5%tannin addition on the mechanical properties, thermal behavior, and moisture resistance of gelatin-based adhesives was also investigated herein.

### 2 MATERIALS AND METHODS

#### 2.1 Gelatin Preparation

Gelatin was commercially obtained from Knox (Kraft Foods Group, Inc.) in powder form. To prepare the gelatin adhesives, 100 g of water was first heated to 40°C. Powdered gelatin was added and dissolved under continuous agitation for 10 minutes. The amount of gelatin added to the water depended upon the desired percent (%) of gelatin by weight of the resulting samples. For example, 10 g of gelatin added to 100 g of water resulted in a 10% sample. Six sample formulations were prepared, namely 5%, 10%, 20%, 30%, 40%, and 50% samples.

### 2.2 Tannin Modification

Powdered wine tannin was supplied by LD Carlson Company. The tannin-modified adhesives were prepared using the same procedure outlined in Section 2.1. Tannin and gelatin were simultaneously added to 100 mL of 40°C water and mixed for 10 minutes under constant agitation. The amount of tannin added depended upon the desired tannin content. For example, 0.5 g of tannin and 9.5 g of gelatin were added to 100 g of water to achieve a sample with 5% tannin content by total solid mass. Three tannin-modified sample formulations were prepared: 1%, 3%, and 5%. The sample identification for the gelatin and gelatin-tannin films and adhesive are shown in Table 1.

#### 2.3 Composite Manufacture

For testing the adhesive strength of gelatin and the commercial wood glues, oak wood veneers, supplied by Sure-Wood Forest Products, were cut into strips 4"  $L \times 0.75''$  W (101 mm  $L \times 19$  mm W). The thickness of the oak wood samples was 0.25" (6.4 mm). The gelatin and gelatin-tannin adhesives were prepared as described in Section 2.1 and Section 2.2, respectively. A thin layer of the adhesive sample was placed on a  $0.75'' \times 0.75''$  (19 mm  $\times$  19 mm) splice area (shown in Figure 1) to secure two oak wood substrates to the ends of one oak wood substrate. To fabricate the composite, a total of three oak strips were glued at two locations and allowed to cure for 7 days in ambient conditions. The geometry of the tensile test specimens is shown in Figure 1. Composites using commercial wood adhesives, namely Gorilla Glue (GG), Liquid Nails (LN), Titebond (T), and Weldbond (W), were fabricated in a similar fashion.

#### 2.4 Mechanical Property Characterization

The breaking (bond) strength of the adhesive-bonded wood samples was characterized according to a modified ASTM D1002-10 standard tensile test method using an Instron 5869 Universal Testing Machine. Samples were tested in tension using a displacementcontrolled rate of 5 mm/min. Six specimens were tested for each sample formulation. Ultimate breaking strength was calculated by dividing the maximum experimental load at break,  $P_{max}$ , by the adhered area.

# 2.5 Thermal Property Characterization

Glass transition and melt temperature data was collected using a TA Instruments Q2000 DSC in a nitrogen environment using a purge rate of 50 mL min<sup>-1</sup>. Samples with a mass between 3 and 10 mg were first equilibrated at 15°C followed by heating at a rate of 10°C/min to 80°C. The range of temperatures was used to ensure melting temperature was observed but limited to 80°C to avoid the vaporization of water.

Thermal property data for samples aged seven days or greater was collected using a Mettler Toledo 823e differential scanning calorimeter (DSC) in a nitrogen environment using a purge rate of 40 mL min<sup>-1</sup>. Samples with a mass between 2 and 6 mg were heated at a rate of 10°C/min from 25°C to 90°C and held for 5 minutes to erase thermal history. Cooling was carried out at 5°C/min to -10°C and held for 5 minutes. Samples were then reheated at 5°C/min to 90°C to ensure the retention of bound water and to simulate ambient conditions for construction and building materials.

