Dopamine-Mediated Pre-Crosslinked Cellulose/Polyurethane Block Elastomer for the Preparation of Robust Biocomposites

Shujun Zhao,†‡ Zhong Wang,†‡ Wei Zhang,†‡ Jianzhang Li,†‡ Shifeng Zhang,*†‡§ and Anmin Huang†‡§

†MOE Key Laboratory of Wooden Material Science and Application and ‡Beijing Key Laboratory of Wood Science and Engineering, Beijing Forestry University, Beijing 100083, China
§Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing 100091, China

ABSTRACT: The development of micro- and nanofibril cellulose to improve strength while reducing the side effects of toughness and water resistance can benefit integrated polymer performance. Inspired by the interior microstructure of mussel byssus, this paper proposed an efficient means of generating an active block microfibrillated cellulose/polyurethane elastomer using an epoxy monomer as a pre-crosslinked agent with the addition of a poly(dopamine) layer. The block elastomer served as a multifunctional crosslinker, constructing a covalent network and interfacial hydrogen bonding that interlinked the elastomer with a soy protein isolate (SPI) matrix. Compared with the pristine SPI film, the introduction of the block elastomer induced remarkable improvements in tensile strength and toughness (146.7 and 102.1%, respectively). Additionally, the block elastomer was employed to further estimate its reinforcing effect in SPI resin modification, which also exhibited favorable water resistance and adhesion performance. This strategy may provide a new approach for constructing superior elastomers to reinforce applicable biomass composites.

1. INTRODUCTION

Biobased materials may allow tomorrow’s engineers to tap renewable feedstocks instead of petrochemical resources.1,2 Despite significant progress in biobased polymers for various application fields, some shortcomings persist, especially in terms of mechanical performance compared to petroleum-based materials.3–5 The introduction of nanofillers as a reinforcement phase for polymers has been shown to be a facile and effective strategy to improve the mechanical properties of composites.6,7 The incorporated various nanofillers can serve as the reinforcing center to accelerate the composite transformation of an amorphous and/or semicrystallized structure into a crystallized structure to obtain enhanced mechanical performance of biomaterials.8–9 However, most nanofillers are nonbiodegradable, opposing the concept of green and sustainable biobased materials. As one of the most abundant biopolymers in nature, cellulose can be obtained from multiple sources such as plants, bacteria, or tunicates ranging in size from macroscale to nanoscale; cellulose has been employed as an environmental reinforcing filler in an array of polymers.10,11 Similar to other nanofillers, cellulose nanofillers exhibit poor interfacial activity, thus, limiting the movement of molecular chains for stress concentration and reducing the ductility of biomaterials.

Nature provides a wealth of inspiration to remedy the above problems. As a typical biological material, mussel threads display a superior combination of strength and ductility.12 Such superior strength is reportedly due to the formed dense dopamine-Fe(III) crosslinkers, while high ductility is the result of crosslinking molecules that induce a flexible granular microphase-separated structure in the continuous protein matrix.13,14 Researchers have explored the structure of strong and ductile composites by mimicking the granular microphase-separated structure in the polymer matrix.8,15,16 Song et al. designed a facile biomimetic microphase-separated nanostructure in a polyvinyl alcohol matrix by introducing a sulfonated styrene–ethylene/butylene–styrene triblock copolymer, achieving a remarkably strong and tough composite.17 For block copolymers, stress can be transferred through the bridging chains from one entangled domain to its neighbors, thus preventing crack propagation within the entire polymer and improving the integrated mechanical performance.18,19 Meanwhile, the block copolymer can self-assemble into a granular microphase-separated structure in the waterborne composite matrix due to the strong competitive hydrophilic–hydrophobic interactions that endow the matrix with superior toughness.15 In practice, however, the development of a block
polymer with regulable chain architecture and morphology has been proven to be challenging. Polyurethane (PU) is a family of block copolymers composed of alternating soft and hard segments, forming a microphase-separated structural assembly owing to thermodynamic incompatibility. PU has been used effectively in polymer enhancement and operates via the same modification mechanism as the block copolymer. Recent research has revealed that the introduction of nano-fillers could optimize the microphase-separated structure of PU, which exhibits more interconnected hard phases and markedly enhances the mechanical properties of the materials. As such, various micro- and nanofibrils have been applied to improve PU performance, mainly through water-dispersible reinforcement incorporation. To further modify the interfacial interaction, cellulose derivatives have been surface-modified by various groups and presented as reactants to be synthesized directly into PU chains. In this way, the modified cellulose derivatives, as hard segments, can be grafted onto PU molecular chains to construct a generalized polymer-filler block copolymer, which can then optimize the PU microstructure and provide a new avenue by which to synthesize directly into PU chains. In this way, the modified cellulose derivatives, as hard segments, can be grafted onto PU molecular chains to construct a generalized polymer-filler block copolymer, which can then optimize the PU microstructure and provide a new avenue by which to synthesize directly into PU chains.

2. RESULTS AND DISCUSSION

2.1. PM Characterization. A facile dopamine dip-coating method was used for the surface modification of MFC. Catechol groups of dopamine underwent a self-polymerization process, forming an adherent PDA layer that then served as a versatile reaction platform to increase the interfacial activity of the polymer. Physical characteristics and chemical structure of PM were characterized by scanning electron microscopy (SEM), thermogravimetric (TG), Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS).

