# A Novel Wood-Binding Domain of a Wood–Plastic Coupling Agent: Development and Characterization

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**ABSTRACT:** Poly(*N*-acryloyl dopamine) (PAD) was successfully synthesized through free-radical homopolymerization of *N*-acryloyl-*O,O'*-diphenylmethyldopamine and subsequent deprotection. The adhesive ability of PAD to wood was studied in detail. PAD underwent substantial oxidation and crosslinking reactions at about 80°C. Therefore, maple veneer samples bonded with PAD powder at a press temperature of 120°C had high shear strength and high water resistance. In contrast to conventional wood adhesives such as phenol-formaldehyde and urea-formaldehyde resins, PAD resulted in an increase, rather than a decrease, in the shear strengths of two-ply laminated maple veneer test specimens that had undergone a water soaking and drying treatment. A mixture of PAD and polyethylenimine (PEI) resulted in much higher shear strength than PAD alone. To achieve high shear strength and high water resistance, the maple specimens bonded with PAD–PEI mixtures had to be cured above 150°C because reactions between PAD and PEI occurred at about 150°C. The water resistance of the maple specimens bonded with the PAD–PEI mixtures was dependent on the PAD:PEI weight ratio and the curing temperature. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1078–1084, 2003

**Key words:** compatibilization; composites; adhesives

## INTRODUCTION

Various fillers such as glass fibers and mineral fillers are extensively used in the plastics industry to increase the strength and stiffness of thermoplastics. Wood fibers are currently gaining in popularity because they are inexpensive, readily available, and have low abrasiveness, keeping machine wear low and reducing damage to processing equipment. Wood-filled plastics, also called wood–plastic composites (WPC), are one of the fastest-growing sectors in the wood composite industry.[1] The most commonly used thermoplastics in a WPC are polyethylene and polypropylene. The most common filler used in WPCs is ground wood waste. In addition, cellulosic natural fiber materials such as bagasse, corncobs, and cereal straw, have also been used as fillers.[2] WPCs are used as outdoor decking materials, interior door panels, window moldings, interior automobile parts, and a large variety of other molded products.[3] WPCs have many advantages over traditional wood products such as reduced water absorbance, reduced thickness swelling, and enhanced durability against biodeterioration. When compared to unfilled thermoplastics, WPCs exhibit higher strength and stiffness, higher resistance to ultraviolet degradation, and higher thermal stability.

How WPCs ultimately perform is greatly dependent on the properties of the interface between the thermoplastic matrix and the wood filler. This interface is normally weak and fails to transfer stress between the phases because the wood is hydrophilic and the thermoplastic is hydrophobic. To address this problem, a coupling agent (commonly called a compatibilizer) that can bridge the interface and improve the stress transfer between phases is often added to the composite formulation during the manufacture of WPCs.

The results of an extensive number of studies suggest that an ideal compatibilizer should contain two domains: one domain able to form entanglements or segmental crystallization with the polymer matrix and the other able to form a strong adhesive bond with wood. An ideal compatibilizer for wood-filled polypropylene (PP) composites, as an example, would be a diblock copolymer with one block made up of PP and the other containing wood-binding functional groups. Maleic anhydride (MA)-grafted polypropylene (MAPP) is by far the most effective compatibilizer for wood-filled PP composites. In MAPP the succinic anhydride groups bind to wood via ester linkages, whereas the PP chains form an adhesion with the PP matrix.[4,5] MAPP is normally produced through grafting of MA to PP via a free-radical process. The succinic anhydride groups in MAPP are irregularly

distributed along the PP chain.[5] Therefore, MAPP does not have an optimum structure for compatibilization. Maleic anhydride is also not a good material to make PP–poly(MA) diblock copolymer because maleic anhydride is known to have a low tendency to form a homopolymer.[6,7] Therefore, improvement of WPC properties would benefit from the development of a new wood-binding domain that is able to form a diblock copolymer with PP.

