

Glycidyl Methacrylate Grafted onto Enzyme-Treated Soybean Meal Adhesive with Improved Wet Shear Strength

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In order to decrease the viscosity and improve the wet shear strength of soybean meal (SM) adhesive, in this study, SM adhesive, enzyme-treated SM adhesive (ESM), and the ESM grafted GMA (ESM-g-GMA) adhesive were prepared. The properties of these adhesives were characterized by rheological measurement, mechanical performance testing, Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). The results indicated that the apparent viscosity of the adhesives decreased due to the enzymatic treatment and the presence of GMA. The wet shear strength of the plywood panels bonded with ESM-g-GMA adhesive was significantly improved from 0.45 Mpa to 1.05 MPa, which met the interior plywood requirement (≥ 0.7 MPa) of the China National Standard. This study also investigated the pot life of the ESM-g-GMA adhesive and the impact of hot pressing. The change in wet shear strength was not obvious within 24 h. The optimum hot press temperature and time were 150 °C and 6 min, respectively. FTIR showed that GMA was successfully grafted onto the ESM adhesive. TGA indicated that the peak degradation temperature of the ESM-g-GMA adhesive was higher than that of the SM adhesive due to the cross-linking reaction that created the macromolecular dense structure between the ESM adhesive and the GMA monomer.

Keywords: Soybean-based adhesive; Bromelain; Graft; Glycidyl methacrylate; Wood adhesive; Non-formaldehyde

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INTRODUCTION

Recently, formaldehyde-based adhesives have played a dominant role in the wood adhesive market (Kumar *et al.* 2008). The emission of formaldehyde from wood-based panels and its products, however, is harmful to human health, as formaldehyde is a human carcinogen. In addition, formaldehyde-based adhesives are derived from nonrenewable fossil resources, which leads to an urgent need for the development of environmentally friendly wood adhesives from renewable materials (Huang and Li 2008; Li *et al.* 2004; Li *et al.* 2009; Liu and Li 2007; Schwarzkopf *et al.* 2009; Wang *et al.* 2008a; Wang *et al.* 2008b).

Attempts have been made to synthesize a bio-adhesive with good bonding strength, comparative water resistance, and reasonable pot life, and one that is free of formaldehyde emission (Li *et al.* 2009; Schwarzkopf *et al.* 2009; Wang *et al.* 2008a). Soybean, a renewable and abundant industrial raw material, can provide an alternative to formaldehyde-based resins. It is considered a promising alternative adhesive in the wood

industry and in other applications because of the previously mentioned advantages. Modified soy-based adhesive has the potential to partly or completely replace urea formaldehyde (UF) resin, which is widely used in the wood industry. It also has no formaldehyde emission and can reduce dependence on petroleum products (Kumar *et al.* 2008; Mo *et al.* 2004). It has potential use in the wood-based panel industry and is desirable as a potential method to increase the value of agriculture byproducts.

In recent decades, many studies have investigated methods to modify soybean protein to improve water resistance (Wang *et al.* 2007; Yang *et al.* 2008). Common approaches used by researchers to modify soybean protein include the use of chemicals such as alkali (Cheng *et al.* 2004; Wang *et al.* 2008a), urea (Zhang and Hua 2007), sodium dodecyl sulfate (Li *et al.* 2009; Mo *et al.* 2004; Zhong *et al.* 2003), and guanidine hydrochloride (Zhong *et al.* 2003). The current focus on soybean protein modification is the expectation that the polymer may change its conformation. During modification, the conformation of soybean protein becomes an unfolded, random loose structure, which causes the wet shear strength to increase; however, the viscosity is also increased, which prohibits widespread use in the wood industry. The objective of this study was to investigate whether enzyme treatment and grafting a GMA monomer onto soybean meal adhesive could reduce the protein's viscosity and increase the wet shear strength, making it suitable for the wood industry.

EXPERIMENTAL

Materials

Soybean meal (SM) was purchased from Sanhe Hopefull Group Oil Grain Food Co. Ltd., with an average protein content of 45.2% and moisture content of 5.0%. It was milled into powder with an airflow crusher before use. An emulsifier was prepared according to a method mentioned in previous literature (Qiu *et al.* 2012). Poplar veneer was obtained from Wen'an County with a moisture content of 8.0%. Bromelain and ammonium persulfate were analytical-grade reagents from Beijing Chemical Reagents Co.