SEM results of MFC and PM were compared as shown in Figure 1a. The unmodified MFC exhibited a random orientation distribution with a diameter in the range of 5−10
μm, whereas the modified MFC was seemingly coated with a polymer layer indicating successful adhesion of the PDA layer.

The TG results (Figure 1b) showed a difference in residual weights of 24.75% for MFC and 23.65% for PM along with a clear difference in the region of 200−300 °C, primarily attributable to PDA-layer degradation.

FTIR spectra confirmed successful coating of the PDA layer on the MFC surface. As shown in Figure 1c, new absorption peaks appeared at 1515 and 1456 cm−1 in PM particles associated with N−H and C−H bonds, respectively, indicating the presence of the PDA layer. Additionally, the absorption peak of the C−H bond at 1423 cm−1 shifted to a lower region, whereas the peak of the C−O bond at 1032 cm−1 shifted toward a higher region. It was suggested that the incorporation of PDA changed the chemical environment of atoms on the MFC. The XPS measurement was performed to further investigate the chemical components of MFC and PM as shown in Figure 1d−f. The wide PM scan (Figure 1d) shows a clear peak of N elements and C−N bonds at the C 1s...
PM spectra (Figure 1f), implying that MFC was successfully surface-modified by PDA.

2.2. Construction of PMEU Elastomer. A polyurethane prepolymer, which was isocyanate-terminated, was dispersed in the functionalized PM suspension to in situ polymerize PM onto polyurethane and construct the block polymer. The epoxy monomer was then employed to enhance the inherent crosslinking degree and interfacial activity for an active pre-crosslinked block elastomer (Scheme 1). The construction of the PMEU elastomer was confirmed by FTIR and TG analyses.

In the FTIR spectra (Figure 2a), the EU elastomer exhibited absorption peaks at 3319, 2858, 1713, and 1532 cm⁻¹, attributed to the N–H, C–H, C=O and N–H, and C–N groups, respectively.³⁰ For the MEU, the peaks at 3319 shifted to 3323 cm⁻¹, mainly due to hydrogen bonding between −OH of MFC with N–H and C–H groups of polyurethane chains.²³,²⁶ Comparatively, two new bands at 2741 and 998 cm⁻¹ were observed in PMEU, suggesting that the PDA layer caused PM to graft onto the polyurethane prepolymer via chemical reactions. The shift and increase in intensity of the peak at 2858 cm⁻¹ was thought to result from the ring-opening reaction of epoxy groups with a PDA layer, leading to an increase in −CH₂ groups.¹⁵ Therefore, the PDA layer of PM caused MFC to graft onto the polyurethane prepolymer for the block elastomer and provided reaction sites to accelerate the introduction of epoxy groups into the elastomer to obtain the pre-crosslinked block elastomer.

TG measurement was performed to further verify the interactions within the PMEU block elastomer (Figure 2b). EU reflects the two-step degradation stages of hard segments in the low-temperature region followed by soft segments in the higher-temperature region.³¹ Enhanced thermal stability was observed for MEU per smaller degradation rate caused by the crystalline effects of the filler and the presence of a hydrogen bonding network structure.²⁰ A significant improvement in thermal stability was observed in the PMEU elastomer, which showed more residual mass at all stages, a lower degradation rate, and a higher maximum degradation temperature. The enhanced thermal properties can be attributed to the PDA layer causing MFC to react with the polyurethane prepolymer, constructing a high-performance block elastomer. The PDA layer may have also acted as a crosslinking site for strong interactions with the epoxy monomer.³² The interactions between the block elastomer and the SPI matrix were certainly notable.

2.3. Interactions between PMEU and SPI Matrix. FTIR measurement was applied to pristine and modified SPI-based films to investigate the interactions between PMEU and SPI molecules. In Figure 3a, characteristic peaks of SPI were observed at 3283 cm⁻¹ (O–H and N–H stretching vibration), 1651 cm⁻¹ (C=O stretching vibration of amide I), 1544 cm⁻¹ (N–H bending of amide II), and 1238 cm⁻¹ (C–H and N–H stretching of amide III).⁸,³³ Compared to the pristine SPI film, the main changes in the FTIR spectra of SPMEU films were located within 3000–3500 cm⁻¹, mainly due to hydrogen bonding. The absorption peak at 1651 cm⁻¹ also blue-shifted toward a relatively higher wavenumber after incorporating the PMEU block elastomer owing to intermolecular hydrogen bonding between the elastomer and SPI.²¹ In addition, the absorption peak at 2928 cm⁻¹ shifted to 2932 cm⁻¹ because new −CH₂ groups formed due to the chemical reactions...
between the epoxy groups of PMEU and −NH₂ groups of SPI molecules,34–36 collectively indicating the presence of multiple interactions between PMEU and SPI.