In this study a novel wood-binding domain was developed through mimicking the strong adhesion of mussels to rock and other substances in seawater. To cope with tides and strong turbulence, mussels secrete adhesive proteins, typically called marine adhesives. From extensive study it has been found that marine adhesives contain 8–18 mol % L-3,4-dihydroxyphenylalanine (DOPA).[8,9] To further determine the specific functions of individual amino acids such as tyrosine, DOPA, lysine, and cysteine in marine adhesive proteins, various polypeptides have been chemically synthesized and studied for their binding abilities to various substrates[10–13] Several key conclusions are apparent from these studies: (1) "Functionality, and not amino acid sequence, was the only feature necessary for moisture-resistant adhesion"[13]; (2) DOPA residues appear to play an essential role in both adhesion and crosslinking in marine adhesives; and (3) other amino acids such as lysine significantly improved the binding of marine adhesives.

Inspired by the strong binding of marine adhesives, poly(N-acryloyl dopamine), a polymer that contains DOPA-like phenolic hydroxyl groups, was investigated as a good candidate for the wood-binding domain of a diblock copolymer compatibilizer.

## EXPERIMENTAL

### General information

All IR samples were recorded on a Nexus 470 FTIR spectrometer equipped with a Golden Gate–heated diamond ATR (attenuated total reflectance) accessory. The $^1$H-NMR spectra were recorded on a 300-MHz spectrometer. All chemicals and NMR solvents were purchased from commercial sources and used as received. Polyethylenimine was purchased from the Sigma–Aldrich Company (Milwaukee, WI). Thin-layer chromatography (TLC) was performed with Alugram Sil G/UV254 plates (Fisher Scientific, Pittsburgh, PA) with UV light. Column chromatography was performed with Whatman silica 60 [230–400 mesh (63–38 $\mu$m), Fisher Scientific (Pittsburgh, PA)] using a standard flash chromatography apparatus (Ace Glass, Vineland, NJ).

### Synthesis of O,O′-diphenylmethyldopamine hydrochloride (2)

O,O′-diphenylmethyldopamine hydrochloride (2) was synthesized according to a procedure in the literature.[14]

### Synthesis of N-acryloyl-O,O′-diphenylmethyldopamine (3)

Triethylamine (5.15 g, 50.91 mmol) was added to a suspension of 2 (6 g, 16.96 mmol) in $CH_2Cl_2$ (150 mL). The reaction mixture was chilled in an ice-water bath, and acryloyl chloride (2 g, 22.07 mmol) in $CH_2Cl_2$ (10 mL) was then added dropwise over 30 min. The cooling bath was removed, and the mixture was stirred for 3 h at 25°C. The solvents were removed under vacuum and the residues dissolved in EtOAc. The residual solids were removed by filtration, and the EtOAc solution was washed three times with 1$M$ $NH_4Cl$, then three times with 5% $NaHCO_3$ and once with brine. The organic layer was processed in a standard fashion to afford crude 3 that was subsequently purified by silica gel chromatography ($CHCl_3$:EtOAc 9:1) to provide 3 (5.01 g, 80%).

$^1$H-NMR ($CD_3SOCD_3$): 8.15 (1H, t), 7.54 (4H, m), 7.46 (6H, m), 6.93 (2H, t), 6.70 (1H, d), 6.20 (1H, q), 6.09 (1H, d), 5.56 (1H, d), 3.35 (2H, q), 2.69 (2H, t).

### Synthesis of poly(N-acryloyl-O,O′-diphenylmethyldopamine) (4)

Compound 3 (4.46 g, 12.01 mmol) and 2,2′-azobisisobutyronitrile (0.02 g, 0.122 mmol) were dissolved in acetonitrile (30 mL) in a 100-mL flask. The solution was degassed by bubbling $N_2$ for 3 min. The flask was sealed and heated to 70°C for 3 days. The polymerized product 4 was then washed with ethyl ether ($Et_2O$) and dried under vacuum (4.40 g, 98%).

