A Highly Water-Resistant Soy-Based Bioadhesive with 1,4-Butanediol Diglycidyl Ether and its Application on Plywood

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ABSTRACT: The objective of this study was to use soybean meal and 1,4-butanediol diglycidyl ether (BDDE) to develop a highly water-resistant, soy-based bioadhesive for plywood fabrication. The physical properties and performance characteristics of the resulting adhesive, including solid content, viscosity, water resistance, crystallinity, fracture morphology, thermal behavior, and cracks, were evaluated. The proposed adhesive was compared against the traditional soy adhesive with polyamidoamine-epichlorohydrin (PAE). Results showed that adding 8 g of BDDE into the adhesive formulation improved the solid content up to 32.83% and reduced the viscosity to 27340 mPa·s. The wet shear strength of plywood bonded with the adhesive was improved by 417% to 1.19 MPa, which was 17.8% higher than that of the PAE adhesive. BDDE effectively reacts with soy protein to form a dense network, thus enhancing the water resistance of the adhesive by creating a smooth and compact fracture surface that prevents moisture intrusion. The adhesive with BDDE was also found to be tougher after curing than the adhesive with PAE, which reduced the interior force of the adhesive layer and further enhanced its water resistance.

KEYWORDS: Soybean meal, 1,4-butanediol diglycidyl ether, toughness, wet shear strength, plywood

1 INTRODUCTION

Biobased adhesives are considered excellent materials whose rapid rise has attracted a great deal of attention owing to their environmental sustainability and low energy production costs. A series of bioadhesives, including starch adhesive [1], tannin adhesive [2], and protein-based adhesive [3], have been researched as adhesive for plywood fabrication. However, the starch and tannin types of adhesives have exhibited some major weaknesses—poor water resistance and complicated preparation process—which have limited their practical application. The functions on starch are inert, which make it hard to modify. Tannin reacts easily with other chemicals, which leads to a short pot life that is unacceptable for plywood application. Research addressing these disadvantages is still being conducted. As is known to all, soy-based

adhesives have garnered research attention as a substitute for conventional petroleum-based adhesive because they are renewable, biodegradable, and nontoxic [4, 5]. Poor water resistance is a major drawback to soy-based adhesives, which limits their practical application. Soy protein has a lot of active functions on the molecule, which can be used to improve the water resistance. A variety of modification methods, such as denaturing agent modification (e.g., alkali [6], urea [7], sodium dodecyl sulfate (SDS) [8]), molecular modification [9], and crosslinker modification [10, 11], have been developed in an effort to improve the water resistance of soy-based adhesives. The use of denaturing agents or molecular modification for this purpose remain limited, however, and plywood bonded with adhesives modified in this way do not meet interior use requirements.

The use of crosslinkers, especially polyamidoamine-epichlorohydrin (PAE) [10], has proven to be the most effective method of improving the water resistance of soy-based adhesives. Based on our previous research, epoxides like ethylene glycol

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diglycidyl ether and triglycidylamine, also can effectively improve adhesive water resistance; plywood bonded with the modified adhesive meets interior use requirements. The performance of adhesive with epoxide is comparable to that of adhesive with PAE, however, the cured soy-based adhesive with PAE or epoxide is brittle and can be readily broken under the interior force caused by moisture intrusion. Reducing the brittleness of the soy-based adhesive will balance the interior force and further improve its performance.

1,4-Butanediol diglycidyl ether (BDDE) is a long chain compound with two highly reactive epoxy groups, which can be successfully utilized to prepare advanced composites. It is commonly used as a reactive diluent for epoxy resin due to its reactivity and low cost. BDDE can react with the active groups on proteins to form a highly dense network while its long chain structure changes the cured structure of the adhesive to produce an inner toughening effect [12], which may reduce adhesive brittleness and further improve its water resistance.