#### 2.6 Moisture Absorption Characterization

Moisture absorption experiments were conducted according to a modified ASTM D5229. Gelatin solutions were prepared for 10% and 40% weight of gelatin to weight of water (g/w) concentrations (i.e., G10, G40). Before the powered gelatin was added, 100 mL of water was heated to 60°C in order to ensure complete dissolution. The gelatin-water solution was allowed to mix under continuous agitation for 15 minutes. To investigate the effect of tannin modification on the moisture resistance of gelatin, a tannin addition of 2.5% was added to the 40% g/w sample gelatin to yield a tanninmodified sample, G40T2.5. The tannin was added to the 40% g/w solution that had been prepared as previously described and continuously agitated for 15 minutes. Once the tannin was added, the solution was allowed to mix under continuous agitation for 45 minutes. The solutions were cast in rectangular forms



Figure 1 Geometry of the adhesive breaking strength tensile-test specimens.

until gelation occurred. After gelation, the samples were placed between grates, secured with ties, and cured in ambient conditions for 3 days. After ambient curing, the samples were weighed and placed in an oven at 60°C for conditioning to remove any unbound moisture. During oven drying, the sample weights were measured at intermittent time intervals until the weight loss was negligible.

Three samples measuring 15 mm  $\times$  15 mm were laser cut from each sample (10G, 40G, and G40T2.5) using an Epilog Legend 36EXT laser system. The samples were weighed and measured before complete immersion in distilled water at room temperature (21 ± 1°C). Their weight gain was recorded at intermittent time intervals in order to compare the swelling ratios (defined herein as a percent weight gain due to the absorption of water by preconditioned sample) for the G10, G40, and G40T2.5 and determine the effect of tannin addition on moisture absorption.

# 2.8 Mechanical Performance during High Humidity Conditioning

The effect of high humidity on the breaking strengths of gelatin-based adhesives was determined for adhesive-bonded wood samples using a plain gelatin (G10) and a tannin-modified gelatin (G10T5) adhesive sample. The preparation of the adhesive-bonded wood samples is described in Section 2.3, and the preparation of the G10 and G10T5 adhesives is described in Section 2.1 and 2.2, respectively. The samples were cured in ambient conditions for 7 days. On day 7, three unconditioned samples were tested for breaking strength as described in Section 2.4. The rest of the samples were placed in a high humidity chamber. The high humidity chamber was prepared by placing a supersaturated solution of sodium phosphate in a sealed plastic container. The sealed plastic containers were 60 cm  $\times$  45 cm  $\times$  20 cm airtight storage boxes from IRIS USA, Inc. The temperature and humidity in

the chamber were recorded using an EL-USB-2-LCD temperature and humidity data logger from Lascar Electronics. For the high humidity chamber, the data logger recorded an average relative humidity (RH) of 95.4% with a standard deviation of 2.3% and an average temperature of 22.4°C with a standard deviation of 0.5°C. All the samples were placed on grates in the chamber to ensure full exposure to the humidity condition. Three conditioned samples were tested for breaking strength, as described in Section 2.4, after 1, 3, and 7 days of being in the high humidity chamber.

# **3 RESULTS AND DISCUSSION**

# 3.1 Effect of Gelatin-to-Water Content on Mechanical and Thermal Properties

Figure 2 shows the effect of gelatin-to-water ratio on the breaking strength of the gelatin-based adhesives. All of the tests resulted in true adhesive breaks wherein the failures occurred only through the adhesive and not through the wood substrate. In general, higher gelatin-to-water ratios resulted in increased breaking strengths. For example, the G5 samples exhibited a breaking strength of  $3.1 \pm 0.3$  MPa, while the G40 samples achieved a breaking strength of  $7.5 \pm 2.6$  MPa, which corresponds to an increase of 141%.

Figure 2 also shows that the strengths of the gelatin-based adhesives are greater than, or comparable to, commercially available wood adhesives. For example, the breaking strengths of the GG and LN adhesives were 87% and 82% less, respectively, than the G40 samples, which exhibited the highest strength for the gelatin-based adhesives. The average breaking strength of the G40 adhesives was also comparable to the strengths of the T and W samples. The breaking strength of G40 only varied -4.1% and +1.5% from the T and W adhesives, respectively.