$^1$H-NMR ($CD_3SOCD_3$): 7.41 (4H, broad), 7.22 (6H, broad), 6.74 (2H, broad), 6.47 (1H, broad), 3.35 (2H, broad), 3.15 (2H, broad), 2.00 (1H, broad), 1.58 (2H, broad).

### Synthesis of poly(N-acryloyl dopamine) (PAD) (5)

To a suspension of 4 (4.2 g) in 30 mL of trifluoroacetic acid (TFA) was added 33 wt % HBr in acetic acid with stirring. The mixture was stirred for 3 h at 25°C. The product was washed with $Et_2O$ and dried under vacuum (2.29 g, 98%).

### Differential scanning calorimetry analysis

Calorimetric measurements were obtained on a DSC-2920 (TA Instruments, Inc., New Castle, DE) with argon as a purge gas. Argon flow was adjusted to a rate of 40 mL/min. The calorimeter was calibrated

against indium (m.p. 156.6°C, $\Delta H = 28.45$ J/g) at 10°C/min. Test samples of about 2–5 mg were weighed in standard aluminum pans with lids. An empty aluminum pan with a lid was used as a reference. The samples were first cooled to 5°C–8°C with ice, and the thermograms were then recorded at a heating rate of 10°C/min from 5°C to 300°C. For the differential scanning calorimetry (DSC) analysis of a preheated sample, the sample was heated quickly to a preset temperature (120°C or 180°C) and held at that temperature for 5 min. The hot sample was cooled to 8°C with ice at an approximate rate of 50°C/min. The thermograms were then recorded at a heating rate of 10°C/min from 5°C to 300°C. If the sample was the mixture of PAD and polyethylenimine (1:1 weight ratio), PEI was first dried under high vacuum to completely remove water prior to mixing with PAD. The Universal Analysis V3.3B software, supplied by TA Instruments, Inc. (TA Instruments, Inc., New Castle, DE) was used to plot and analyze the thermal data. The DSC spectra were normalized to represent 1 g of sample.

### Adhesion test specimen preparation

Maple veneer 0.6 mm thick was cut into $100 \times 60$ mm pieces. When only PAD was used, the PAD powder was brushed directly onto maple veneer surfaces. When mixtures of PAD and PEI were used, PAD was first added to an aqueous PEI solution with a predetermined weight ratio of PAD to PEI and then mixed well. The PAD–PEI mixtures were brushed onto the veneer surfaces. The bonded area of each piece of veneer was $100 \times 10$ mm. The adhesive spread rate was 40 g/m$^2$ (dry weight).

One piece of PAD- or PAD–PEI mixture–brushed veneer and another piece of unaltered veneer were mated with the wood grain parallel in the samples and hot-pressed to form two-ply wood composites. The press time and temperature varied with the requirements of the experiment. After pressing the bonded two-ply wood composite was cut into 10 specimens. Each specimen had a bonded area of $10 \times 10$ mm.

### Determination of shear strength

The shear strength of a bonded wood specimen was tested with an Instron TTBML testing machine with the specimen in tension. The crosshead speed was 1 mm/min. The maximum shear strength at breakage was recorded and the degree of cohesive or adhesive failure observed.

### Determination of water resistance

Water resistance of the wood composites was determined by soaking the bonded specimen in water at
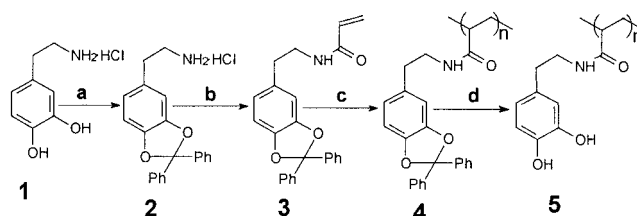


**Scheme 1** Synthesis of PAD. Reaction conditions: a, Ph2CCl$_2$; b, acryloyl chloride/Et$_3$N; c, AIBN/CH$_3$CN; d, HBr/AcOH/TFA.

room temperature for 24 h, then drying it at room temperature in a fume hood for 24 h, then measuring its shear strength. This water soaking and drying cycle (WSAD) was repeated up to three times. A separate boil test was performed in accordance with U.S. Voluntary Product Standard PS l-95 for Construction and Industrial Plywood (published by the U.S. Department of Commerce through APA–The Engineered Wood Association, Tacoma, WA), that is, test specimens were boiled in water for 4 h and then dried for 20 h at 63°C $\pm$ 3°C. The specimens were boiled in water again for 4 h, cooled down with tap water, and evaluated for shear strength while still wet. The shear strengths were also measured after the specimens were dried again at room temperature in a fume hood for 24 h.

