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Shear Strain and Microscopic Characterization of a Bamboo Bonding Interface with Poly(vinyl alcohol) Modified Phenol–Formaldehyde Resin

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ABSTRACT: The study of the shear strain distribution at the bonding interface helped us to understand the bamboo bonding interface response mechanisms to solve problems of ply bamboo deformation or bonding failure. The shear strain distribution across a two-ply bamboo sheet bonded with a ductile phenol–formaldehyde resin (PF) modified by poly(vinyl alcohol) (PVA) was measured by means of electronic speckle pattern interferometry, along with tensile strength measurements to prove the shear stain distribution on a macroscopic scale. This research effectively combined macroscopic mechanical properties with microcosmic interfacial mechanical properties. The shear strength and shear strain results showed that PF modified with 20% PVA performed better than common PF and PF modified with 5 and 10% PVA. Microscopic fluorescent characterization of the bonding interface also provided evidence that a new bonding mechanism was adequate for bamboo bonding under the ductile PF modified with 20% PVA. Moreover, we suppose that the results of this study will help in the choice of bamboo-specific adhesives under different strain conditions. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1345–1350, 2013

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INTRODUCTION

Fundamental studies of bamboo adhesives and adhesion have been characterized by uncertainty because of poorly characterized initial and final conditions.[1–3] The interface of the bamboo substrate and adhesive plays an important role in composite material applications.[4] Water-soluble, low-molecular-weight phenol–formaldehyde (PF) resol resin is commonly used in the bamboo-based panel industry to manufacture products such as bamboo mat plywood, laminated bamboo lumber, and recombined bamboo timber (Japan), and its utility for many bamboo-based applications[5–7] is beyond question. However, questions persist regarding the observation of a nanomechanical interlock formed by PF impregnation in bamboo as compared to wood, because bamboo is intrinsically short of horizontal organization like wood rays and so on. To a large extent, the bondline thickness and bondline strength formed by the adhesive specifically have a great influence on the composite material's shear strength.[8,9] At the same time, under high-moisture and high-heat conditions, the stress transition between ductile bamboo substrates and rigid PF seems unduly severe in the zone of the bonding interface.[10] All of these unusual and notable factors affect the widespread use of PF in bamboo-based engineered materials.

In consideration of these facts, PF flexible processing is especially valuable in the manufacturing of bamboo-based materials with poly(vinyl alcohol) (PVA) as the modifier for PF resin. In general, PVA is widely used as water-soluble or water-dispersible polymer, and partially hydrolyzed grades are used mainly as protective colloids in emulsions.[11] These factors make PVA particularly suitable for modifying the PF resol resin commonly used in bamboo-based materials. Many researchers have attempted to improve the ductility of brittle concrete materials with PVA.[12–15] The incorporation of PVA into concrete provides a practical and substantial means of improving its tensile strength, bending toughness, and impact toughness and reducing its tendency to crack. Furthermore, under microscopic characterization, the addition of PVA fiber to plain concrete greatly enhances its postpeak tensile-softening behavior under a tensile load. Ductile fibers cross the paths of potential cracks and transmit stress between those fibers and the matrix and throughout the interfacial bond.

Many researchers have attempted to characterize the interaction of wood surfaces and adhesives in various ways but often with contradictory conclusions. Sonnenschein et al.[3] provided evidence that the most important interfacial aspect of building board strength is the adhesive surface coverage of the wood particles or fibers. However, in Frihart's[16] opinion, if the adhesive penetrates into the cell wall to form a bridge, the role of the primary and secondary chemical bonds at the adhesive–wood interface might be less important, whereas penetration into the cell walls can change the material's mechanical strength. Thus, it can be seen that the characterization of the interaction between the adhesive and matrix is of vital importance.

In this study, we manufactured two-ply bamboo panels with PF resin modified by different levels of PVA. We tested the micro-scale strain distribution and strain concentration in the vicinity of the bonding interface by means of electronic speckle pattern interferometry (ESPI) and the bonding line shear strength to speculate on a possible bonding interface model illustrating the interaction of the modified PF with the bamboo matrix. We also investigated the morphology of the adhesive bondlines in the bamboo matrix with fluorescence microscopy.