In this study, soybean meal flour (SM) as a raw material, SDS as a denaturing agent, and BDDE as a crosslinker, were used to develop a high performance soy-based adhesive. The resultant adhesive was used to fabricate three-ply plywood and its water resistance was measured to investigate the properties and the performance of the adhesive. The functions, crystallinity, fracture morphology, thermal behavior, and cracks in the cured adhesive were examined to determine why the water resistance of the adhesive was improved. An adhesive with PAE was also prepared and compared against the proposed adhesive, as discussed below.

2 MATERIALS AND METHODS

2.1 Materials

Soybean meal flour (SM) with 43.5% soy protein content was obtained from Huifu Grain and Oil Company of Hebei province, China. The soybean meal was ground into 200 mesh powder using a fluid-energy mill. SDS, BDDE, PAE and the other chemicals were obtained from Beijing Chemical Reagent, Beijing, China. Poplar veneer (*Populus cathayana*, 8–12% moisture content) was obtained from Hebei Province of China.

2.2 Adhesive Preparation

For SM adhesive (A): SM (30 g) was mixed with water (70 g) and stirred for 10 min at 25 °C using a stirrer.

For SM/SDS adhesive (B): SDS (1 g) was added into SM adhesive and stirred for another 10 min at 25 °C.

For SM/SDS/BDDE2 to 5 adhesive (C to E): BDDE (2, 5, 8, 11 g) was added into SM/SDS adhesive and stirred for 10 min at 25 °C, respectively.

For SM/PAE adhesive (G): PAE (50 g, 12% solid content) was mixed with water (20 g) and then SM (30 g) was added into the mixture and stirred for 10 min at 25 °C.

2.3 Plywood Preparation

The procedure was adapted from a previous study by Luo *et al.* [13]. The adhesive was applied on a single side of the veneer at a ratio of 55 g/m² (100% solid content of adhesive). Two coated veneers were placed in different directions and an uncoated veneer was placed on top to form a slab. The slab was prepressed for 10 min before hot pressing at 120 °C for 5 min under 1.0 MPa of pressure. After hot pressing, the plywood was put into a conditioning room for 24 h before testing its strength.

2.4 Solid Content

The procedure was also adapted from Luo *et al.* [14]. Three adhesive samples (3 g, weight α) were dried in an oven at 105 °C ± 2 °C for 2 h, then weighed and recorded as weight β. The solid content of the adhesive was calculated via Equation 1. The average of three samples was calculated to obtain the final value.

$$\text{Solid content}(\%) = \frac{\text{Weight}\,\beta\,(\text{g})}{\text{Weight}\,\alpha\,(\text{g})} \times 100\% \quad (1)$$

2.5 Dynamic Viscoelasticity

The procedure was adapted from a previous study by Li *et al.* [3]. A HAAKE RS1 rheometer with a P35 parallel plate was used to measure the adhesive viscosity. The gap between two plates was set to 1 mm and the temperature to 20 °C. The viscosity of the adhesive was obtained at a rate of 1 s⁻¹.

2.6 Fourier Transform Infrared (FTIR) Spectroscopy

The procedure was adapted from a previous study by Luo *et al.* [14]. The adhesive was placed into a 120 °C ± 2 °C oven for 2 h to cure completely, then the cured adhesive was ground into a 200 mesh powder. The powder was first mixed with KBr crystals at a ratio of 1/70 and then pressed to form an adhesive folium. The FTIR spectra were then recorded on a Nicolet 7600 spectrometer (Nicolet Instrument Corp., Madison, WI) from 500 to 4000 cm⁻¹ with a 4 cm⁻¹ resolution using 32 scans.

2.7 Thermogravimetry (TGA)

The procedure was adapted from one previously reported by Li *et al.* [3]. The cured adhesive powder (200 mesh) was prepared in the same manner as for FTIR measurement. The weight loss of the sample was recorded using a TGA instrument (TA Q50, Waters Corp., USA). About 5 mg of the powder was scanned from 30 °C to 600 °C at a heat rate of 10 °C/min.