## RESULTS AND DISCUSSION

The synthesis of poly(*N*-acryloyl dopamine) (PAD) **5** is shown in Scheme 1. The protection of phenolic hydroxyl groups in **1** with dichlorodiphenylmethane readily produced a 73% yield of **2**. The reaction of **2** with acryloyl chloride in the presence of triethylamine afforded a 80% yield of **3**. Polymerization of **3** provided **4**, which was readily deprotected to give **5**. Deprotection of **4** was verified through Fourier transform infrared (FTIR) spectroscopy (spectra not shown).

PAD powder bonded maple veneers strongly (Fig. 1). Shear strengths of PAD-powder-bonded wood composites at curing times of 2 and 5 min were comparable to each other and slightly higher than those at curing times of 10 and 20 min. Most interesting, the shear strengths significantly increased after the specimens underwent the WSAD cycle. The gain in shear strength was highest at a cure time of 5 min. Reported shear strengths of specimens bonded with conventional wood adhesives such as phenol–formaldehyde and urea–formaldehyde resins typically decrease after a WSAD cycle.[15,16] Therefore, this big strength gain is an unprecedented phenomenon in wood adhesion.

Visual inspection revealed an even distribution of PAD on the veneer surfaces for those specimens cured at 120°C. Optical microscopic inspection showed that
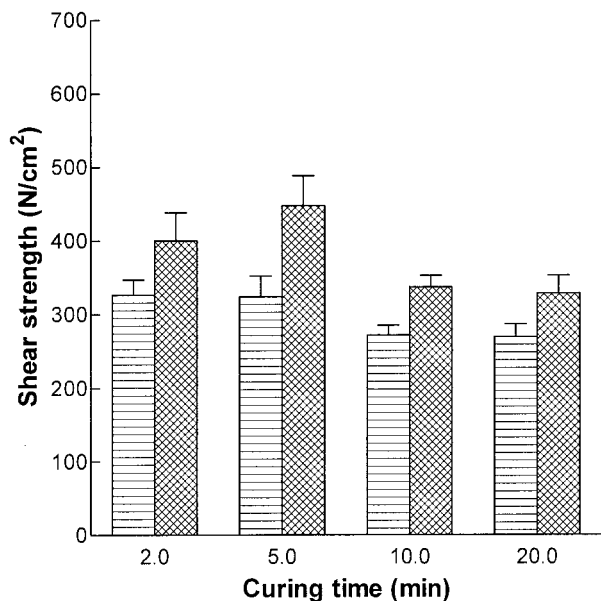
**Figure 1** Effects of curing time on shear strengths of wood composites bonded with PAD at a curing temperature of 120°C: (▤) without a WSAD test, (▩) after a WSAD test. Error bars show the standard deviation of the data (minimum of eight independent measurements).



**Figure 2** Effects of the number of WSAD cycles on shear strengths of wood composites bonded with PAD at a curing temperature of 120°C for 5 min. Error bars show the standard deviation of the data (minimum of eight independent measurements).

the adhesive could penetrate up to four woody cells (microscopic image not included). We concluded that the PAD flowed well and penetrated the wood substrate at 120°C.

The gain in shear strength occurred only after the first WSAD cycle, that is, the shear strength did not further increase after the specimens underwent a second or third WSAD cycle, but instead decreased slightly (Fig. 2). However, the shear strength value after soaking always remained higher than that of an unsoaked specimens (Fig. 2). We concluded that the PAD adhesive was very water resistant.