Preparation of adhesives

The following is a representative procedure for the preparation of SM adhesive, enzyme-treated SM adhesive (ESM), and ESM grafted GMA (ESM-g-GMA) adhesive.

SM adhesive: SM (25g) was suspended in the emulsifier solution (75 mL) and stirred uniformly.

ESM adhesive: 0.125g bromelain (0.5% based on weight of SM) was added into the SM adhesive at 50 °C and stirred for 30 min.

ESM-g-GMA adhesive: Different amounts of GMA monomer and ammonium persulfate (2% based on GMA by weight) were added into the ESM adhesive, and the samples were reacted for 1 h at 75 °C. All the resulting adhesives were stored at ambient temperature before use.

Rheological Properties of Adhesives

Rheological measurements of the SM adhesive, ESM adhesive, and ESM-g-GMA adhesive were performed on a rheometer with a parallel plate fixture (20 mm diameter).

The distance was set to 1 mm for all measurements. Experiments were conducted with shear rates ranging from 10 to 240 s⁻¹ at 23 °C.

Solid Content Measurement

The solid content of the adhesives was measured based on the weight method according to the China National Standard (GB/T 14074-2006). About 3 g (weight α) adhesive was placed into an oven with the temperature set at 105 °C for drying until a constant weight (weight β) was obtained. The value of the solid content was calculated with the following equation. The average value of solid content was calculated from three parallel samples.

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

Preparation of Plywood Samples

Three-layer plywood (400 × 400 × 4.5 mm) was pressed on a laboratory hot press under the following conditions: adhesive spread rate of 150 to 160 g/m² at 150 °C of hot pressing temperature, 1.0 MPa of the hot pressing pressure, and 6 min of hot pressing time. After hot pressing, the plywood was stored under ambient conditions for at least 24 h before the wet shear strength was tested. Two panels of plywood were made for each formulation of the adhesive.

Wet Shear Strength Test

The wet shear strength of the plywood was determined in accordance with the procedure described by China National Standard GB/T 9846.3-2004 (Standardization Administration of the People's Republic of China 2004) for Type II plywood. The plywood prepared above was first cut into shear specimens and submersed in water at 63 °C for 3 h. The wet shear strength of wood specimens was then determined using a common tensile machine operating at a speed of 10.0 mm/min.

The force (N) at which the bonded wood specimen was damaged was recorded. The reported strength data of the adhesives are the averages of ten replications from two panels of plywood. Wet shear strength (MPa) was calculated using the following equation:

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

Fourier Transform Infrared Spectroscopy (FTIR) of ESM-g-GMA

The ESM-g-GMA adhesive (with a GMA monomer content of 10%) was precipitated with acetone and collected by centrifugation. The resulting precipitate was extracted with acetone for 3 h to remove the unreacted GMA monomer and the polyglycidyl methacrylate homopolymer. The FTIR spectra of the SM adhesive and the ESM-g-GMA adhesive were recorded on a Nicolet 380 spectrometer over the range of 400 to 4000 cm⁻¹ with a 4 cm⁻¹ resolution and 32 scans.

Thermal Stability of Cured Adhesives

The SM adhesive and ESM-g-GMA adhesive (with a GMA monomer content of 10%) were placed in an oven at 150 °C until reaching a constant weight and then ground into powder. The stabilities of the cured adhesives were tested using a TGA instrument (TA Q50, WATERS Company, USA). About 5 mg of the ground powder was weighed in a platinum cup and scanned from room temperature to 600 °C at a heating rate of 10 °C/min. The maximum degradation rate was calculated as mass (%) at peak temperature divided by peak temperature.

RESULTS AND DISCUSSION

Physical and Rheological Properties of the Different Adhesives

High viscosity adhesive is not accepted in the wood composites industry. One of the most effective methods for reducing the viscosity of soybean-based adhesive is to decrease the intermolecular forces in soy protein. In the present work, bromelain was used to decrease the viscosity of adhesives. The flow behaviors of the SM adhesive, ESM adhesive, and the ESM-g-GMA adhesive are shown in Table 1. The apparent viscosity of all the adhesives decreased when the shear rate increased, which showed a shear thinning behavior of non-newton fluid. As expected, the viscosity of the ESM adhesive was the lowest. The apparent viscosity of SM adhesive decreased from 2263 mPa·s to 133 mPa·s at a shear rate of 240 s⁻¹ with enzymatic treatment, which was in accordance with the result of Kumar' research (Kumar *et al.* 2004a). The viscosity of ESM-g-GMA adhesive was increased with the increase of the amount of GMA added, but still lower than that of SM adhesive.