Kim and Netravali [13] suggest the sizeable amount of hydroxyproline present in gelatin creates hydrogen



Figure 2 Comparison of ultimate breaking strength of gelatin-based and commercial wood adhesives. Error bars represent minimum and maximum experimental value.

bonds when in contact with the cellulose on the surface of the wood substrate, which results in increased strength of the adhesive assembly. In the context of this study, the higher concentration of gelatin, namely 40%, may provide sufficient hydroxyproline to produce the maximum number of hydrogen bonds with the cellulose at the wood surface. Once saturated, additional gelatin concentration would not provide additional strength as evident by the similar breaking strength for the G40 and G50 samples.

Data collected from adhesive manufacturers also suggest that the commercially obtained adhesives contain elevated levels of VOCs. For example, the GG and LN samples contain 12 g/L [27] and 46 g/L [28], and the T and W contain 5.6 g/L [29] and 9.0 g/L [30] of VOCs, respectively. According to manufacturers, the GG adhesives are polyurethane-based and contain various forms of diisocyanates and polyisocyanates. The LN adhesives contain acrylic and formaldehyde. No publically disclosed information was obtainable on the chemical formulation of the T and W samples. Together, these data demonstrate that the gelatinbased adhesives are both mechanically and, potentially, environmentally preferred to the commercial adhesives investigated herein.

Figures 3 and 4 show evidence that for the 10% gelatin (G10) and 40% gelatin (G40) samples, the melting peaks disappear after aging in ambient conditions. For these samples containing gelatin only, the melting temperature increased over the course of two days of curing, and no melting was observed after three days. As shown in Figure 5, samples containing tannin displayed no melting after two days. The addition of 1%, 3%, and 5% tannin (G40T1, G40T3, G40T5) did, however, increase the melting temperature from 45°C to approximately 50°C. These results indicate a) an interaction between the gelatin network and tannin (e.g.,



**Figure 3** DSC thermogram of 10% gelatin (G10) after 1 day, 2 days, and 3 days of curing at ambient conditions. Note the disappearance of the melting peak in the 3-day thermogram.

J. Renew. Mater., Vol. 3, No. 3, August 2015

crosslink formation) and b) a non-thermoreversible gelation after sufficient aging.

Reported melt temperatures for gelatin vary based on preparation, storage conditions, and gelatin source. For example, type A porcine skin gelatin has been reported to have a melting temperature of 223°C [26], while type A bovine gelatin has been reported to have a melting temperature of 52°C [23]. Type B bovine skin gelatin has been reported to have a melting temperature of 31°C [31]. Previous work has also concluded that the gelatin-to-water ratio does not lead to an increase in a melting temperature for gelatin from the same source, but rather it increases the heat of melting [31]. Although a variety of melting temperatures have been reported in literature, this study is the first report of the non-melting behavior of gelatin. This finding may be due, in part, to high g/w concentrations investigated herein. The studies reported in [26] and [23] both investigated gelatin films with g/w concentrations less than 10% (~5% and ~4%, respectively). The authors of another study reported a melting temperature of ~  $31^{\circ}$ C for a 40% film, which is comparable to the 45°C melt temperature observed in this study [31].

The lack of melting in the adhesive samples can be attributed to gelatin origin, casting temperature, and aging. Regardless of source, gelatin cast at room temperature is well known to form helical structures [32]. The helical structures behave as junctions in a network [33]. Upon gelation, hydrogen bonds form and continue to form well after gelation. Over time, hydrogenbond crosslinks can form [33]. As hydrogen/intermolecular bonds are formed, water is forced out of the system, and the remaining water is tightly bound in the gelatin network [34]. The increasing number of bonds after the initial gelation explains the lack of melting after 2 days of curing at room temperature.