Results from the boil test indicated the wood composites did not delaminate, although the shear strengths of the wet specimens were significantly lower than those of the unexposed (and dry) wood composites (Fig. 3). However, when the exposed wood composites were subsequently dried, the shear strengths increased greatly and became higher than those of the original unexposed specimens. The gain in shear strength was larger for specimens cured at 180°C than for those cured at 120°C (Fig. 3).

Results of the DSC measurements on PAD showed a strong heat absorbance peak around 80°C (Fig. 4). When PAD was preheated at 120°C for 5 min and then analyzed by DSC, the strong peak at 80°C was greatly reduced, indicating that a chemical reaction of PAD, presumably with itself, had occurred. Possible reactions of PAD at elevated temperatures are discussed in detail later in this article.

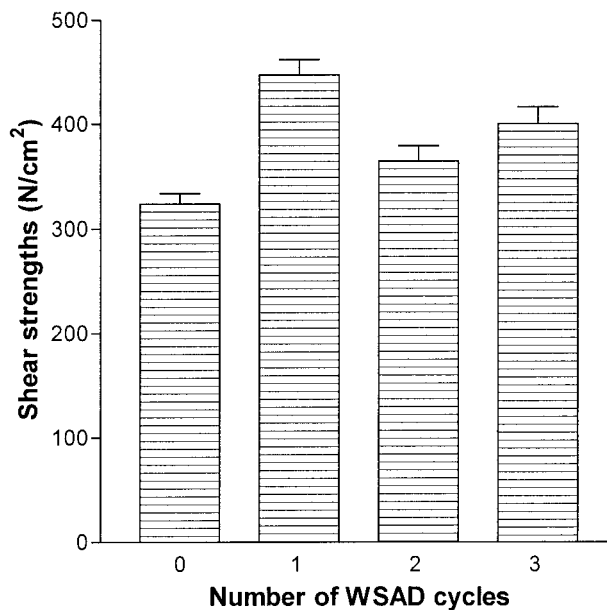In addition to phenolic hydroxyl groups, an amino group is also one of the major functional groups in mussel adhesive proteins.[17] Polyethylenimine (PEI) was combined with PAD to mimic marine adhesives. When mixed, PAD dispersed well in an aqueous PEI (50% wt) solution, although it did not completely dissolve. Under the same press conditions as those shown in Figure 1, a mixture of PAD and PEI (1:1
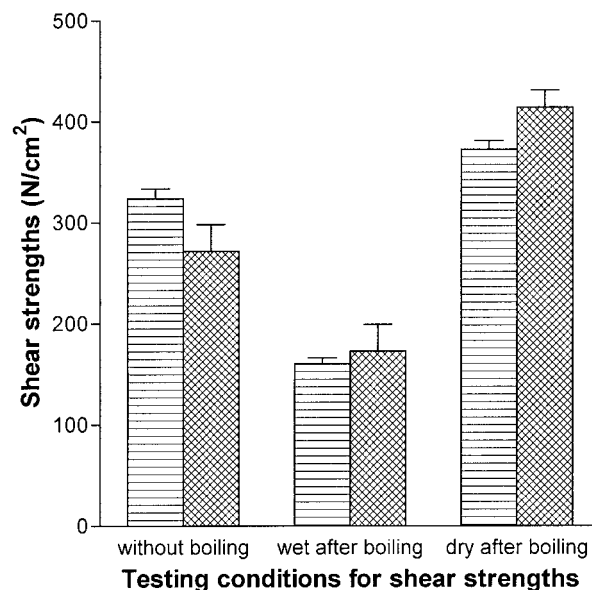