2.8 Scanning Electron Microscopy (SEM)

The procedure was adapted from the one reported by Li *et al.* [3]. The adhesive was cured in an oven at 120 °C ± 2 °C for 2 h, then the cured adhesive was cracked into small pieces. Several pieces of cured adhesive were placed into a desiccator for 2 days prior to testing. The surface of the adhesive piece was sputter-coated with gold before observation under a Hitachi S-3400N scanning electron microscope (Hitachi Science System, Ibaraki, Japan).

2.9 Crack Observation

Adhesive samples were first coated evenly on glass slides (about 5 g), then cured in an oven at 120 °C ± 2 °C for 15 min. The samples were then held at 25 °C for 20 min and their surfaces imaged to observe cracks.

2.10 Plywood Wet Shear Strength

The procedure was adapted from the one previously described by Li *et al.* [3]. Twelve plywood specimens (25 × 100 mm) were first cut from two plywood panels, then six specimens submersed in water at 63 °C for 3 h and the other six specimens at 10 °C for 3 h, respectively, then held at room temperature for 10 min prior to testing. The speed of the crosshead was 1.0 mm/min. The force (N) at the bond break of each wood specimen was recorded and the wet shear strength (MPa) was calculated via Equation 2. The reported strength values of the adhesives are the average of six replications.

$$\text{Wet shear strength } (\text{MPa}) = \frac{\text{Tension Force}(\text{N})}{\text{Gluing area}(\text{m}^2)} \quad (2)$$

3 RESULTS AND DISCUSSION

3.1 Solid Content

Most wood adhesives are water based; the water in the adhesive significantly affects its performance. Generally, an adhesive with a higher solid content is preferred in the plywood fabrication industry [15]. As shown in Figure 1, the solid content of SM adhesive was recorded at 28.3%, the lowest of all the adhesives. After adding BDDE to the formulation, the solid content of the resulting adhesive increased from 30.39 to 35.08% with BDDE addition from 2 to 11 g, which can be attributed to the high solid content of BDDE. When 8 g of BDDE was added, the solid content of the SM/SDS/BDDE8 adhesive was measured at 32.83%—a 16% increase compared to the SM adhesive. The sample meets the plywood adhesive requirement (≥ 32%) set by previous researchers [16, 17]. The solid content of the SM/PAE adhesive was 33.32%, which was similar to adhesive E.

3.2 Viscosity

Viscosity is another important property of a wood adhesive which greatly affects its process performance. Adhesive with a high viscosity causes a hard distribution on the veneer; while an adhesive with overly low viscosity leads to over-penetration into the veneer. Both of them cause an insufficient bond of the resultant adhesive [18]. From Table 1, the viscosity of adhesive A was measured at 38,490 mPa·s, which had a flow issue and was hard to distribute uniformly on the veneer. A protein denature agent can unfold the protein molecules and decrease the distance between protein molecules, which will increase the adhesive viscosity [19]. As expected, introducing SDS increased the viscosity of adhesive B to 108,380 mPa·s. After incorporating BDDE from 2 to 11 g, the viscosity
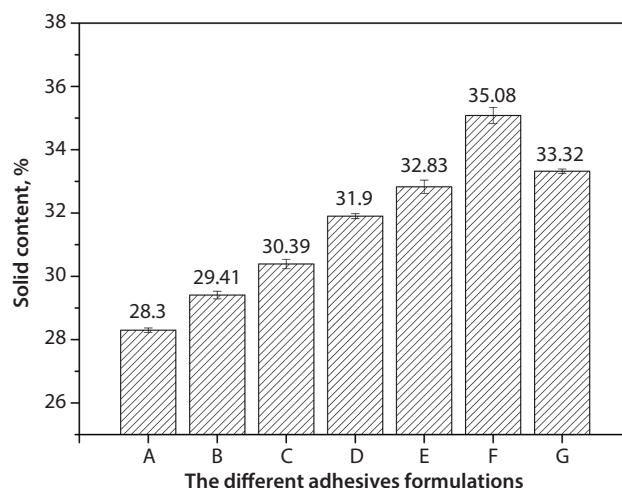

Figure 1 The solid content of the different adhesives: A (SM adhesive), B (SM/SDS adhesive), C (SM/SDS/BDDE2 adhesive), D (SM/SDS/BDDE5 adhesive), E (SM/SDS/BDDE8 adhesive), F (SM/SDS/BDDE11 adhesive), G (SM/PAE adhesive).