EXPERIMENTAL

Modification of PF Resin with PVA

A reactor equipped with a mechanical stirrer, a reflux condenser, and a thermometer was charged with appropriate levels of PVA and water. The temperature of the reaction mixture of PVA and water was raised to 100°C with agitation in a thermostatic water bath. After the PVA had dissolved completely, the temperature of the reaction mixture was lowered to 50°C; phenol and sodium hydroxide were added to the solution along with formaldehyde (up to 80% of the total), and agitation was continued for 10 min. After these additions, the mixture temperature in the reaction still was again raised to 92°C at a constant heating rate for 50–60 min, and the reaction was maintained at this temperature for 15 min. This heating and cooling cycle was conducted one more time through the addition of the leftover formaldehyde and the measurement of the reaction mixture viscosity over 60 min at a constant temperature of 92°C. The reaction mixture was obtained by rapid cooling until the solution viscosity met the requirements. Ductile PF modified by different contents of PVA (5, 10, and 20%) was manufactured via the experimental methods explained previously.

Sample Preparation

These modified adhesives were used to glue two-ply bamboo panels, and the specimens were then press-cured for 15 min under 2 MPa of pressure at a temperature of 140°C. After curing, the specimens were maintained in a conditioning chamber held at 65% relative humidity and 20°C for 1 week until equilibration was attained.

Shear Testing

Shear testing was conducted to measure the bonding strength of the modified adhesives at the bamboo surface. Shear specimens were produced for this experiment in accordance with DIN EN 302-1-2004 with a total length of 150 mm, a width of 20 mm, and a thickness of 10 mm (2 × 5). Incisions were saw-cut to direct the notches toward the glue line and allow for an effective bond length of 10 mm, as suggested by DIN EN 302-1-2004. The shear strength tests were performed on a universal testing machine with the load applied at a speed of 2.5 mm/min. We tested a sufficient number of specimens to get 10 valid samples, and the bamboo failure rate was close to 30%.

ESPI Measurement

To monitor the shear displacement on the surface of the two lap-joint specimens, shear testing corresponding to DIN EN 302-1-2004 was performed on a universal testing machine equipped with a TS-S1-1XP ESPI system. The basic principle of the ESPI technique was explained and detailed in a previous article.[17] With the optical setup used here, the size of the field of view (FOV) observed with ESPI was 44 × 35 mm^2, and the working distance between camera and specimen was about 300 mm. The specimens were preloaded to 50 N and then strained in 14 steps of 5 N each. We conducted the shear testing twice in two directions, *x* and *y*. Because ESPI caught the deformation from only the *x* direction, each deformation of two-ply bamboo was controlled in its elastic stage. At each displacement step, an interference fringe image of the observed FOV was taken. The displacement maps were computed by the summary of the information from all 14 displacement steps. Each adhesive with five specimens was tested at least five times until all of the specimens showed similar results, and then, we chose only one specimen for calculation.

Sample Sections and Fluorescent Microscopic Observation

The bonding interface regions were stained by fluorescent dye so that we could better observe the morphology of the adhesive bondlines in the bamboo matrix. A cross section in the area of interest on each sample was created with a Reichert-Jung Ultracut E microtome equipped with a sapphire knife at room temperature and after the specimens had been softened by soaking. The cross section was then dehydrated with graded ethanol (30, 50, 75, 95, and 100%), and Toluidine Blue O fluorescent dye was added (0.5%) via a droplet method over 30 min. Each sample was then washed twice in distilled water, glycerin was added, and they were covered for observational purposes. Fluorescent microscopic observations were made, and the images were recorded digitally. The penetration situation, such as the depth and color, was studied and analyzed with Image J software.

RESULTS AND DISCUSSION

Shear Strength

Clear differences in the shear strength values were observed in specimens glued with different PVA contents. As depicted in Figure 1, we observed that with an increasing percentage of PVA, the shear strength started to descend at first but then rebounded to values higher than the starting point. The maximum strength was 16.39 MPa with a PVA content of 20%, whereas the minimum strength was 11.95 MPa with a PVA content of 5%.