**Figure 3** Effects of the boil test on shear strengths of wood composites bonded with PAD–PEI mixtures: (▤) cure temperature of 120°C, (▩) cure temperature of 180°C. Error bars show the standard deviation of the data (minimum of eight independent measurements).
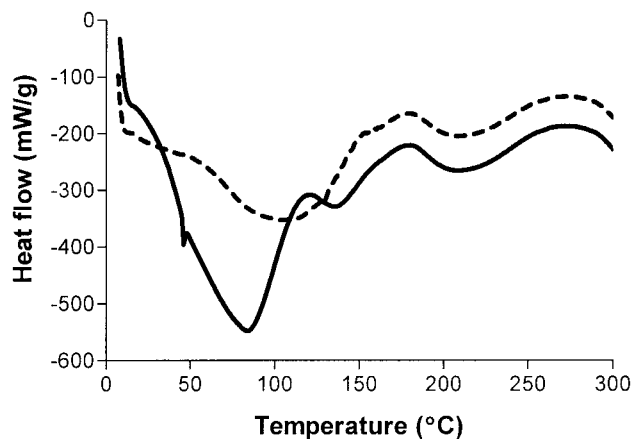
**Figure 4**  DSC characterization of PAD: (–) unheated before testing, (– – –) preheated at 120°C for 5 min.

weight ratio, dry basis) resulted in much higher shear strengths than PAD alone (Fig. 5), reaching 600 N/cm² when the press time was 20 min. However, shear strengths decreased significantly after the specimens bonded with PAD–PEI mixtures underwent a WSAD treatment. Increasing the press time from 5 to 20 min had little impact on shear strength after a WSAD treatment. Comparison of the data shown in Figure 5 with those in Figure 1 reveals that the water resistances of the wood composites bonded with a PAD–PEI (1:1 weight ratio) mixture at a press temperature of 120°C were lower than those bonded with PAD alone.
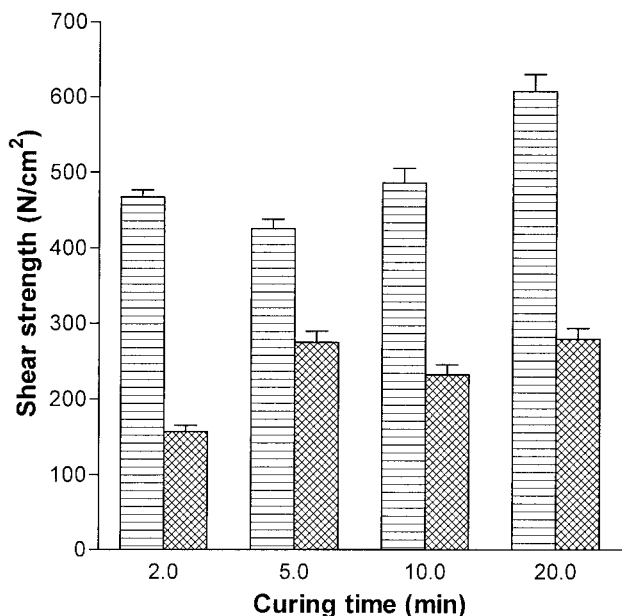


**Figure 5**  Effects of cure time on shear strengths of wood composites bonded with PAD–PEI (1:1 weight ratio) at a cure temperature of 120°C: (▤) without a WSAD test, (▨) after a WSAD test. Error bars show the standard deviation of the data (minimum of eight independent measurements).
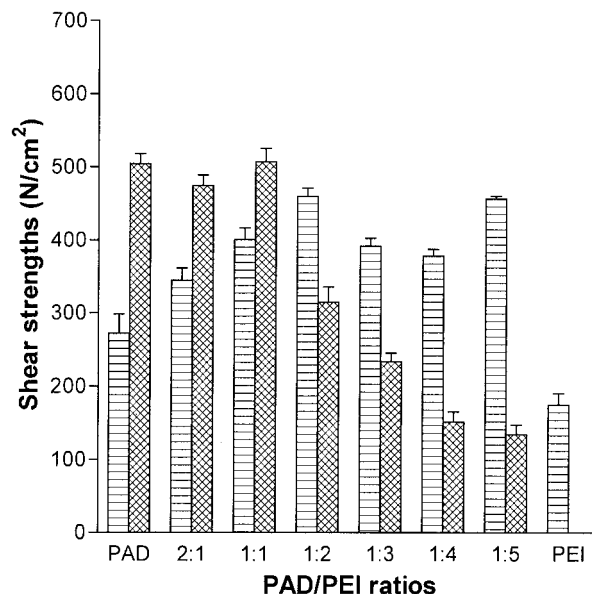