Table 1 The viscosity of the different adhesives at the rate of 1 s^{-1}: A (SM adhesive), B (SM/SDS adhesive), C (SM/SDS/BDDE2 adhesive), D (SM/SDS/BDDE5 adhesive), E (SM/SDS/BDDE8 adhesive), F (SM/SDS/BDDE11 adhesive), G (SM/PAE adhesive).

Types of adhesive	A	B	C	D	E	F	G
Initial viscosity (mPa·s)	38490	108380	76850	61480	37340	20730	48240

of the resulting adhesive decreased from 76,850 to 20,730 mPa·s. The adhesives E and F were easy flow. Compared to soy protein, BDDE has a small molecule and can embed protein molecule to reduce the intermolecular force, which reduces its overall viscosity. The viscosity of adhesive G was recorded at 48240 mPa·s, which had a flow issue. This is attributed to the fact that PAE possesses an electric charge which increases the forces between protein molecules, and thus presents a high viscosity. But, adhesive G had initial adhesion, leading to a good distribution on the veneer. Compared with PAE, the crosslinker BDDE has the ability to reduce adhesive viscosity, which benefits the improvement of adhesive solid content and adhesive distribution.

3.3 Wet Shear Strength of Plywood

The water resistance can be evaluated by measuring the wet shear strength of the resulting plywood. The wet shear strength of the plywood bonded by different adhesives is shown in Figure 2. In the testing of 63 °C water, the wet shear strength of the plywood bonded by the adhesive A was measured at 0.23 MPa and the wet shear strength increased to 0.54 MPa after adding SDS. Adding 2 g BDDE in adhesive formulation (adhesive C), the wet shear strength of plywood increased by 322% to 0.97 MPa compared to that of adhesive A. When the BDDE addition was 8 g, the wet shear strength of plywood reached a highest value of 1.19 MPa. As seen in Figure 2, the wet shear strength of the plywood with 10 °C water showed the same tendency with that of 63 °C water. The BDDE possesses active epoxy groups, which react with the active groups of the protein and increase the adhesive crosslinking degree, thus increasing the water resistance of adhesive. In theory, the plywood with adhesive F presented a better water resistance when compared to adhesive E. In reality, the wet shear strength of the plywood (63 °C) with adhesive F decreased 12% compared with that of adhesive E, which was attributed to the resulting low viscosity of the adhesive (Table 1) after adding 11 g BDDE which caused the adhesive over-penetration into veneer surface. Furthermore, the BDDE is oil soluable and overdosage of BDDE reduces the bond strength of the resultant plywood. The wet
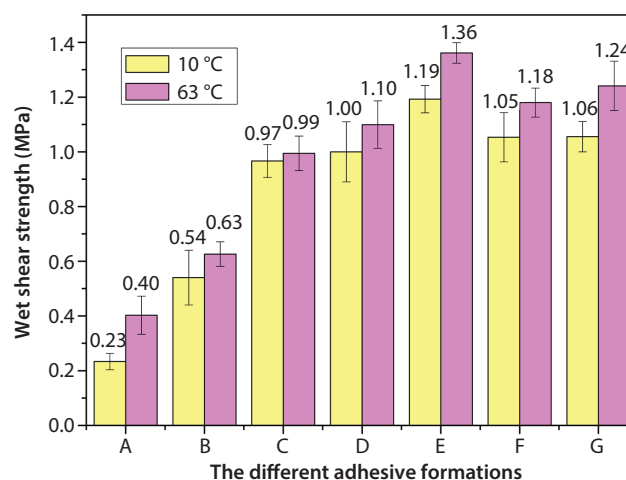