Table 1. Physical and Apparent Viscosity Dependence on Shear Rate of the Different Adhesives

Sample	Viscosity (mPa.s)				Solid content (%)	pH value
	60*	120*	180*	240*		
SM adhesive	11123	6760	3241	2263	24.1	6.58
ESM adhesive	199	167	145	133	23.8	6.04
2%	654	512	430	382	25.6	6.37
4%	2227	1316	950	789	27.3	6.51
6%	5089	2510	1612	1247	29.1	6.55
8%	5900	2910	1790	1374	30.7	6.60
10%	9573	4463	2660	1958	32.5	-

* means of the shear rates (1/s) of 60,120,180,240, respectively.

The high viscosity caused poor flowability on the veneer surface. It also caused the distribution issue, which made it difficult to form mechanical interlocking between the wood and the adhesive during hot pressing, resulting in the low water resistance. The apparent decrease in viscosity of the ESM-g-GMA adhesive may be due to the protein being hydrolyzed into free amino acids or short peptides because of the effect of

bromelain. The modified ESM-g-GMA adhesive had a better flowability than that of the control, which allowed it to be easily sprayed onto wood veneer to make plywood.

Table 1 also shows that the solid content of adhesives was increased gradually from 23.8% to 32.5% with the increase of the amount of GMA added. The higher the solid content and lower the viscosity, the better the wet shear strength (Gao *et al.* 2012). And the change of pH value was not obvious.

Wet Shear Strength of the Adhesives

The wet shear strength of the plywood bonded with the SM adhesive and the SM-g-GMA adhesive are shown in Fig. 1. The wet shear strength of the plywood bonded by the SM adhesive was measured to be 0.45 MPa, which was much lower than the interior plywood requirement (0.7 MPa) according to the China National Standard (GB/T 9846.3-2004).

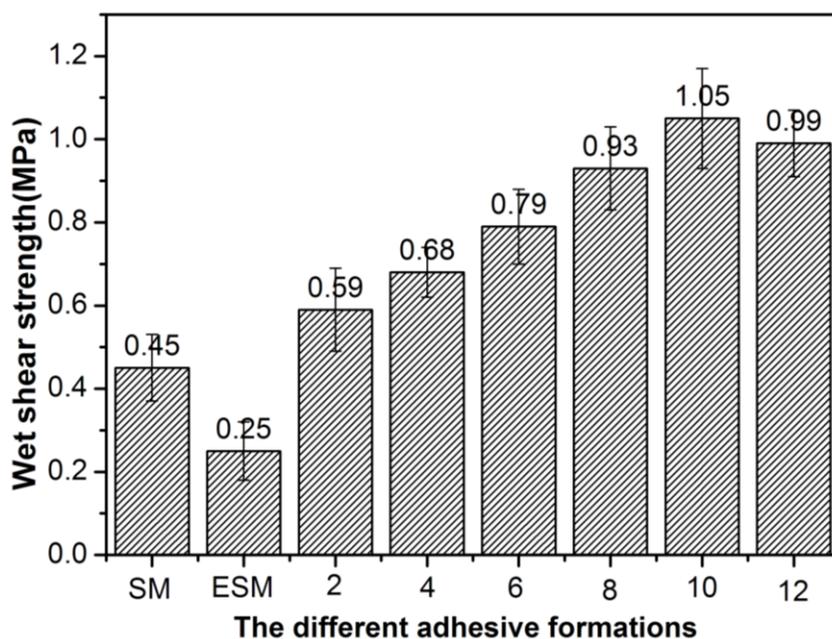


Fig. 1. Wet shear strength of plywood panels bonded with the SM adhesive, ESM adhesive, and the ESM-g-GMA adhesive as a function of the amount of GMA added