The active PMEU elastomer reacted with SPI chains constructing multiple crosslinked networks as further confirmed by 13C NMR measurement. Noticeable peaks corresponding to carbonyl (160–180 ppm), aromatic (115–130 ppm), α-carbon (45–70 ppm), β-carbon (25–45 ppm), and methylene and methyl groups (15–25 ppm) of the SPI backbone were observed as shown in Figure 3b.37 Compared to the pristine SP composite, new peaks for polyurethane-modified SPI at 26.9 and 70.3 ppm corresponding to the methyl carbon of isophorone diisocyanate (IPDI) and −C−CH₂−OH groups revealed that polyurethane exhibited satisfactory compatibility and crosslinked SPI through the ring-opening reactions of epoxy groups.38,39 Meanwhile, the signal at 134.9 ppm for SPI lost its resolution after introducing polyurethane, which could because the residual isocyanate groups formed interactions with SPI molecules. Moreover, in SEU, the new resolution at 41.8 ppm could be explained due to the fact that EU further reacted with SPI via ring-opening of epoxy groups forming aliphatic CH₂ groups.40 After further incorporating the PMEU elastomer, another new peak at 44.8 ppm was observed possibly because of the fact that the PDA layer reacted with SPI via Schiff base reactions forming double bond groups,8,41 in accordance with FTIR results.

The interactions between PMEU and SPI were also evidenced by the XRD data. As mentioned in previous studies, in Figure 3c, the diffraction peaks at approximately 8.5 and 20.0° were attributed to α-helix and β-sheet structures of SPI molecules.32 After the introduction of the PMEU pre-crosslinked block elastomer, nearly no changes appeared compared to pristine SPI, indicating that PMEU did not significantly affect the SPI structure.

TG analysis was used to further confirm the effective interactions in the SPMEU films as shown in Figure 3d and Table 1. Pristine SPI mainly exhibited two-step degradation: glycerol degradation in the lower-temperature region, and backbone peptide degradation in the higher-temperature region.42 After incorporating the MEU block elastomer, the degradation peak around 170 °C decreased and a new peak appeared around 240 °C, indicating a favorable combination and effective interaction between MEU and SPI.43,44 Significantly enhanced thermal stability was observed in the SPMEU film compared to the control samples. The first degradation peak of SPI disappeared, and the maximum degradation temperature increased with the addition of PMEU as shown in Figure 3d and Table 1, possibly because multiple interactions formed and accelerated heat consumption. These results confirm strong interactions between the PMEU and SPI matrix, which were supported by the FTIR, XRD, and NMR results.

To some extent, the surface morphology of a composite reflects the interaction properties of a filler in its matrix as confirmed by SEM images (Figure 4). The pristine SPI exhibited a scale-like morphology with a rough fractured surface as shown in Figure 4a.43 The surface of the SEU film (Figure 4b) presented a relatively dense and smooth cross-
section morphology with sheet-like structures and fiber-like polymers appearing on the film surface. The EU formed strong interfacial interactions with SPI via a ring-opening reaction of epoxy groups, thus improving the interior network structure; the microphase-separated structure of EU could then disperse stress in the SPI matrix.31,36,45 After the addition of the MEU elastomer (Figure 4c), the sheet-like structure increased because MFC was used as hard segments to optimize the microphase-separated structure of the elastomer and improved the mechanical performance of the SPI-based film.20,24 However, the unmodified MFC was pulled out, forming several pits due to weak surface activity. After incorporating PMEU into the SPI matrix (Figure 4d), some fibers embedded in the matrix were again pulled out, and the surface presented a dense multi-layer structure. These observations suggested improved interfacial interactions in the SPMEU films.

2.4. Applied Performance of SPMEU Composites. 2.4.1. Mechanical Properties. As two important mechanical parameters, tensile strength (TS) and toughness were examined to further determine the effects of the PMEU block elastomer on the mechanical defects of the SPI-based film. As shown in Table 2 and Figure 5a,b, the pristine SPI exhibited TS, elongation at break (EB), and W values of 5.05 MPa, 128%, and 5.82 MJ/m3, respectively.3,8 After the addition of the EU elastomer, the TS and W values increased to 8.09 MPa and 8.33 MJ/m3 because the existence of active groups (e.g., epoxy groups) formed crosslinking reactions with SPI while the interior microphase-separated structure and particle cavitation effect of EU enhanced the toughness of the composite.35,36,40 Compared to the SEU film (Figure 5c), the sheet-like structure increased while the interior microphase-separated structure and particle cavitation effect of EU enhanced the TS and W values increased to 8.09 (0.94) MPa and 104.48 (0.54)% respectively.3,8 After the addition of MFC decreased due to the poor surface activity of MFC, reducing the limitations of polymer chain mobility.20,22 Compared to the control groups, the modulus of the SPMEU film was much higher with the same addition, mainly because the interactions between the PMEU block elastomer and SPI increased the inherent crosslinking degree and reduced the mobility of polymer chains in the SPMEU film.50 The introduction of PMEU also decreased the loss factor in the composites while increasing the glass transition temperature (Tg), reflecting an improvement in the interfacial interactions of SPMEU films.