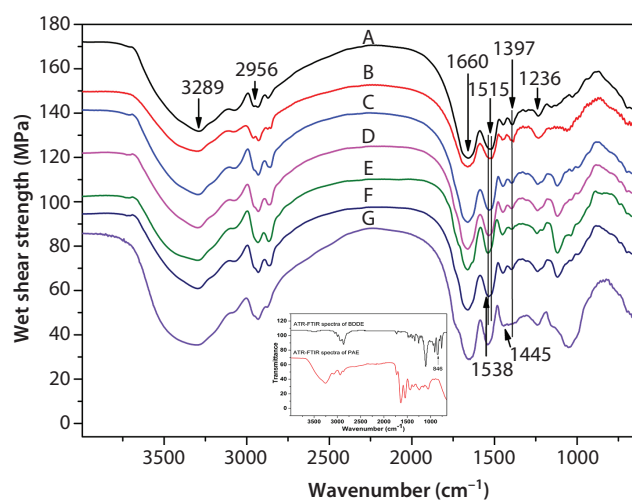**Figure 2** The wet shear strength of the different adhesives: A (SM adhesive), B (SM/SDS adhesive), C (SM/SDS/BDDE2 adhesive), D (SM/SDS/BDDE5 adhesive), E (SM/SDS/BDDE8 adhesive), F (SM/SDS/BDDE11 adhesive), G (SM/PAE adhesive).

shear strength of plywood (63 °C) with adhesive G was 1.01 MPa, which is 15.1% lower than that of adhesive E, which may be attributed to the toughness improvement of adhesive after using BDDE, thus decreasing the interior force and increasing the water resistance.

3.4 FTIR Analysis

In the spectra of adhesive A (Figure 3), the primary characteristic absorption bands appeared at 1660 cm^{-1} (amide I), 1515 cm^{-1} (amide II), and 1236 cm^{-1} (amide III), which were assigned to C=O stretching, N-H bending, and C-N and N-H stretching, respectively [20]. After using BDDE in the adhesive, the absorption peaks of amide II shifted from 1515 to 1538 cm^{-1} (blue shift) in the spectrum of the adhesive with BDDE, indicating a denser structure was formed in the adhesive. This denser structure was formed by the chemical reaction between BDDE and soy protein molecule. The absorption at 846 cm^{-1} was attributed to the peak of the epoxy group in the BDDE [21]. The epoxy group peak disappeared in the adhesive with BDDE, suggesting that the epoxy group of the BDDE

reacted with the protein molecules during the curing process, which crosslinked protein molecules and formed a crosslinking network in the adhesive. A schematic illustration of the reaction is shown in Figure 4. For the adhesive G, the peak of COO- (1397 cm^{-1}) [11] dropped lower than the peak at 1445 cm^{-1} of adhesive A, which was due to the reaction between azetidinium rings of PAE and the –COOH groups of soy protein and formation of crosslinking networks during the curing process [10].

3.5 DTG Analysis

Figure 5 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the different adhesives. From our previous research [3], for a soy protein-based adhesive, the breaking of unstable chemical bonds in the cured adhesive happens at the range of 210–290 °C (stage II). And the main structure degradation process is at 290 to 600 °C (stage III), indicating the breakage of C-C and C-N.