The wet shear strength of the ESM-g-GMA adhesive increased gradually with increasing GMA and exceeded the minimum industrial requirement (horizontal dashed line) when the amount of GMA added reached 6%. With the addition of more GMA monomer (10%), the wet shear strength of the ESM-g-GMA adhesive reached 1.05 MPa, more than 130% higher than that of the control. More GMA monomer resulted in higher crosslinking density and lower water absorption values of the networks in water, which increased the interactions between the adhesive and the substrate and hence resulted in a higher wet shear strength. Possible cross-linking of the functionalized protein may be another reason to improve the shear strength. When the added amount reached a certain value (12%), the higher monomer concentration of GMA in the ESM-g-GMA adhesive solution became prone to homopolymerization reactions, which caused the adhesive strength and water resistance to decrease. The wet shear strength of the SM adhesive, ESM adhesive, and ESM-g-GMA adhesive were also compared. It was shown that the

ESM adhesive had the lowest wet shear strength due to the soy protein macromolecule being hydrolyzed into small molecules.

Figures 2 through 4 show the effect of pot life, press temperature, and press time on the wet shear strength of plywood bonded by ESM-g-GMA adhesive (with a GMA monomer content of 10%). Figure 2 shows that the change in wet shear strength was not obvious within 24 h, which is long enough for use in the factory. Both hot press temperature and hot press time are important factors that affect the water resistance of the plywood bonded by the adhesives. As shown in Fig. 3, the wet shear strength increased as the hot press temperature increased from 110 °C to 160 °C.

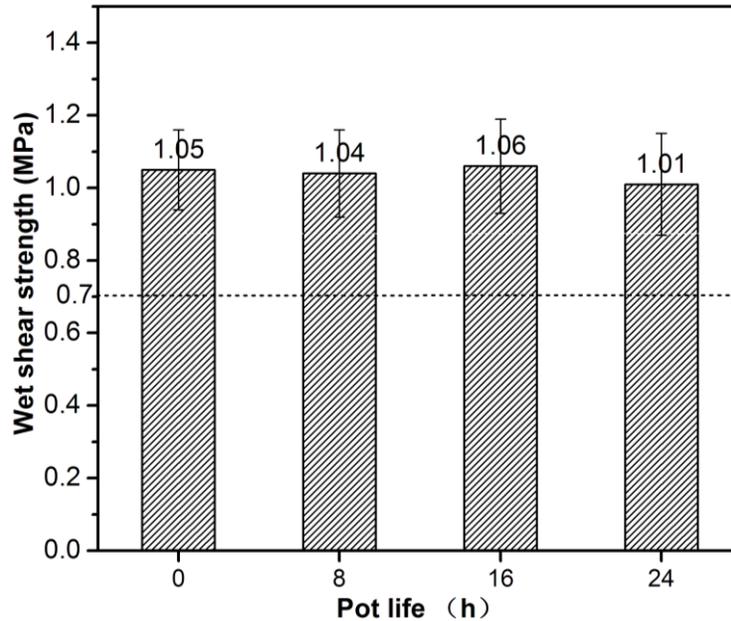


Fig. 2. The wet shear strength of plywood panels bonded with the ESM-g-GMA adhesive as a function of pot life

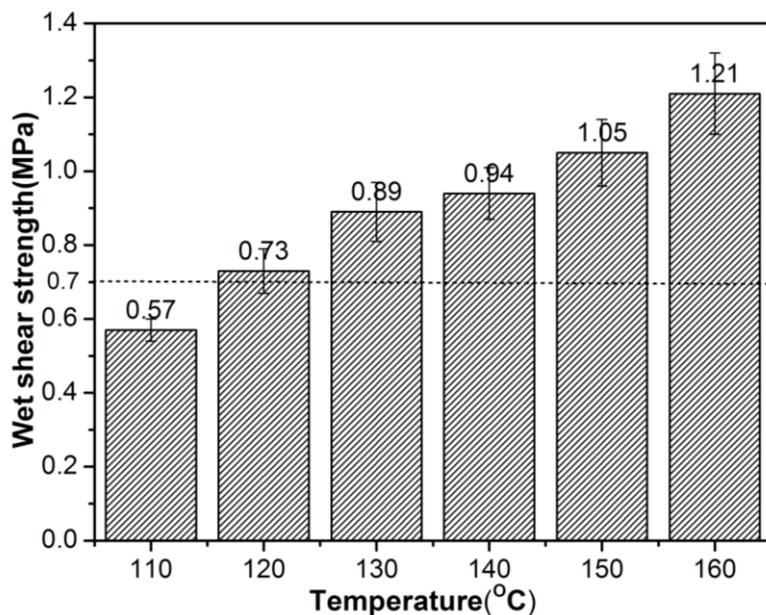


Fig. 3. The wet shear strength of plywood panels bonded with the ESM-g-GMA adhesive as a function of temperature (hot press time: 300 s; hot press pressure: 1.0 MPa)