Although adhesives represent another important application field of SPI, poor adhesive and water-resistant properties render SPI unsuitable for load-bearing engineering materials. To further confirm the high-performance of the PMEU pre-crosslinked block elastomer, PMEU was applied in modifying the SPI adhesives by the process of hot-pressing under 120 °C and 1.0 MPa for 315 s. The wet shear bonding strength of SPI-based adhesives modified by the PMEU elastomer is shown in Figure 7. The introduction of PMEU produced a much better-performing adhesive compared to the same addition of the EU or MEU elastomer. The PDA layer likely served as a particularly versatile interface to react with the polyurethane prepolymer and produce a robust block structure while also interacting with the epoxy polymer to enhance the interior crosslinking degree and interfacial activity of the elastomer.51,36,50 The incorporated PMEU provided multiple interaction sites to form a strong crosslinking structure with the SPI molecules.

When the PMEU was added in the range of 1–3 wt%, the wet shear strength of the protein adhesive increased to 1.35 MPa marking an increase of 118% compared to the pristine SPI adhesive, which also meets the industrial plywood production standard for interior applications (≥0.7 MPa).42 This change was mainly attributed to the formation of multiple interactions between the PMEU elastomer and SPI, preventing moisture intrusion to improve the material’s water-resistant properties. However, the wet shear strength decreased to 1.27 MPa upon the increased addition of PMEU to 5 wt % of the SPI content, related to the competition reaction mechanism of active groups of the PDA layer/polyurethane and –NH2 groups of SPI with the epoxy polymer.56,40 Figure 8 illustrates the reinforcement mechanisms of SPMEU films and adhesives reinforced by the PMEU pre-crosslinked block elastomer.

2.4.2. Water Resistance of SPI-Based Composites. Total soluble matter (TSM) and water contact angle (WCA) measurements were conducted to investigate the effects of the block PMEU elastomer on the water resistance and surface hydrophilicity of pristine and modified SPI-based films (Table 3). The incorporation of EU, MEU, and PMEU led to the integrated improvement of mechanical performance.69 As expected, the addition of PMEU increased TS and W values by 146.7 and 102.1% compared to the pristine SPI film, indicating a considerable improvement to address the mechanical drawbacks of the pristine SPI film as supported by the SEM images of SPMEU (Figure 5d) with pulled-out fibers.

Dynamic mechanical analyses (DMA) analysis was carried out for the SPI-based films (Figure 6) to further determine the reinforcing effects of the PMEU elastomer on the SPI composite. In the storage modulus (E′) diagram, SPI exhibits a relatively small E′ at low temperatures but higher E′ at high temperatures. The introduction of EU formed a robust crosslinking structure with SPI molecules to significantly increase E′; however, the addition of MEU decreased E′ due to the poor surface activity of MFC, reducing the limitations of polymer chain mobility.20,22 Compared to the control groups, the modulus of the SPMEU film was much higher with the same addition, mainly because the interactions between the PMEU block elastomer and SPI increased the inherent crosslinking degree and reduced the mobility of polymer chains in the SPMEU film.50 The introduction of PMEU also decreased the loss factor in the composites while increasing the glass transition temperature (Tg), reflecting an improvement in the interfacial interactions of SPMEU films.

Table 2. Mechanical Properties of Pristine and Modified SPI Films

| sample entry | thickness (mm) | tensile strength (MPa) | elongation at break (%) |
|---------------|---------------|-----------------------|------------------------|
| SPI           | 0.257 (0.012) | 5.05 (0.120)          | 128.54 (0.10)          |
| SEU           | 0.259 (0.016) | 8.09 (0.94)           | 104.48 (0.54)          |
| SMEU          | 0.225 (0.019) | 10.11 (0.26)          | 92.03 (0.43)           |
| SPMEU         | 0.252 (0.031) | 12.46 (0.43)          | 102.92 (0.26)          |
| increment     | 146.7         | −19.9                 |

“Mean (standard deviation).” Increase as-calculated from SPMEU to the pristine SPI-based film.
notable increase in WCA values; these activated polyurethane elastomers formed interactions with SPI, which consumed the surface hydrophilic groups and enhanced surface hydrophobicity. The TSM of pristine SPI films declined by 11.2% after the addition of the PMEU block elastomer. This could be explained due to the fact that the PDA layer in PMEU induced MFC to react with the polyurethane prepolymer to form a superior block elastomer. The incorporated epoxy monomer further improved the crosslinking degree and interfacial activity of the PMEU elastomer, which accelerated the connection with the SPI chain for a strong crosslinking network, significantly enhancing the water-resistant properties of SPI-based films.

3. CONCLUSIONS

In summary, a superior pre-crosslinked PMEU elastomer was prepared via in situ polymerizing PM onto polyurethane by means of a PDA layer with an epoxy monomer as a pre-crosslinking agent, which improved the crosslinking degree and interfacial activity of the PMEU elastomer. The incorporated PMEU block elastomer served as a physical and chemical crosslinker, which is able to form multiple interactions with the SPI matrix to improve the crosslinking network and significantly enhance the mechanical strength compared to pristine SPI-based films. Meanwhile, the improvement in the microphase-separated structure of PMEU effectively reduced the stress concentration and smoothed out energy upon deformation, endowing SPMEU films with superior toughness. Compared to pristine SPI films, the addition of the PMEU elastomer resulted in an increase in TS, toughness, and WCA values of 146.7, 102.1, and 49.1%, respectively. In addition, the PMEU elastomer was applied to the SPI-based adhesive to further substantiate its superior performance, exhibiting particularly high wet shear strength (1.35 MPa) compared to

Figure 5. Mechanical properties of SPMEU films: (a, b) Stress–strain curves and comparison of strength and roughness of SPI and modified SPI composites; (c, d) cross-sectional fracture SEM images of SMEU and SPMEU under the same load of neat SPI and modified SPI films.