Figure 3 The FTIR spectrum of the different adhesives: A (SM adhesive), B (SM/SDS adhesive), C (SM/SDS/BDDE2 adhesive), D (SM/SDS/BDDE5 adhesive), E (SM/SDS/BDDE8 adhesive), F (SM/SDS/BDDE11 adhesive), G (SM/PAE adhesive).
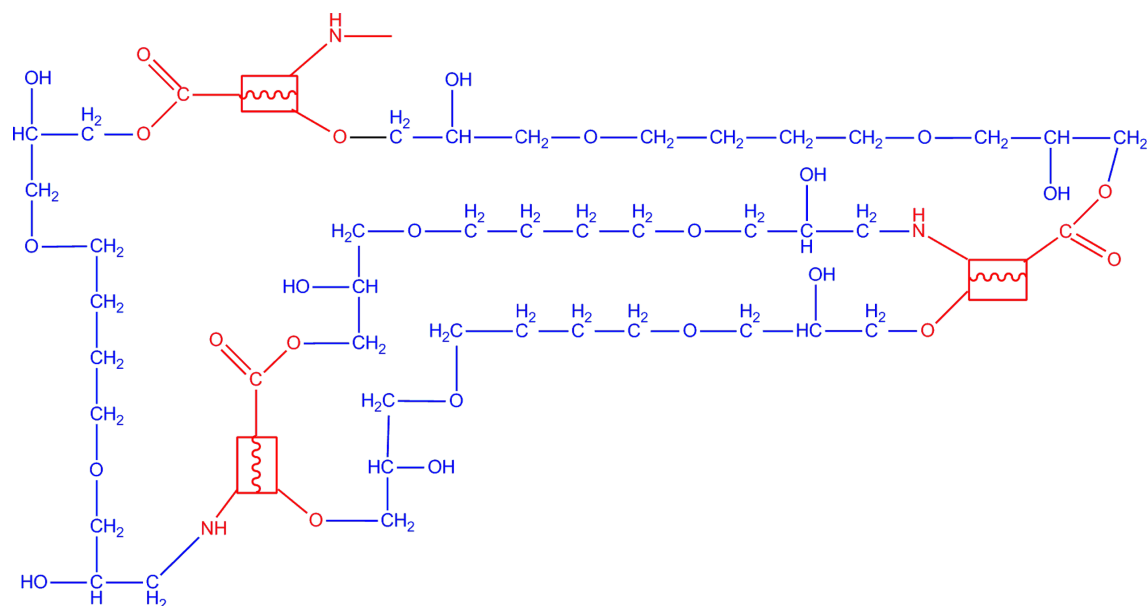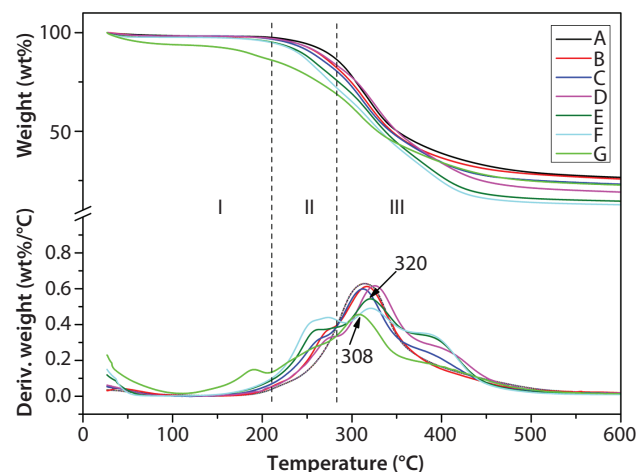

Figure 5 The TGA and DTG curves of the different adhesives: A (SM adhesive), B (SM/SDS adhesive), C (SM/SDS/BDDE2 adhesive), D (SM/SDS/BDDE5 adhesive), E (SM/SDS/BDDE8 adhesive), F (SM/SDS/BDDE11 adhesive), G (SM/PAE adhesive).

Figure 4 Schematic illustration of the reaction between BDDE and soy protein.

Compared with the SM adhesive, the adhesives with BDDE showed a strong peak (derivative weight) in stage II, indicating a different structure formed in the cured adhesive system after adding BDDE. This new structure was formed by the reaction between BDDE and protein molecules according to the analysis of FTIR. At stage III, the thermal degradation behavior showed an evident distinction between the adhesive with and without BDDE. The SM adhesive had the highest degradation rate and decreased significantly with the increasing addition of BDDE in the adhesive formulations, indicating that the adhesive with BDDE had a better thermal stability. This is probably due to the crosslinking structure formation between the BDDE and soy protein molecules, which also effectively improves the water resistance of the adhesive. Compared with the adhesive with BDDE, the SM/PAE adhesive showed a different thermal degradation behavior. A new peak was observed at stage I in the SM/PAE adhesive, indicating that the crosslinking structure formed between protein and PAE was more unstable than that with BDDE.