To better understand the diversity of the shear strength, in reference to Frihart's[16] bonding model, we set up a model to illustrate the difference between the bonding interface and the substrate considering the influence of PVA and bamboo. As shown in Figure 2, PF, composed of oligomers and monomers, easily forms a polymer chain and crosslinks by hot pressing. These bonds have a high content of aromatic or resonance-stabilized structure with limited flexibility,[18] and they easily lead to stress concentration and a rigid backbone, which is incompatible with ductile bamboo. In contrast, PVA, with its branched hydroxy, which makes it prone to combining with the hydroxymethyl of PF, belongs to the prepolymerized adhesive group with a flexible backbone.[10] Therefore, more energy resulting from strain concentration in the vicinity of the glue line will be

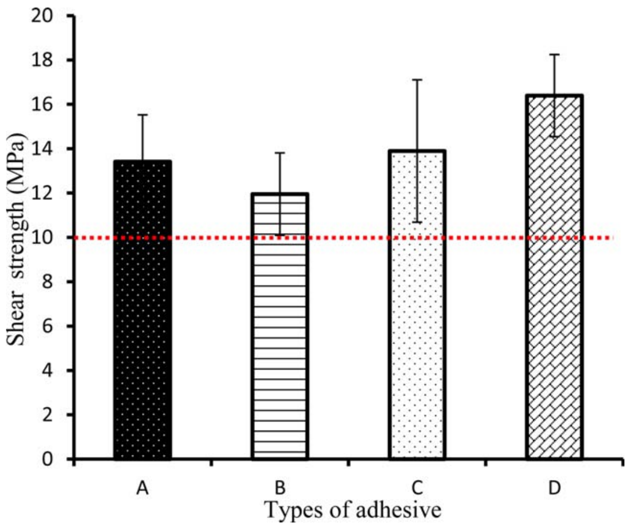

Figure 1. Shear strength of the bamboo bonding with PF modified by PVA: (A) without PVA, (B) with 5% PVA, (C) with 10% PVA, and (D) with 20% PVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorbed by interfacial slipping, and this will impart a higher shear strength. As shown in Figure 1, the shear strength decreased with low levels of PVA because of a lack of entanglement networks; this led to a strain concentration between the two adhesives, whereas the interface slipped without any obvious overall effect. However, as the percentage of PVA increased, a sufficient entanglement of PVA ensured strain transmission.[19] Interface slipping removed the strain concentration, eliminated interfacial energy, and led to an increase in shear strength.

In addition, because of the unidirectional shear deformation in bamboo, ductile PF may be more suitable for bamboo-based materials than the commonly used stiff PF because ductile bamboo fibers usually bear more deformation, which is highly incompatible with stiff PF.

Shear Strain Distribution

Two-dimensional patterns of the in-plane strain distribution across the FOV on the tensile specimens glued with different adhesives are shown in Figure 3. For both glues, the ESPI measurements of single lap-joint samples showed that the normal and shear strains along the glue line were comparably low in the middle of the overlapping area but increased steeply at both ends of the bonded area. These increased values of the normal and shear strains were localized in the thin bondline itself and in an area not extending further than 1 mm from the bondline. With regard to the type of glue, higher levels of the normal and shear strains were measured for the ductile PF than for the stiff PF sample, and the strain gradients and transmission areas were much more pronounced for the former adhesive than for the latter. In the region of the bonding interface, strains from 4.6×10^{-3} to 6.4×10^{-3} mm were observed for the PF samples compared with strains from 5.2×10^{-3} to 7.2×10^{-3} mm for the PF sample with 20% PVA.

According to Frihart's models,[16] prepolymerized adhesives could offset the energy created from the stress concentration through slippage during application of a lateral load. So, it was reasonable for PVA to drive all of the stiff PF slippage when a lateral load was being applied because of its branched hydroxyl combining with the hydroxyl of hydroxymethyl from PF on hot pressing. As shown in Figure 3(b,c), there were discontinuous breaks in the strain distribution with as little as 5–10% PVA.