Figure 6. (a) Storage modulus and (b) Tan Delta of neat SPI and modified SPI films.
the pristine SPI-based adhesive (0.62 MPa) with an increase of 117.7% to reach the industrial application standard for plywood fabrication. The results indicate that the proposed strategy is an effective and feasible approach to construct a high-performance elastomer, which may show promise for various biomass applications.

4. EXPERIMENTAL SECTION

4.1. Materials. SPI with 95% protein content was provided by Yuwang Ecological Food Industry Co., Ltd. Microfibrillated cellulose (MFC; solid content of 1.5 wt %) aqueous dispersion was acquired from Tianjin Haojia Reagents Co., Ltd., China, as-prepared from homogenized wood pulp. Dopamine (97% purity), tris(hydroxymethyl)aminomethane, poly(tetrahydrofuran) (Tris) (PTMG; $M_n = 2000$), 2,2-bis(hydroxymethyl) propionic acid (DMPA), tannic acid (TA), and 1,6-hexanediol diglycidyl ether (HDE) were obtained from Tianjin Heowns Biochem Co., Ltd. Butane diol (BD) was purchased from Shanghai TCI Co., Ltd., and isophorone diisocyanate (IPDI) was obtained from Aladdin Biochem Co., Ltd. PTMG, DMPA, TA, and BD were used after being dried in a vacuum oven at 110 °C. Glycerol, triethylamine (TEA), and other chemical reagents were purchased from Beijing Chemical Reagents Co., Ltd (Beijing, China) and used without further purification.

4.2. Preparation of PMEU Pre-Crosslinked Block Elastomer. The PMEU elastomer was prepared via the conventional two-step method. In the first step, quantitative IPDI, PTMG, and DMPA (6 wt % of total prepolymer weight), with a molar ratio of isocyanate and hydroxy groups of 1.80, were introduced into a four-necked flask outfitted with a thermometer, nitrogen inlet, condenser, and mechanical stirrer and then heated for 3 h at 70–80 °C under nitrogen protection with the addition of a few drops of the catalyst. Next, a certain proportion of BD and TA (polyol molar ratio of BD/TA = 1:9; the amount of hydroxyl groups in TA molecular metered to 3) was dissolved in acetone and added dropwise as the $-\text{NCO}/-\text{OH}$ ratio approached 1.05 to avoid any sudden reaction.30 The mixture was mechanically stirred for 5 h at 70 °C; the isocyanate ($-\text{NCO}$) content was continually tested during the reacting time. After being cooled to room temperature, the required TEA was used to neutralize $-\text{COOH}$ groups and stirred for 45 min.

Next, the MFC (5 wt % of solution weight) was immersed in a dopamine buffer solution to prepare a PM suspension as reported in the references of our group.3 The prepolymer was then dispersed in the prepared PM aqueous solution with an epoxy monomer (3 wt % of the PM solution content) added and vigorously stirred for shearing-emulsification. Finally, the pure waterborne polyurethane PMEU was obtained after removing any remaining acetone through a rotary steaming instrument. The PU/epoxy monomer (EU) and MFC/epoxy monomer/PU (MEU) elastomer were prepared using a similar synthesis method, where the EU contained no fillers and MEU

![Figure 7](image1)

**Figure 7.** Wet shear strength of SPI-based adhesive plywood samples with different amounts of EU, MEU, and PMEU elastomers (the number represents the addition percentage of total adhesive weight).

![Figure 8](image2)

**Figure 8.** Enhancement mechanism in SPMEU composites.

| Table 3. Water Resistance Measurement Results (TSM and WCA) of SPI-Based Films |
|-----------------------------|-----------------|-----------------|
| sample entry | total soluble matter (%) | water contact angle (°) |
| SPI | 25.8 (0.70)$^a$ | 37.1 (0.12) |
| SEU | 24 (2.98) | 41.7 (1.15) |
| SMEU | 24.4 (0.93) | 52.4 (1.90) |
| SPMEU | 22.9 (1.63) | 55.3 (2.26) |
| increment (%)$^b$ | -11.2 | 49.1 |

$^a$Mean (standard deviation). $^b$Increase in SPMEU compared to pristine SPI film.
was prepared with unmodified MFC compared to the PMEU elastomer.