In addition, the main decomposition temperature of SM/PAE adhesive at stage III was observed at 308 °C and was lower than that of the adhesive E at 320 °C, suggesting that the thermal stability of adhesive E was better than that of adhesive G.

3.6   Fracture Morphology

The fracture surface micrographs of the different cured adhesives are shown in Figure 6. A large number of holes and cracks were observed on the fracture surface of the SM adhesive (Figure 7A) where moisture readily penetrated (i.e., water resistance was low). Fewer cracks were observed on the fracture surface of the cured adhesive B (Figure 7B), indicating that adhesive B had a better water resistance, which was in accordance with the result of wet shear strength measurement. After BDDE was introduced, a smoother and more homogeneous surface with no holes and cracks was observed, indicating that the cured adhesive with the BDDE became denser than that without the BDDE. However, compared with the adhesives modified by BDDE, the number of holes and cracks of the SM/PAE adhesive on the fracture surface micrograph increased. A smooth surface with no holes and cracks can effectively prevent moisture intrusion, thus improving the water resistance of the adhesive.

3.7   Crack Observation

The toughness measurements of the different cured adhesives are shown in Figure 7. A large number of cracks were observed on the surfaces of adhesives A and B, suggesting that the cured SM adhesive is brittle and easily broken under an interior force caused by moisture intrusion. After introducing BDDE, the cracks disappeared and the cured adhesive became more flexible and compact. The BDDE has a long chain structure and produces an inner toughening effect, which reduces adhesive brittleness. Furthermore, with the SEM imaging performance, we observed plenty of
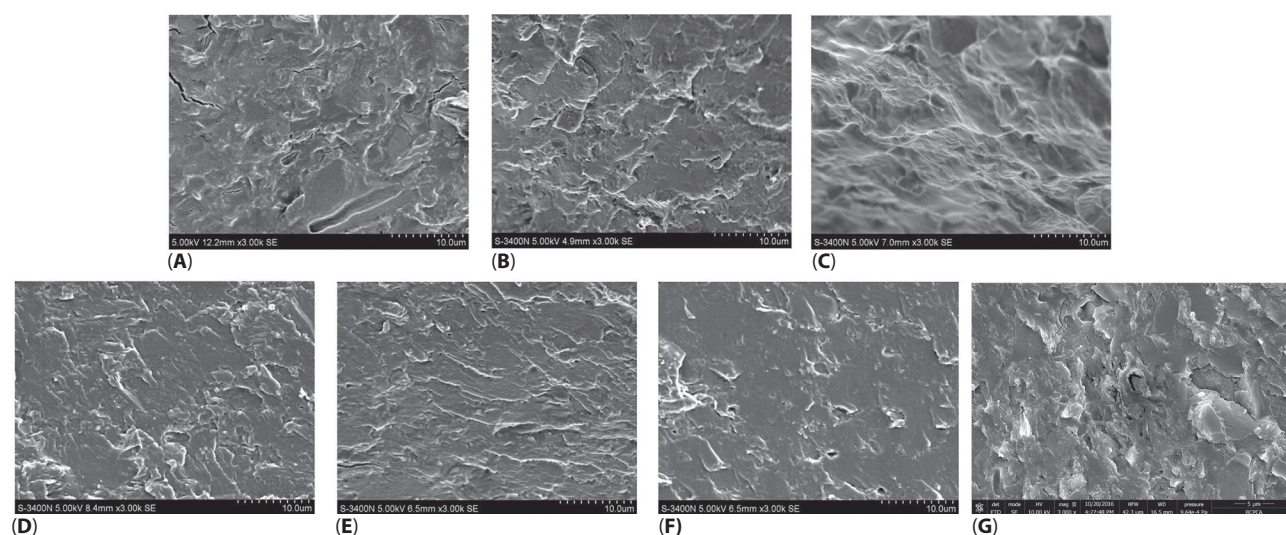