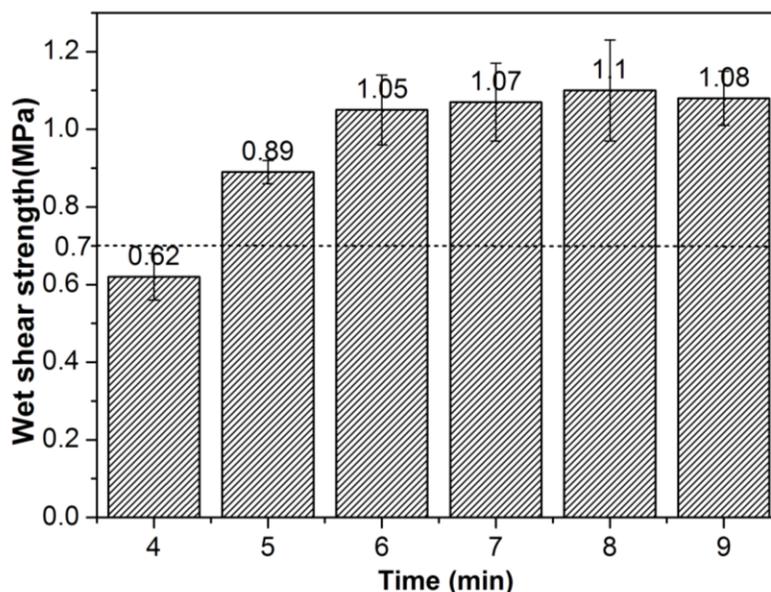


Fig. 4. The wet shear strength of plywood panels bonded with ESM-g-GMA adhesive as a function of temperature (hot press temperature: 150 °C; hot press pressure: 1.0 MPa)

The adhesives cured more completely because of the elevated temperature, which caused the core temperature of the plywood to increase. Generally, specimens made with a long hot press time had a higher wet shear strength. Figure 4 shows the effect of time on the wet shear strength from 4 min to 9 min. The wet shear strength of the plywood species improved during this time, and the wet shear strength of the plywood species bonded with the ESM-g-GMA adhesive reached 1.05 MPa after 6 min of hot pressing, which was much higher than the interior plywood requirement (0.7 MPa) of the China National Standard (GB/T 9846.3-2004).

As time increased, the wet shear strength did not change significantly. A suitable hot pressing time allowed more adhesive molecules to be pushed into the pore structure of the wood veneers to form a mechanical interlock to enhance the adhesion. Additionally, an adequate hot pressing time ensured chemical crosslinking reactions between the active functional groups of the wood and the adhesive, leading to a high wet shear strength.

GMA Grafted onto the ESM Adhesive

The FTIR spectra of the SM adhesive and the ESM-g-GMA adhesive are shown in Fig. 5. The broad band at 3200 to 3500 cm^{-1} corresponds to the stretching vibration of N-H and -OH groups in the SM and ESM-g-GMA adhesive. Three typical characteristic absorption bands at 1659 cm^{-1} (amide I), 1542 cm^{-1} (amide II), and 1235 cm^{-1} (amide III), which are related to C=O stretching, N-H bending, and -C-NH₂ bending, respectively, were also observed in the SM spectra.

As shown in Fig. 5, the amide I shifted from 1659 cm^{-1} to 1664 cm^{-1} in the SM-g-GMA sample. For the SM adhesive spectra, absorption peaks were found at 1732.2 cm^{-1} and 1170 cm^{-1} , related to the absorption peak of the carbonyl group of the ester bond in GMA. The absorption bands arising from the C-O strength vibration of esters consisted of C(C=O)-O and C-O-C and normally occurred in the region of 1300 to 1100 cm^{-1} .