**Figure 4** DSC thermogram of 40% gelatin (G40) after 1 day, 2 days, and 3 days of curing at ambient conditions. Note the disappearance of the melting peak in the 3-day thermogram.







Figure 6 Adhesive breaking strengths of G10 and 1%, 3%, and 5% tannin addition (by weight).

# 3.2 Effect of Tannin Addition on Mechanical, Thermal and Moisture Absorption Properties

As shown in Figure 6, the tannin modification did not affect the mechanical properties of the gelatin adhesive strength. The 1%, 3%, and 5% tannin addition to the G10 adhesive samples exhibited neither benefit nor negative impact on the strength of the glue.

As shown for G40T3 in Figure 5, the DSC thermograms for gelatin samples with a 3% tannin addition showed no phase transitions in the range of 15°C to 80°C after two days of curing. A similar result was also found for all tannin-modified gelatin adhesives that were investigated. Furthermore, all gelatin samples with and without the addition of tannin showed no phase transitions in the range of -10°C to 90°C upon heating and cooling. The existence of no phase transitions, together with an increased initial melting temperature and decreased time to a lack of melting, indicates that the tannin molecules chemically interact with the gelatin system. Peña *et al.* [26] found that the addition of tannin up to 10% by weight resulted in minimal changes to endothermic peak locations, but increasing tannin concentration decreased enthalpy of the corresponding peaks. Broad endothermic peaks were observed for gelatin and gelatin-tannin samples centered at approximately 100°C, with some peaks forming at temperatures as low as 50°C.

Figure 7 shows the swelling ratios for G10, G40, and G40T2.5. It is observed that the increase in gelatin concentration from 10% to 40% improved moisture resistance. When compared to the swelling ratio of the G10 samples at equilibrium, the G40 samples absorbed 38.5% less water. Moreover, the addition of tannin further improved the moisture resistance of the gelatin-based adhesive. When compared to G40 swelling ratio at equilibrium, G40T2.5 absorbed 15.6% less water. The results of this study support the findings of Peña *et al.* [26] in which tannin modification reduced the water absorption of gelatin films.



**Figure 7** Swelling ratios of G10, G40, and G40 with 2.5% tannin addition (by weight of tannin to weight of gelatin). Error bars represent  $\pm$  one standard deviation.



Figure 8 Time-dependence of adhesive breaking strengths of gelatin (G10) and gelatin-tannin (G10T5) samples conditioned in high humidity (95.4% RH) conditions.

Figure 8 shows the time evolution of breaking strengths of G10 and G10T5 wood adhesive samples conditioned in a high humidity environment (95.4% RH). The breaking strengths of G10 and G10T5 were comparable for unconditioned samples, but the tannin-modified conditioned sample (G10T5) demonstrated improved properties through 3 days of high humidity exposure. When compared to G10, G10T5 exhibited 35.3% and 59.6% higher breaking strengths at 1 and 3 days, but exhibited a reduction of 14.4% and 40.0% in breaking strength at 1 and 3 days compared to the unconditioned sample. As expected, the tannin modification was not effective in providing resistance to moisture beyond 7 days of high humidity exposure. Chemical modifications have been found to delay, not completely prevent, the kinetic transport of water into bulk wood composite in much the same way that traditional wood varnishes, paints, and

J. Renew. Mater., Vol. 3, No. 3, August 2015

coatings slow, but not completely preclude, moisture absorption.

# 4 DISCUSSION

The mechanical property and toxicity data gathered and presented herein suggest that biodegradable gelatin-based wood adhesives demonstrate good potential to become a viable alternative to commercial wood adhesives when both mechanical strength and potential environmental hazards are considered. The strengths of the gelatin-based adhesives, which are expected to emit no VOCs, were equal to or stronger than leading adhesives that contain elevated levels of VOCs, which are known to cause adverse human health effects. Due to its malleability and ability to bond well with wood and other natural fibers, gelatin has a wide variety of adhesive and composite

© 2015 Scrivener Publishing LLC 201

applications in the automotive, packaging, and construction industries.