4.3. Preparation of PMEU Elastomer-Reinforced SPI Composites. The SPMEU films were fabricated using a casting method as shown in Scheme 1. SPI (5 g), deionized water (95 g), and glycerol (2.5 g) were introduced into a beaker and stirred until a uniform mixture was obtained. The pH value of the mixture was adjusted with the NaOH solution (1.0 M) to 9.0 and then stirred continuously for 30 min in a water bath at 85 °C. As listed in Table 4, a certain amount of

| Table 4. Experimental Mass Ratios of SPI-Based Films and adhesives |
|---------------------------------------------------------------|
| sample entry | proportion | |
| film | SPI | M(SPI)/M(glycerol)/M(WPU) = 1:0.5:0 |
|       | SEU | M(SPI)/M(glycerol)/M(EU) = 1:0.5:0.1 |
|       | SMEU | M(SPI)/M(glycerol)/M(MEU) = 1:0.5:0.1 |
|       | SPMEU | M(SPI)/M(glycerol)/M(PMEU) = 1:0.5:0.1 |
| adhesive | SPI-0 | M(water)/M(SPI)/M(WPU) = 85:15:0 |
|          | SEU-1 | M(water)/M(SPI)/M(EU) = 85:15:1 |
|          | SMEU-1 | M(water)/M(SPI)/M(MEU) = 85:15:1 |
|          | SPMEU-1 | M(water)/M(SPI)/M(PMEU) = 85:15:1 |
|          | SPMEU-3 | M(water)/M(SPI)/M(PMEU) = 85:15:3 |
|          | SPMEU-5 | M(water)/M(SPI)/M(PMEU) = 85:15:5 |

“The sample “M” represents the meaning of “mass”.

PMEU elastomer was added to the SPI film-forming solution as the mixture was stirred thoroughly. Next, the obtained solution was poured into plates and vacuum-dried for 24 h at 45 °C. The films were then placed into desiccators containing saturated K₂CO₃ solution (relative humidity of 50 ± 2%) before any further measurements. SEU and SMEU films were fabricated by introducing a certain amount of EU and MEU elastomers into the SPI solution as SPMEU was prepared according to Table 4.

Samples of PMEU-reinforced SPMEU resin were prepared using a simple blending method. Briefly, SPI (15 g) was added into deionized water (85 g) via mechanical stirring for 10 min at 20 °C. Then, the required amount (Table 4) of elastomer was introduced and stirred uniformly at 20 °C. Three-layer plywood samples were prepared at a spread rate of 180 g/m² per side. The glued veneers were then hot-pressed under 1.0 MPa for 315 s. The prepared plywood samples were stored at ambient temperature for more than 12 h before further testing. The control adhesive group was synthesized under the same conditions without the addition of the polyurethane elastomer.

4.4. Characterization of PMEU Elastomer and SPMEU Composites. Fourier transform infrared (FTIR) spectra of the SPMEU film, PMEU elastomer, and PM were detected by attenuated total reflection (Nicolet 6700) ranging from 650 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹ with 32 scans. X-ray diffraction (XRD) results were obtained using a commercial X-ray D8 Advance diffractometer (Cu Kα, λ = 0.154 nm; Bruker AXS; Karlsruhe, Germany) with a voltage of 40 kV at 40 mA ranging from 5 to 60° at a rate of 2°/min. X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific) was performed to analyze the elements via a monochromatized Al Kα X-ray source of 148.6 eV at room conditions. The thermal stability indicators of the SPI-based PMEU elastomer, and PM were measured on a thermogravimetric (TG Q50; TA Instruments) machine at a constant heating rate of 10 °C/min in the range of 30–600 °C under nitrogen conditions. The cross-sectional morphologies of the PM filler and SPI-based hybrid films were examined using scanning electron microscopy (SEM; Hitachi S-3400 N) with the accelerating voltage of 5 kV. The solid-state ¹³C NMR spectra of SPI-based films were obtained using an AVANCE III 400WB spectrometer (Bruker, Switzerland) with a 4 mm cross-polarization/magic-angle spinning probe at a spinning speed of 14 KHz; methane carbon atoms of adamantane (29.47 ppm) were applied to correct the chemical shifts.

4.5. Mechanical Testing. The water-resistant bonding strength of SPI-based adhesive plywood was measured according to the type II plywood standard of China National Standard GB/T 9846.3-2004 as described by Li et al.⁵² The plywood specimens were immersed in 63 °C water for 3 h and then tested at a cross-head speed of 10 mm/min on a universal mechanical machine (WDE-200E; Jinan, China). Wet shear strength was calculated as follows

\[ \text{wet shear strength (MPa)} = \left( \frac{\text{tensile force (N)}}{\text{adhesion area (mm}^2)\right. \]

Mechanical performance of SPMEU films was tested on an INSTRON 3365 Universal Material Testing Machine (Norwood, MA) with an initial gauge length of 50 mm and crosshead speed of 50 mm/min at room temperature. The final values of tensile strength (TS) and elongation at break (EB) properties reported below are the averages of at least six specimens.

Dynamic mechanical analyses (DMA) of SPMEU films were conducted with the TA instrument Q800 with the film tension mode. The samples were cut into 4 mm × 20 mm shapes and tested at 1 Hz frequency in the range of 40–180 °C at a heating rate of 5 °C/min.

4.6. Water Barrier Performance. The surface hydrophilicity of films was measured with an OCA 20 water contact angle device (WCA; Dataphysics Instruments Gmbh, Germany) at ambient temperature. To further evaluate the water-resistant properties of films, the total soluble matter (TSM) of specimens was measured according to the following formula

\[ \text{TSM (\%)} = \left( \frac{W_i - W_f}{W_i} \right) \times 100 \]

where \( W_i \) and \( W_f \) denote the initial dry film weight and dry sample weight after dissolution.