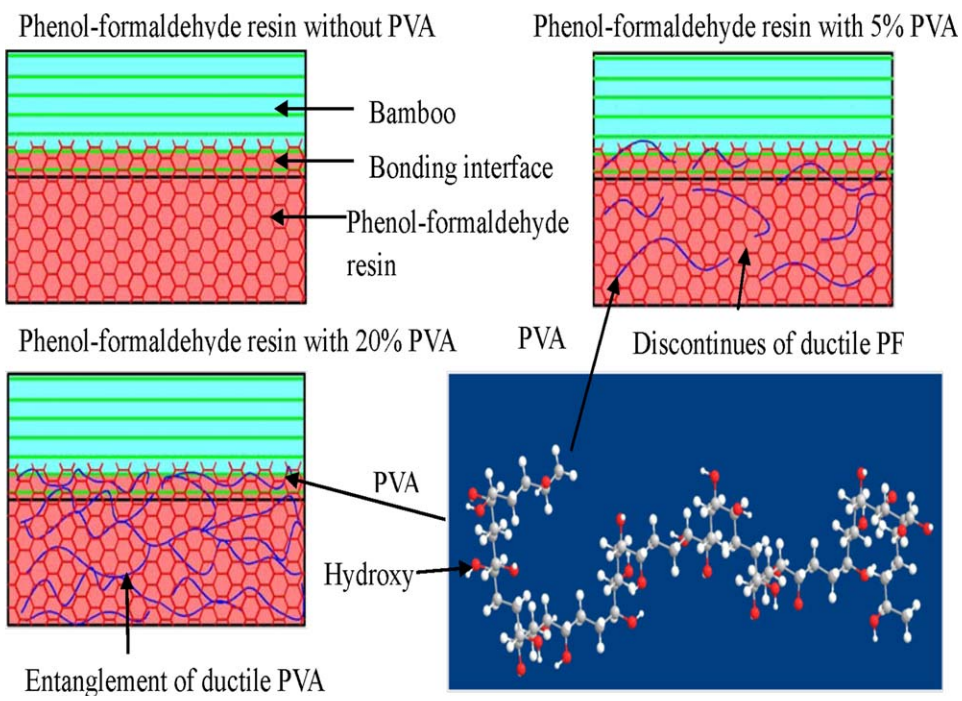

Figure 2. Schematic model of the bamboo/PF modified by the PVA bonding interface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