**Figure 6**  Effects of PAD–PEI weight ratios on shear strengths of wood composites bonded with PAD–PEI mixtures at a cure temperature of 180°C for 5 min: (▤) without a WSAD test, (▨) after a WSAD test. Error bars show the standard deviation of the data (minimum of eight independent measurements).

Because PEI is soluble in water, the amount of PEI in the PAD–PEI mixtures was expected to have a large impact on the water resistance of the wood composites bonded with PAD–PEI mixtures. The shear strengths of wood composites bonded with PAD–PEI mixtures at a press temperature of 180°C are shown in Figure 6. When the wood composites were evaluated without the WSAD treatment, the highest shear strength was reached when the weight ratio of PAD to PEI was 1:2. The shear strengths of wood composites bonded with PAD alone or PEI alone were much lower than those bonded with PAD–PEI mixtures. When the wood composites were evaluated after one WSAD cycle, the PAD–PEI weight ratio of 1:1 resulted in the maximum shear strength. At PAD–PEI weight ratios of 1:2, 1:3, and 1:4, the WSAD treatment decreased the shear strengths of the wood composites. However, when the PAD–PEI weight ratio was 2:1 or 1:1, the WSAD treatment increased the shear strengths of the wood composites. It appears that the higher the PAD content in the PAD–PEI mixtures, the higher is the gain in shear strength after a WSAD treatment.

A comparison of Figure 1 to Figure 6 reveals that the gain in shear strength after WSAD treatment of the wood composites bonded with PAD alone was higher at a press temperature of 180°C than at 120°C. In contrast to the reduction of the shear strengths for the composites bonded with PAD–PEI mixtures (1:1 weight ratio) at 120°C for 5 min after a WSAD treatment (Fig. 5), a press temperature of 180°C resulted in an increase in shear strengths for the wood composites
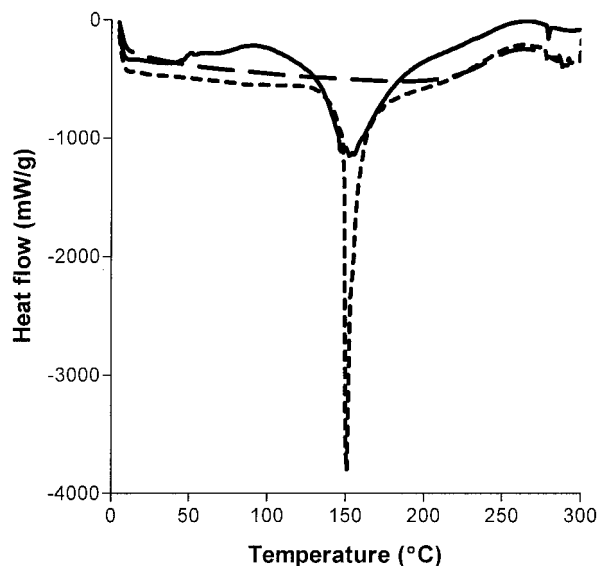
**Figure 7** DSC characterization of PAD–PEI (1:1 wt ratio) mixtures: (–) unheated before testing, (– – –) preheated at 120°C for 5 min, (— —) preheated at 180° for 5 min.

bonded with PAD–PEI mixtures (1:1 wt ratio), as shown in Figure 6. Press temperature had an important impact on the shear strength of the wood composites.