### ACKNOWLEDGMENTS

This work was financially supported by the National Key Research and Development Program of China (2017YFD0601205), the National Natural Science Foundation of China (Project 51779005/E090301), and the Fundamental...
References

1. Song, F.; Tang, D. L.; Wang, X. L.; Wang, Y. Z. Biodegradable soy protein isolate-based materials: a review. Biomacromolecules 2011, 12, 3369−3380.

2. Benali, S.; Khelifa, F.; Lerari, D.; Mincheva, R.; Habibi, Y.; Lahem, D.; Deblyquy, M.; Dubois, P. Supramolecular Approach for Efficient Processing of Polylactide/Starch Nanocomposites. ACS Omega 2018, 3, 1069−1080.

3. Kang, H.; Song, X.; Wang, Z.; Zhang, W.; Zhang, S.; Li, J. High-Performance and Fully Renewable Soy Protein Isolate-Based Film from Microcrystalline Cellulose via Bio-Inspired Poly(dopamine) Surface Modification. ACS Sustainable Chem. Eng. 2016, 4, 4354−4360.

4. Lu, Y.; Ye, G.; She, X.; Wang, S.; Yang, D.; Yin, Y. Sustainable Route for Molecule Thin Cellulose Nanoribbons and Derived Nitrogen-Doped Carbon Electrocatlysts. ACS Sustainable Chem. Eng. 2017, 5, 8729−8737.

5. Han, J.; Lei, T.; Wu, Q. High-water-content mouldable polypivin alcohol-borax hydrogels reinforced by well-dispersed cellulose nanoparticles: Dynamic rheological properties and hydrogel formation mechanism. Carbohydr. Polym. 2014, 102, 306−316.

6. Xie, D.-Y.; Qian, D.; Song, F.; Wang, X.-L.; Wang, Y.-Z. A Fully Biobased Encapsulant Constructed of Soy Protein and Cellulose Nanocrystals for Flexible Electromechanical Sensing. ACS Sustainable Chem. Eng. 2017, 5, 7063−7070.

7. Naseri, N.; Deepa, B.; Mathew, A. P.; Okman, K.; Girandon, L. Nanocellulose-Based Interpenetrating Polymer Network (IPN) Hydrogels for Cardilage Applications. Biomacromolecules 2016, 17, 3714−3723.

8. Wang, Z.; Kang, H.; Zhang, W.; Zhang, S.; Li, J. Improvement of interfacial interactions using natural polyphenol-inspired tannic acid-coated nanoclay enhancement of soy protein isolate biofilms. Appl. Surf. Sci. 2017, 401, 271−282.

9. Xu, F.; Chen, R.; Lin, Z.; Qin, Y.; Yuan, Y.; Li, Y.; Zhao, X.; Yang, M.; Sun, X.; Wang, S.; Peng, Q.; Li, Y.; He, X. Superflexible Interconnected Graphene Network Nanocomposites for High-Performance Electromagnetic Interference Shielding. ACS Omega 2018, 3, 3599−3607.

10. Fei, X.; Wei, W.; Zhao, F.; Zhu, Y.; Luo, J.; Chen, M.; Liu, X. Efficient Toughening of Epoxy−Anhydride Thermosets with a Biobased Tannin Acid Derivative. ACS Sustainable Chem. Eng. 2017, 5, 596−603.

11. Zhang, S.; Xia, C.; Dong, Y.; Yan, Y.; Li, J.; Shi, S. Q.; Cai, L. Soy protein isolate-based films reinforced by surface modified cellulose nanocrystal. Ind. Crop. Prod. 2016, 80, 207−213.

12. Filippidi, E.; Cristiani, T. R.; Eisenbach, C. D.; Waite, J. H.; Israelachvili, J. N.; Ahn, B. K.; Valentine, M. T. Toughening elastomers using mussel inspired iron-catechol complexes. Science 2017, 358, 502−505.

13. Lee, B. P.; Messersmith, P. B.; Israelachvili, J. N.; Waite, J. H. Mussel-Inspired Adhesives and Coatings. Annu. Rev. Mater. Res. 2011, 41, 99−132.

14. Ye, Q.; Zhou, F.; Liu, W. Bioinspired catecholic chemistry for surface modification. Chem. Soc. Rev. 2011, 40, 4244−4258.

15. Yang, L.; Phua, S. L.; Teo, J. K.; Toh, C. L.; Lau, S. K.; Ma, J.; Lu, X. A biomimetic approach to enhancing interfacial interactions: polydopamine-coated clay as reinforcement for epoxy resin. ACS Appl. Mater. Interfaces 2011, 3, 3026−3032.

16. Wang, Y.; Li, T.; Wang, X.; Ma, P.; Bai, H.; Dong, W.; Xie, Y.; Chen, M. Superior Performance of Polyurethane Based on Natural Melanin Nanoparticles. Biomacromolecules 2016, 17, 3782−3789.

17. Song, P.; Xu, Z.; Dargusch, M. S.; Chen, Z. G.; Wang, H.; Guo, Q. Granular Nanostructure: A Facile Biomimetic Strategy for the Design of Supertough Polymeric Materials with High Ductility and Strength. Adv. Mater. 2017, 29, No. 1704661.
(35) Zhao, S.; Wang, Z.; Kang, H.; Li, J.; Zhang, S.; Han, C.; Huang, A. Fully bio-based soybean adhesive in situ cross-linked by interactive network skeleton from plant oil-anchored fiber. *Ind. Crop. Prod.* **2018**, *122*, 366–374.