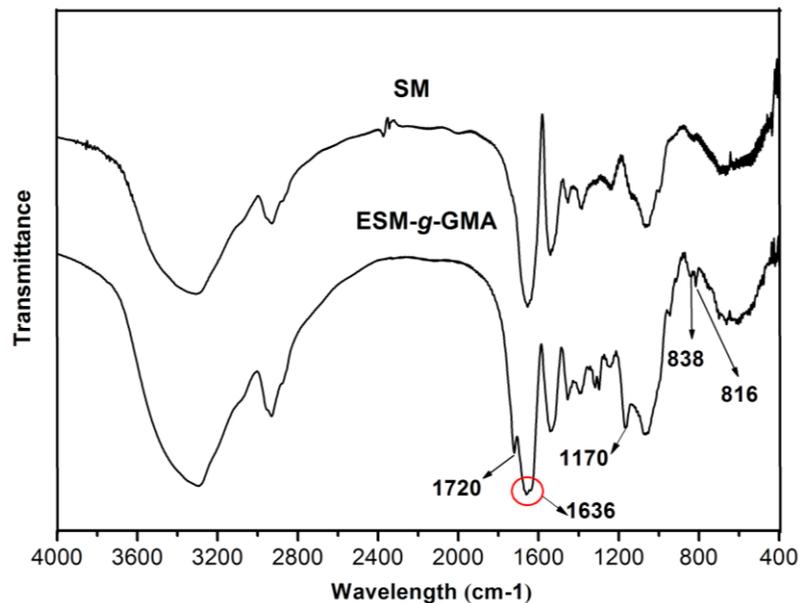
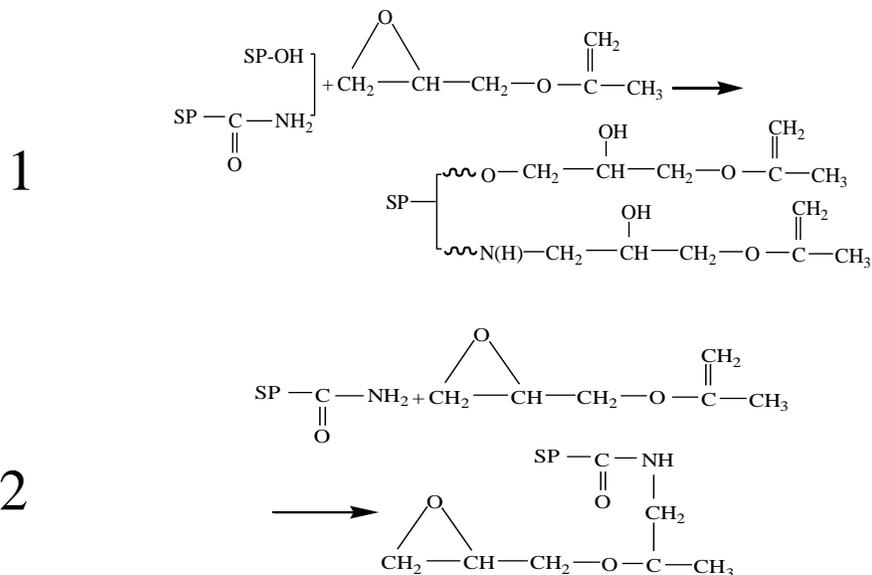


Fig. 5. FTIR spectra of the SM adhesive and the ESM-g-GMA adhesive

All the described observations suggest that GMA was successfully grafted to SM (Xiao *et al.* 2007). With the GMA being introduced into the adhesive, the addition and etherification reaction could possibly take place between the amino acid residues of SM containing hydroxyl groups or active NH_2 with the epoxy group of GMA monomer; the hydrogen bonds of intra- and intermolecular soy protein were destroyed, and the molecular chains were unfolded (Duanmu *et al.* 2007). The bands at 838 cm^{-1} and 816 cm^{-1} are characteristic bands of the epoxy groups, and the faint peak at 1636 cm^{-1} is related to $\text{C}=\text{C}$ stretching. These observations may be due to the characteristic groups of the unreacted GMA monomer. The SM adhesive grafted with GMA not only successfully increased the solid content of the adhesive but also improved the hydrophobic nature of the adhesive; the apparent increase in performance is due to the improvement of the wet shear strength. As a result, the SM units can form a cross-linking network with GMA by the following possible reactions:



Thermal Behavior of the SM and ESM-g-GMA Adhesive

The TGA and differential TGA curves of the cured SM and ESM-g-GMA adhesive are shown in Fig. 6. The adhesives degraded in three weight loss stages. In the first stage, from 25 °C to 200 °C, the weight loss for the adhesive was attributable to the evaporation of residual moisture, and the weight loss ratio were very small. No degradation of soy protein was found. Weight loss in the second stage, between 200 °C and 450 °C, was due to the degradation of the soy protein through broken intermolecular and intramolecular hydrogen bonds, electrostatic bonds, and bond cleavage. Further heating caused breakages of S–S, O–N, and O–O linkages, and finally, protein backbone peptide bonds were decomposed, producing various gases, such as CO, CO₂, NH₃, and H₂S (Qi and Sun 2011; Kumar *et al.* 2004b).

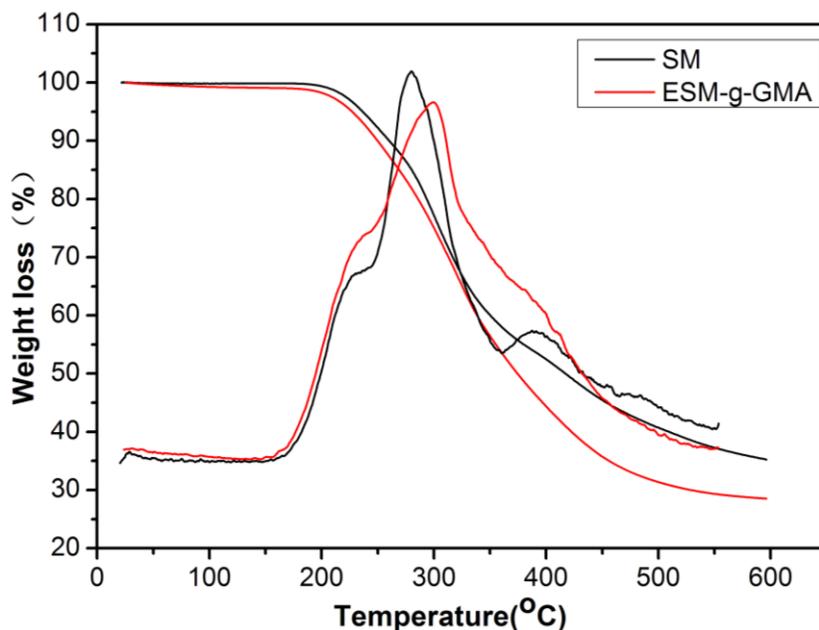


Fig. 6. TGA and differential TGA curves for the cured adhesives

The peak degradation temperature of the ESM-g-GMA adhesive was higher than that of the SM adhesive. A reverse trend was observed for the final residue weights corresponding to the temperature. With and without GMA, the peak temperatures were 301 °C and 323 °C, respectively, probably due to the cross-linking reaction that created the macromolecular dense structure between the ESM adhesive and the GMA monomer. This also further illustrated that the GMA effectively grafted onto the SM adhesive; the range of the degradation temperatures of the SM adhesive (200 to 450 °C) was wider than that of the ESM-g-GMA adhesive (200 to 550 °C).

This study does not sufficiently account for the enzymatic concentration and time. Therefore, further research should explore and discuss these values.

CONCLUSION

1. The apparent viscosity of the adhesives decreased upon introduction of bromelain and GMA into the SM adhesive.

2. The wet shear strength of the ESM-g-GMA adhesive was significantly improved, meeting the interior plywood requirement (0.7 MPa) of the China National Standard (GB/T 9846.3-2004). The ESM adhesive had the lowest wet shear strength due to the soy protein macromolecule being hydrolyzed into small molecules.
3. The change in wet shear strength was not obvious within 24 h; the optimum hot press temperature and time were 150 °C and 6 min, respectively.
4. FTIR showed that GMA was successfully grafted onto the ESM adhesive.
5. TGA curves indicated that the peak degradation temperature of the ESM-g-GMA adhesive was higher than that of the SM adhesive.

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