In an effort to better understand the effects of press temperature on strength properties and water resistance, PAD–PEI mixtures were analyzed using a DSC. The PAD–PEI mixtures showed a heat absorbance peak around 150°C (Fig. 7). When the PAD–PEI mixtures were preheated at 120°C for 5 min and then analyzed with the DSC, the heat absorption peak remained but became very sharp. However, this heat absorption peak at 150°C disappeared when the PAD–PEI mixtures were preheated at 180°C for 5 min. Thus, it appears there is a reaction between PAD and PEI occurring at 150°C. These DSC results suggest that the PAD–PEI mixture has a cure temperature of about 150°C. This is consistent with the shear strength data of the wood composites. The wood composites prepared at 120°C were weaker and less water resistant than those prepared at 180°C. The DSC results and the strong adhesive bond data suggest that the PAD reacted with PEI to form a highly crosslinked polymer network.

The reactions that take place here may be similar to those in the byssal threads secreted by mussel feet, which are initially soft and colorless and then gradually harden and turn brown. This process is called quinone tanning,[18–20] which is a very complex process that includes various oxidation reactions and crosslinking reactions among phenolic structures and between phenolic structures of DOPA–tyrosine and amino groups of lysine.[20] Some possible reactions of PAD and PAD–PEI mixtures at elevated temperatures

are outlined in Scheme 2. The phenolic hydroxyl groups in PAD and the imino groups in PEI could form hydrogen bonds with each other and with the hydroxyl groups on the wood surface. The phenolic hydroxyl groups in PAD should be easily oxidized to phenolic free radicals and quinones. A redox pair (one catechol and one quinone) dismutate to form two free radicals. These free radicals can couple in many ways to form various crosslinks. One of the coupling reactions is shown in Scheme 2. DSC characterization of PAD revealed that oxidation reactions and crosslinking reactions of PAD would occur at 80°C or higher.

Imino groups might react with o-quinones through Michael reaction and Schiff-base formation reactions (Scheme 2). The DSC spectra of PAD-PEI mixtures indicate that these reactions between PAD and PEI would primarily occur at about 150°C.

## CONCLUSIONS

PAD was successfully synthesized. PAD powder yielded high adhesive strengths for parallel laminated, two-ply maple veneer specimens. PAD should be able to serve as a wood-binding domain for a wood-plastic compatibilizer because N-acryloyl-O,O′-diphenyldopamine can be used to prepare a PP–PAD diblock copolymer.

The curing reactions of PAD occurred at about 80°C. The curing temperature for PAD–PEI mixtures was about 150°C. A combination of PAD and PEI had higher adhesive strengths than did PAD alone. The shear strength was related to the curing time and temperature. The adhesion mechanisms of PAD and PAD–PEI mixtures are not fully understood but are believed to be similar to those of mussel protein adhesives. The curing mechanisms of PAD and PAD–PEI mixtures are presumably very complex and are believed to be similar to the natural quinone-tanning process. A strength increase, rather than decrease, of wood composites bonded with PAD or PAD–PEI mix-
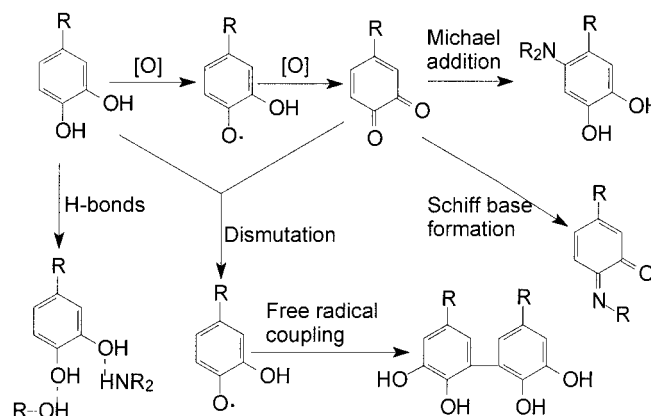


**Scheme 2** Possible reactions of PAD and PAD/PEI mixtures at elevated temperatures.

tures at 180°C was observed when the two-ply maple veneer laminated specimens were soaked in water and then dried. The strength gains were related to the PAD–PEI ratio and to the curing temperature. Further investigation is warranted in order to unveil the mechanism of this unique phenomenon.

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