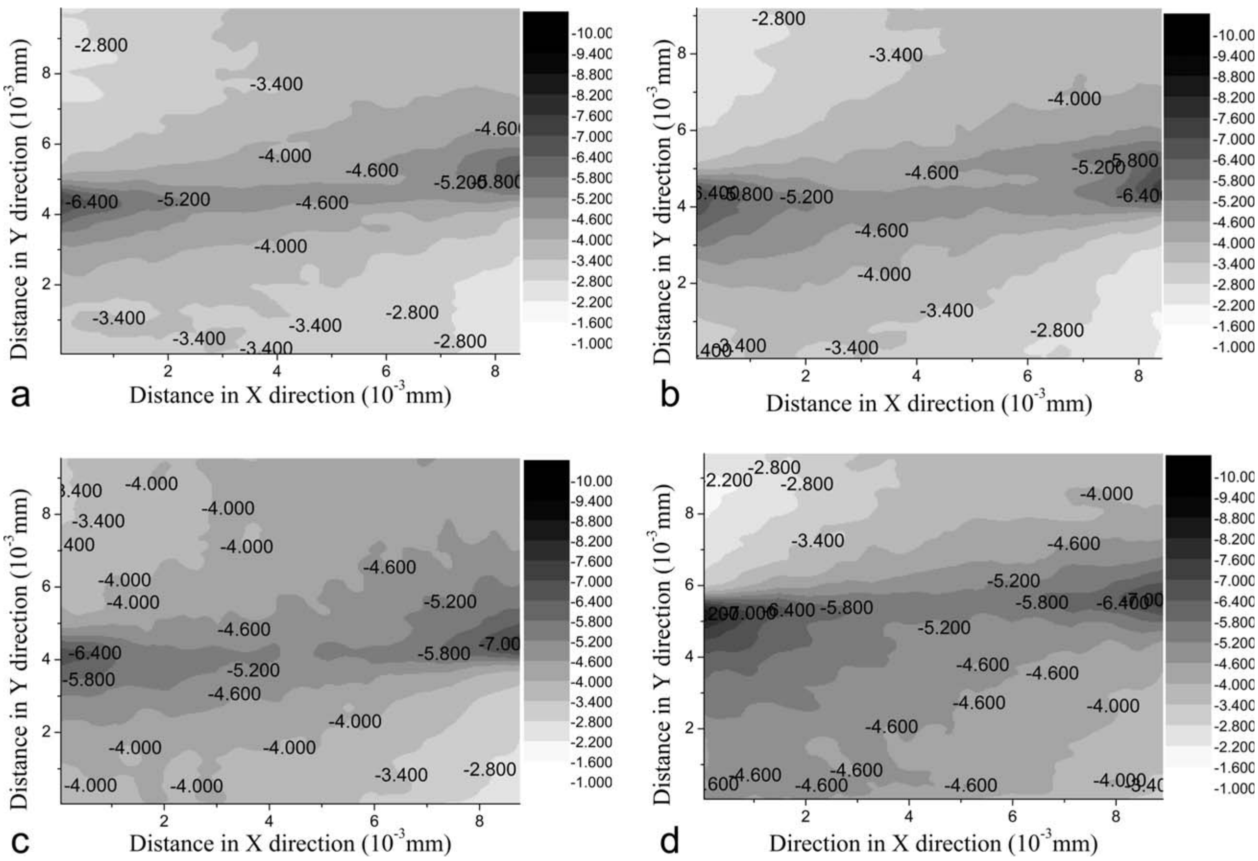

Figure 3. Strain distribution of the bamboo/PF modified by different PVA bonding interfaces: (a) bamboo/PF interface, (b) bamboo/PF interface modified by 5% PVA, (c) bamboo/PF interface modified by 10% PVA, and (d) bamboo/PF interface modified by 20% PVA.

In accordance with previous models, inadequate entanglement networks of each PVA led to strain transmission failure, and this resulted in bonding interface slippage. However, as depicted in Figure 3(d), the breaks of strain transmission disappeared with enough entangling PVA, and this led to an overall effect similar to that in Figure 3(a) without PVA.

Fluorescent Characterization of the Bamboo Bonding Interface

In some previous articles,[20,21] we noted that the fluorescence of wood materials in thin sections of phenol–formaldehyde bondlines could be suppressed by a 0.5% aqueous solution of Toluidine Blue O to yield good color contrast. The *interface* is commonly understood to be the area where bamboo cells and adhesives exist together, whereas the *bondline* is the area where the two parts of the matrix are glued by adhesive. Figure 4 shows the morphology, gray value simulation, and bitmap of the PF bondline in the bamboo matrix by Toluidine Blue O, whereas Figure 5 shows the ductile PF adhesive modified by 20% PVA.

It was clear that the penetration depth shown in Figure 5(a) was less than that shown in Figure 4(a). The low-viscosity PF followed a path of least resistance through cell pits to cell lumens in its penetration of the bamboo structure in hot pressing, often with surprisingly severe inhomogeneity. Adhesive penetration into the microchannels in the bamboo bonding interface could serve as a nanomechanical interlock, and the penetration effect generally depends on the molecular size of the adhesive component.[16] A low-molecular-weight adhesive is helpful for adhesive penetration, but it leads to a reduction in the bonding interface thickness; this decreases the bonding strength of the specimens.[22,23] Along with an irregular fluctuation of the bonding interface, ductile adhesive can spontaneously fill the interfacial gaps by reducing the penetration depth to some extent and thus reducing the mechanical interlock of adhesive penetration into the bamboo cells by a combination of interfacial slippage and interdigitation. Gray value simulations of bonding interface are depicted in Figures 4(b) and 5(b), where the warm color tone represents the bamboo matrix, and the cool color tone stands for adhesive distribution. It was evident from the line plots of the gray value simulation that there was a decrease in the fluorescent effect with modified phenol adhesive. We assumed that the added PVA made it prone to combination with the hydroxymethyl of PF instead of the PF itself crosslinking during hot pressing; this led to a reduction in the bondline fluorescent effect.