(36) Zhu, X.; Wang, D.; Li, N.; Sun, X. S. Bio-Based Wood Adhesive from Camelina Protein (a Biodiesel Residue) and Depolymerized Lignin with Improved Water Resistance. *ACS Omega* **2017**, *2*, 7996–8004.

(37) Zhao, Y.; He, M.; Zhao, L.; Wang, S.; Li, Y.; Gan, L.; Li, M.; Xu, L.; Chang, P. R.; Anderson, D. P.; Chen, Y. Epichlorohydrin-Cross-linked Hydroxyethyl Cellulose/Soy Protein Isolate Composite Films as Biocompatible and Biodegradable Implants for Tissue Engineering. *ACS Appl. Mater. Interfaces* **2016**, *8*, 2781–2795.

(38) Ghosh, T.; Karak, N. Silicone-Containing Biodegradable Smart Elastomeric Thermoplastic Hyperbranched Polyurethane. *ACS Omega* **2018**, *3*, 6849–6859.

(39) Kantheti, S.; Narayan, R.; Raju, K. V. S. N. Click Chemistry Engineered Hyperbranched Polyurethane–Urea for Functional Coating Applications. *Ind. Eng. Chem. Res.* **2014**, *53*, 8357–8365.

(40) Wang, Z.; Zhao, S.; Song, R.; Zhang, W.; Zhang, S.; Li, J. The synergy between natural polyphenol-inspired catechol moieties and plant protein-derived bio-adhesive enhances the wet bonding strength. *Sci. Rep.* **2017**, *7*, No. 9664.

(41) Kurniawan, L.; Zhang, X.; Qiao, G. G. Chemical Modification of Wheat Protein-Based Natural Polymers: Grafting and Cross-Linking Reactions with Poly(ethylene oxide) Diglycidyl Ether and Ethyl Diamine. *Biomacromolecules* **2007**, *8*, 2909–2915.

(42) Liu, C.; Zhang, Y.; Li, X.; Luo, J.; Gao, Q.; Li, J. "Green" bio-thermoset resins derived from soy protein isolate and condensed tannins. *Ind. Crop. Prod.* **2017**, *108*, 363–370.

(43) Xu, F.; Zhang, W.; Zhang, S.; Li, J.; Li, J.; Zhang, Y. Preparation and characterization of poly(vinyl alcohol) and 1,2,3-propanetriol diglycidyl ether incorporated soy protein isolate-based films. *J. Appl. Polym. Sci.* **2015**, *132*, No. 42578.

(44) Liu, H.; Li, C.; Sun, X. S. Soy-oil-based waterborne polyurethane improved wet strength of soy protein adhesives on wood. *Int. J. Adhes. Adhes.* **2017**, *73*, 66–74.

(45) Varganici, C.-D.; Rosu, L.; Rosu, D.; Simionescu, B. C. Miscibility studies of some semi-interpenetrating polymer networks based on an aromatic polyurethane and epoxy resin. *Composites, Part B* **2013**, *50*, 273–278.

(46) Vijayan, P. P.; Puglia, D.; Kenny, J. M.; Thomas, S. Effect of organically modified nanoclay on the miscibility, rheology, morphology and properties of epoxy/carboxyl-terminated (butadiene-co-acrylonitrile) blend. *Soft Matter* **2013**, *9*, 2899–2911.

(47) Pan, H.; Chen, D. Preparation and characterization of waterborne polyurethane/attapulgite nanocomposites. *Eur. Polym. J.* **2007**, *43*, 3766–3772.

(48) Chen, K.; Tian, Q.; Tian, C.; Yan, G.; Cao, F.; Liang, S.; Wang, X. Mechanical Reinforcement in Thermoplastic Polyurethane Nanocomposite Incorporated with Polydopamine Functionalized Graphene Nanoplatelet. *Ind. Eng. Chem. Res.* **2017**, *56*, 11827–11838.

(49) Wu, S.; Qiu, M.; Tang, Z.; Liu, J.; Guo, B. Carbon Nanodots as High-Functionality Cross-Linkers for Bioinspired Engineering of Multiple Sacrificial Units toward Strong yet Tough Elastomers. *Macromolecules* **2017**, *50*, 3244–3253.

(50) Li, Y.; Pan, D.; Chen, S.; Wang, Q.; Pan, G.; Wang, T. In situ polymerization and mechanical, thermal properties of polyurethane/graphene oxide/epoxy nanocomposites. *Mater. Des.* **2013**, *47*, 850–856.

(51) Zhang, M.; Wang, X.-L.; Wang, Y.-Z.; et al. Development of soy protein isolate/waterborne polyurethane blend films with improved properties. *Colloids Surf., B* **2012**, *100*, 16–21.

(52) Li, H.; Li, C.; Gao, Q.; Zhang, S.; Li, J. Properties of soybean-flour-based adhesives enhanced by attapulgite and glycerol poly-glycidyl ether. *Ind. Crop. Prod.* **2014**, *59*, 35–40.