As previously discussed, one challenge for gelatinbased materials is its hydrophilicity. Gelatin inherently absorbs water and water vapor when exposed to moisture. Moisture exposure is inevitable in building and construction applications. The water resistance of gelatins can be improved by incorporating chemical additives (e.g., tannin, starch, chitosan, oligosaccharides) [26]. As observed from the thermal results, the melting peak disappeared at a faster rate and the melting temperature was higher for gelatin-tannin compared to gelatin systems. The data suggest that gelatin-tannin systems form more or stronger bonds at a faster rate than gelatin systems. As observed from the moisture absorption results, tannin addition had lower swelling ratios compared to gelatin systems. The data indicates moisture absorption resistance, which may be attributable to the bonding interactions between gelatin and tannin molecules.

As observed from the high humidity breaking strength results, tannin addition to gelatin adhesives showed increased water resistance as exhibited by the higher breaking strength values through 3 days of high humidity exposure. The observed greater breaking strength may also be attributed to improved bonding between gelatin and tannin molecules. Therefore, the thermal, moisture absorption, and high humidity breaking strength data from this study support the reduction in hydrophilicity from the bonding between gelatin and tannin molecules as proposed by Peña *et al.* [26].

Significantly improving the moisture resistance of gelatin-based materials, however, may reduce the ability of the material to readily degrade. When developing innovative, sustainable materials, a balance must be struck between durability of the material during its service life and deterioration of the material at the end of its service life. While low moisture resistance and biodegradability of gelatin may be seen as a challenge in terms of its long-term durability, it may also be an advantage for green building projects that incorporate strategies for planned obsolescence and that advocate for materials that are designed to degrade in service (e.g., roofing, siding). Advantages of materials that are designed to degrade include reductions in waste and energy for transport, sorting, recycling, and reuse.

Another remaining challenge for gelatin-based materials is the high variability in the achievable thermal and mechanical properties of gelatin, which can differ significantly depending on the source (e.g., porcine, bovine, fish) [16,35]. These differences can be attributed to differences in amino and imino acid content, specifically the imino acids proline and hydroxy-proline [36]. Thus, a grand opportunity exists in

regard to leveraging the tailorability of the mechanical and thermal properties of gelatin-based materials by blending gelatins from various sources for targeted material properties for a wide variety of applications. A notable challenge exists, however, in manufacturing and sourcing consistent fish-derived gelatin, since fish species are well known to demonstrate a varying amino acid content based upon the environmental conditions of the species [36].

# 5 CONCLUSIONS

In this study, the breaking strength and thermal properties of gelatin-based wood adhesives were investigated. When comparing both mechanical and environmental metrics, namely adhesive breaking strength and potentially low-VOC content, a mixture of 40% gelatin-to-water proved to be a more effective wood adhesive than common, commercially available wood adhesives. While the gelatin was modified with 1-5% tannin to improve the hydrophobicity of the adhesives, the tannin addition did not negatively affect the mechanical performance or thermal properties of pure gelatin mixture. Moisture absorption tests confirm that tannin-modified samples improve the shortterm moisture resistance of gelatin-based adhesives. Thermal property data confirm that no phase change was observed with pure gelatin mixtures or gelatintannin mixtures after a minimum aging of two days. The results demonstrate that gelatin-based adhesives may be viable, biorenewable alternatives to the commercial construction adhesives investigated herein, especially for temporary construction applications or applications with minimal moisture exposure.

#### ACKNOWLEDGMENTS

This research was made possible by the Undergraduate Research Opportunities Program, the Department of Civil, Environmental and Architectural Engineering, the College of Engineering and Applied Sciences, and the Sustainable Infrastructure Materials Laboratory (SIMLab) at the at the University of Colorado Boulder. This work represents the views of the authors and not necessarily those of the sponsors. The collaboration with Mr. Torin McCue in the Department of Civil, Environmental and Architectural Engineering and Dr. David Walba in the Department of Chemistry and Biochemistry at the University of Colorado Boulder is gratefully acknowledged.