Bitmaps of the bonding interface are shown in Figure 4(c) and 5(c) and were used to measure the penetration depth. The average penetration depth (AP; μm) was easily calculated from bitmaps according to eq. (1):

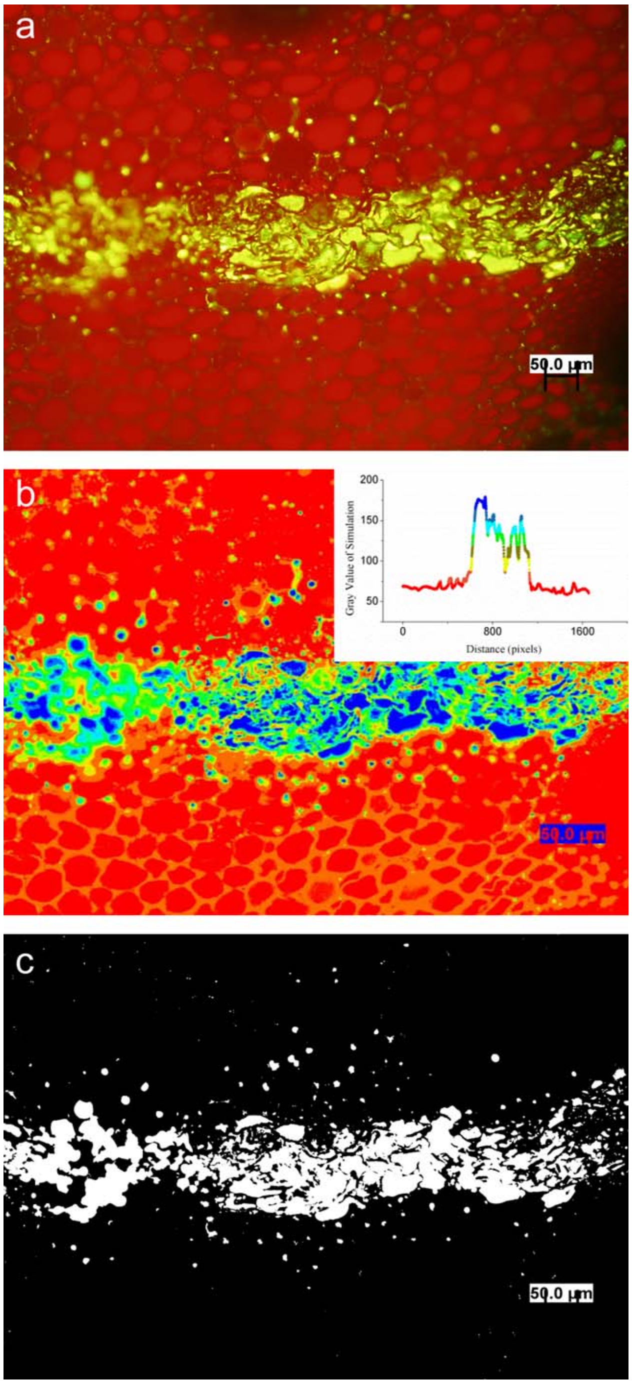

Figure 4. (a) Fluorescence photograph, (b) gray value simulation, and (c) bitmap of the bamboo/PF bonding interface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$AP = \sum_{i=1}^{5} (y_i)/5 \tag{1}$$

where y_i represents the distance from the matrix surface to the five farthest destinations of adhesive in the bonding interface. The penetration depth of normal PF was 178.55 μm, as depicted in Figure 4(c), whereas that of the ductile one was 117.23 μm, as shown in Figure 5(c).