Figure 6 The morphology of the fracture surface for the different cured adhesives: A (SM adhesive), B (SM/SDS adhesive), C (SM/SDS/BDDE2 adhesive), D (SM/SDS/BDDE5 adhesive), E (SM/SDS/BDDE8 adhesive), F (SM/SDS/BDDE11 adhesive), G (SM/PAE adhesive).
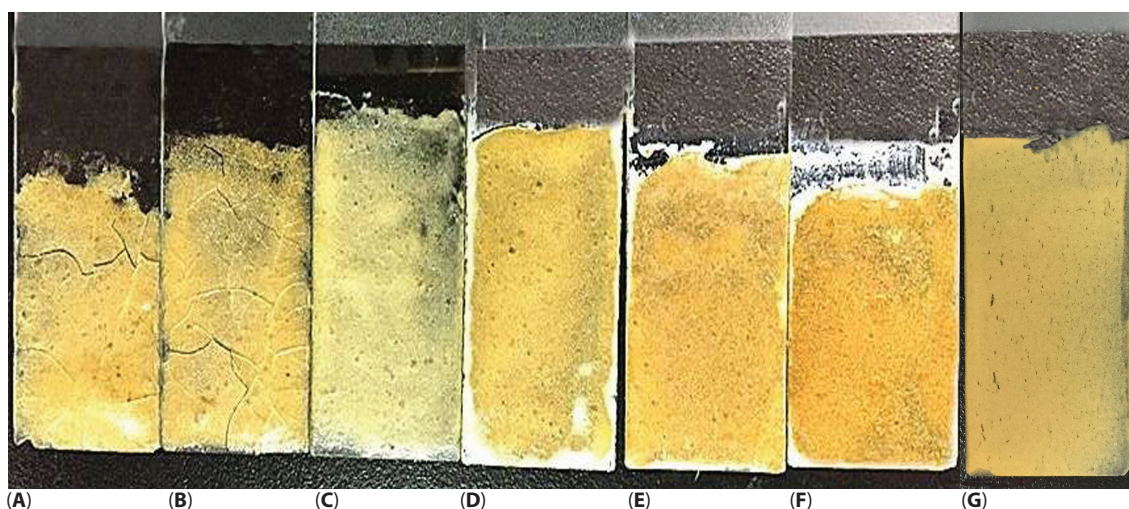
Figure 7 The toughness measurement of the different adhesives: A (SM adhesive), B (SM/SDS adhesive), C (SM/SDS/BDDE2 adhesive), D (SM/SDS/BDDE5 adhesive), E (SM/SDS/BDDE8 adhesive), F (SM/SDS/BDDE11 adhesive), G (SM/PAE adhesive).

holes in adhesive G, which could easily lead to the adhesive's fracture. A toughness adhesive will balance the interior force of the resultant plywood caused by the hot press process and the moisture intrusion, which improved the bond strength of the resultant plywood.

4 CONCLUSIONS

The BDDE reacts with the soy protein molecule to form a denser crosslinked structure, thus greatly improving the wet shear strength of the plywood bonded by the resultant adhesive. This structure also improves the thermal stability and creates a smooth surface, which further improves the performance of the adhesive. The long chain structure of BDDE produces an intrinsic toughness effect in the resultant adhesive and further improves the wet shear strength of the plywood.

By adding 8 g of BDDE into the adhesive formulation, the wet shear strength of plywood improved by 417% to 1.19 MPa compared with that without BDDE, which met the interior use plywood requirements. And the solid content and the viscosity of the resultant adhesive was 32.83% and 27340 mPa·s, respectively, which was acceptable for industrial use.

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