#### REFERENCES

- 1. B. Berge, *The Ecology of Building Materials*, Routledge. (2009)
- 2. C.E. Baukal Jr, (Ed.). *Industrial Combustion Pollution and Control*, CRC Press. (2004).
- 3. M. Kampa and E. Castanas, Human health effects of air pollution *Environ. Pollut.* **151**(2), 362–367 (2008).
- C. Jia, S. Batterman and C. Godwin, VOCs in industrial, urban and suburban neighborhoods, Part 1: Indoor and outdoor concentrations, variation, and risk drivers. *Atmos. Environ.* 42(9), 2083–2100 (2008).
- L.A. Wallace, Human exposure to volatile organic pollutants: implications for indoor air studies. *Annu. Rev. Energ. Env.* 26(1), 269–301 (2001).
- S.H. Imam, S.H. Gordon, L. Mao and L. Chen, Environmentally friendly wood adhesive from a renewable plant polymer: characteristics and optimization. *Polym. Degrad. Stabil* **73**(3), 529–533 (2001).
- Z. Wang, Z. Li, Z. Gu, Y. Hong and L. Cheng, Preparation, characterization and properties of starch-based wood adhesive. *Carbohyd. Polym.* 88(2), 699–706 (2012).
- A. Moubarik, A. Allal, A. Pizzi, F. Charrier and B. Charrier, Characterization of a formaldehyde-free cornstarch-tannin wood adhesive for interior plywood. *Eur. J. Wood Wood Prod.* 68(4), 427–433 (2010).
- 9. Z. Wang, Z. Li, Z. Gu, Y. Hong and L. Chen, Preparation, characterization and properties of starch-based wood adhesive. *Carbohyd. Polym.* **88**, 699–706 (2012).
- S. Imam, L. Mao, L. Chen and R.V. Greene, Wood adhesive from crosslinked poly(Vinyl Alcohol) and partially gelatinzed starch: preparation and properties. *Starch* 51 (6), 225–229 (1999).
- H. Lei, G. Du, Z. Wu, X. Xi and Z. Dong, Cross-linked soy-based wood adhesives for plywood. *Int. J. Adhes. Adhes.* 50, 199–203 (2014).
- L.J. Zhu, M. Arai and K. Hirabayashi, Relationship between adhesive properties and structure of sericin in cocoon filament. J. Sericult. Sci. Jap. 64(5), 270–274 (1995).
- J.T. Kim and A.N. Netravali, Performance of proteinbased wood bioadhesives and development of smallscale test method for characterizing properties of adhesive-bonded wood specimens. *J. Adhes. Sci. Technol.* 27 (18-19), 2083–2093 (2013).
- K.B. Djagny, Z. Wang and S. Xu, Gelatin: A valuable protein for food and pharmaceutical industries: Review. *Crc. Cr. Rev. Food Sci.* 41(6), 481–492 (2001).
- I.J. Haug, K.I. Draget and O. Smidsrød, Physical and rheological properties of fish gelatin compared to mammalian gelatin. *Food Hydrocolloids*, 18, 203–213 (2004).
- M.C. Gómez-Guillén, M. Pérez-Mateos, J. Gómez-Estaca, E. López-Caballero, B. Giménez and P. Montero, Fish gelatin: a renewable material for developing active biodegradable films. *Trends Food Sci. Tech.*, **20**, 3–16 (2009).
- M. Gioffre, P. Torricelli, S. Panzavolta, K. Rubini, and A. Bigi, Role of pH on stability and mechanical propertites of gelatin films. *J. Bioact. Compat. Pol.* 27(1), 67–77 (2011).
- B.S. Chiou, R.J. Avena-Bustillos, J. Shey, E. Yee, P. J. Bechtel, S.H. Imam, G.M. Glenn and W.J. Orts,

Rheological and mechanical properties of cross-linked fish gelatins. *Polymer*, **47**(18), 6379–6386 (2006).