CONCLUSIONS

The research reported in this article demonstrates that the branched hydroxyl of PVA combined with the hydroxyl of hydroxymethyl from PF on hot pressing and led to a reduction in the bondline fluorescent effect. The penetration depth of ductile adhesive in the bamboo bonding interface was less than that glued by rigid PF, and the bonding mechanism changed from a

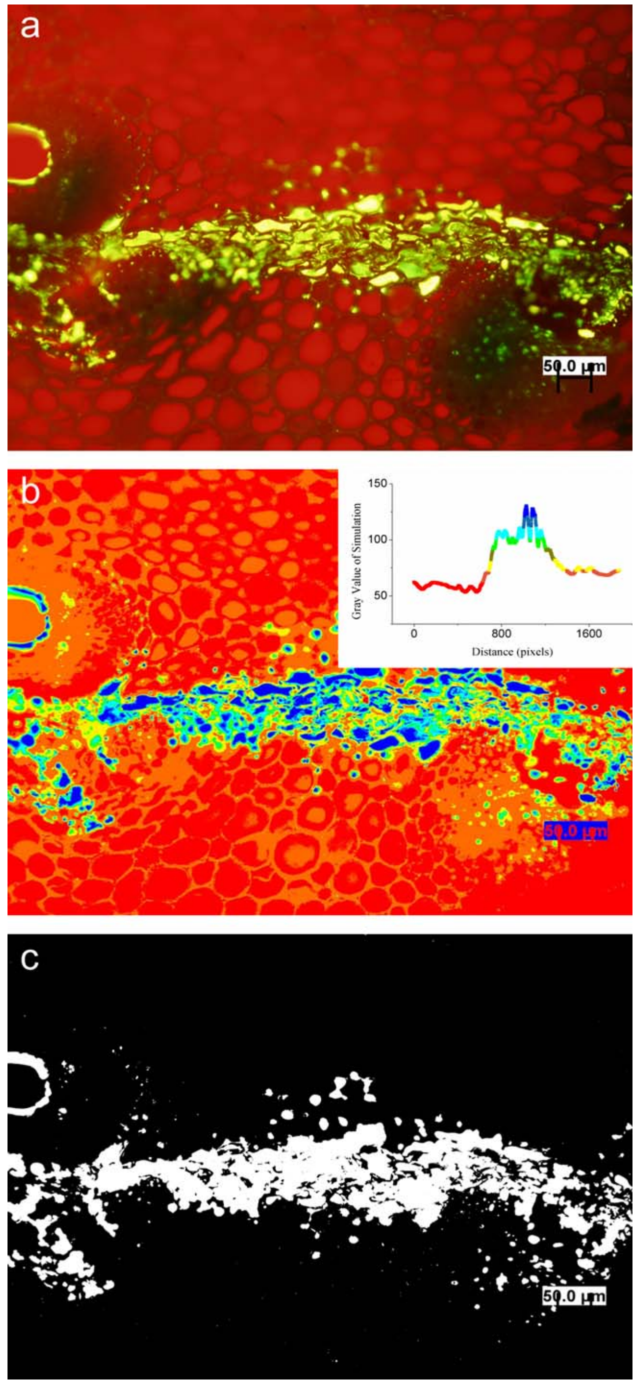

Figure 5. Fluorescence photograph of the bamboo/PF adhesive modified by the 20% PVA interface: (a) fluorescence photograph, (b) gray value simulation, and (c) bitmap. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pure mechanical interlock to a dual function of auto recovery, interfacial slippage, and interdigitation. In terms of shear strength testing and strain distribution by ESPI along the bondline, manifest differences were exhibited among the samples glued by PF resin with different PVA contents. The results also demonstrated that ductile PF diminished the stress distribution in adhesive assemblies and led to bonding interface slippage; this effectively reduced the destructive energy in their overall strength. The amount of prepolymerized adhesive–PVA had a positive influence on the stress transmission and strain distribution in the vicinity of the bonding interface, and this may have contributed to its compatibility with ductile bamboo.

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