- 19. A. Gennadios, (Ed.), *Protein-based Films and Coatings*, CRC Press. (2002).
- S. Leick, P. Degen, B. Kohler and H. Rehage, Film formation and surface gelation of gelatin molecules at the water/air interface. *Phys. Chem. Chem. Phys.* **11**, 2468– 2474 (2009).
- I. Yakimets, S.S. Paes, N. Wellner, A.C. Smith, R. H. Wilson and J.R. Mitchell, Effect of water content on the structural reorganization and elastic properties of biopolymer films: A comparative study. *Biomacromolecules* 8, 1710–1722 (2007).
- M.C. Gómez-Guillén, B. Giménez, M.A. López-Caballero and M.P. Montero, Functional and bioactive properties of collagen and gelatin from alternative sources: A review. *Food Hydrocolloids* 25(8), 1813–1827 (2011).
- J. Gómez-Estaca, M.C. Gómez-Guillén, F. Fernández-Martín and P. Montero, Effects of gelatin origin, bovinehide and tuna-skin, on the properties of compound gelatin-chitosan films. *Food Hydrocolloids*, 25, 1461–1469 (2011).
- A. Bigi, G. Cojazzi, S. Panzavolta, K. Rubini and N. Roveri, Mechanical and thermal properties of gelatin films at different degrees of glutaraldehyde crosslinking. *Biomaterials* 22, 763–768 (2001).
- N. Cao, Y. Fu and J. He, Mechanical properties of gelatin films cross-linked, respectively, by ferulic acid and tannin acid. *Food Hydrocolloids* 21, 575–584 (2007).
- C. Peña, K. de la Caba, A. Eceiza, R. Ruseckaite and I. Mondragon, Enhancing water repellence and mechanical properties of gelatin films by tannin addition. *Bioresource Technol.* **101**, 6836–6842 (2010).
- 27. The Gorilla Glue Company, Gorilla Glue [MSDS], http://www.gorillaglue.com/sites/all/themes/gorilla/pdf/MsdsGorillaGlueEnglishJuly2013.pdf (June 21, 2013).
- Akzo Nobel Paints LLC, Liquid Nails Adhesive [MSDS], http://www.liquidnails.com/LNDatasheets/ MSDS/LN-903\_LNP-903 (March 12, 2013).
- Franklin International. Titebond Extend Wood Glue [MSDS], (May 21, 2014). http://www.franklininternational.com
- Frank T. Ross and Sons Ltd. Weldbond Universal Adhesive [MSDS]. http://www.weldbond.com/files/Weldbond%20Universaladhesive\_0.pdf (February8,2013)..
- I. Dranca and S. Vyazovkin, Thermal stability of gelatin gels: Effect of preparation conditions on the activation energy barrier to melting. *Polymer* 50, 4859–4867 (2009).
- 32. S. Fakirov and D. Bhattacharyya, Gelatin and gelatinbased biodegradable composites: Manufacturing, Properties, and Biodegradation Behavior, in *Handbook of Engineering Biopolymers: Homopolymers, Blends and Composites,* Hanser Publications, Cincinnati, Oh. (2007).
- K. Chen and S. Vyazovkin, Temperature dependence of sol-gel conversion kinetics in gelatin-water system. *Macromol. Biosci.* 9, 383–392 (2009).
- 34. P.V. Kozlov, The structure and properties of solid gelatin and the principles of their modification. *Polymer* **24**, 651–666 (1983).

J. Renew. Mater., Vol. 3, No. 3, August 2015

- 35. P.M. Gilsenan and S.B. Ross-Murphy Rheological characterisation of gelatins from mammalian and marine sources. *Food Hydrocolloids* **14**, 191–?195 (1999).
- 36. M.C. Gómez-Guillén, J. Turnay, M.D. Fernández-Díaz, N. Ulmo, M.A. Lizarbe and P. Montero, Structural and

physical properties of gelatin extracted from different marine species: a comparative study. *Food Hydrocolloids* **16**, 25–34 (2002).