

# Two-Phase Composite Modeling of Polyurea/Wood Interfaces

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**ABSTRACT:** The flexural modulus of oak and pine boards suffused with polymeric methylene diphenyl diisocyanate (pMDI) was measured as a function of the amount of pMDI imbibed. The resulting modulus values were compared to predicted values calculated by assuming a relationship between the composite phases. Specifically, the measured flexural moduli were compared to values obtained from a Kerner model, in which the composite phase consists of isolated and spherical particulate isotropically arranged in the major phase. Results were also compared to a Davies model, in which the two phases exist in a bonded co-continuous morphology. The measured data

was shown to be well fit to the Kerner model and not well described by the Davies model, despite the fact that the Davies model is more physically descriptive of the filled wood pore structure. This incongruous result indicates that the pMDI/wood interface is weak, and the resulting tensile properties are not significantly different from the wood–air composite in the absence of pMDI. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1739–1744, 2009

**Key words:** adhesives for wood; two-phase composite modeling; polymeric isocyanate; wood composites; interfacial interactions

## INTRODUCTION

Fundamental studies on wood adhesives and adhesion are characterized by uncertainty because of poorly characterized initial and final conditions.<sup>1</sup> Wood is a uniquely inhomogeneous substrate, and the interaction of a wood surface with an adhesive is inherently difficult to characterize. Isocyanates are very useful wood adhesives, and their utility for many wood-based applications is beyond question.<sup>2</sup> However, questions have arisen on the characteristics of isocyanate adhesive interactions with wood surfaces. Because isocyanates are intrinsically reactive with hydroxyl groups, which are abundant in wood,<sup>2</sup> it is natural to speculate on the role these presumptive covalent bonds will play in composite wood adhesive properties. Covalent interactions are enhanced by the low viscosity of isocyanate adhesives and their demonstrated ability to wet and penetrate wood. However, difficulty with unambiguous evaluation of the adhesive interface has nonetheless created confusion. This confusion is exacerbated by the fact that the urethane bonds that isocyanates form with the wood surface can revert to more thermodynamically stable urea bonds in the presence of water and elevated temperature.<sup>3</sup> Thus, it has been measured spectroscopically that urethane bonds that

are in abundance when isocyanates are cured with wood at 120°C will be undetectable when cured at 200°C.<sup>4,5</sup>

The nature of isocyanate/wood interactions has been studied by other researchers, often with contradictory conclusions. Some previous studies have documented the formation of a composite wood/isocyanate structure with polymeric methylene diphenyl diisocyanate and found urethane linkages by which the rigid polyurea bulk adhesive could supplement the wood carbohydrate structure.<sup>6,7</sup> Evidence that the resulting composite would actually reinforce the structure was sometimes lacking. A recent article by Frazier and coworkers<sup>8</sup> using model compounds suggests that NMR techniques may greatly overestimate the amount of polyurethane in wood isocyanate composites produced using industrially relevant techniques. Pizzi and Johns<sup>9,10</sup> have argued forcefully that isocyanate does not *ever* form covalent bonds to the wood interface, and instead, it maintains adhesion only via secondary forces (i.e., polar, dispersion, and H-bonding). Sonnenschein et al.<sup>11</sup> have shown that the presence of any wood/isocyanate covalent bonds that may form is not detectable by adhesive strength measurements. This led to the conclusion that the most efficient use of adhesive is to minimize isocyanate penetration into the wood subsurface and maximize the interfacial surface area formed between adhered surfaces. This work was consistent with previous observations that improved dispersion of isocyanate droplets on a wood surface was substantially more efficient in optimizing bond

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formation than procedures which encouraged isocyanate penetration into the subsurface.<sup>12</sup>

This article will further explore the manifestations of isocyanate-to-wood bonding to determine if such interfacial covalent bonds that may exist can be detected via conventional materials science analytical techniques. Our previous studies<sup>11,12</sup> suggest that in the limit of strong adhesion, such interactions may not be observable. However, the effect of a limited volume interfacial interaction may be more subtle and may evidence itself at much lower parts of the stress-strain curve. To explore this possibility, we present data from wood/isocyanate beams, where the flexural modulus is measured as a function of isocyanate loading, cure condition, and wood type. Electron micrographs are presented, which indicate interfacial interactions between the wood and isocyanate phases; however, HalpinTsai composite modeling of the tensile data strongly suggests that the composite phase's interactions may not be very strong. Although such two-phase composite modeling has been previously used to model oriented strandboard,<sup>13</sup> we believe that this is the first example of composite modeling to distinguish mechanisms of adhesion in wood composites.

## METHODS

Polymeric methylene diphenyl diisocyanate (pMDI) was obtained from Dow Chemical (Midland, MI) under the trade-name PAPI. PAPI-94 is a nominally 2.3 functional MDI oligomer having a molecular weight of 290 g/mol and a specified viscosity of 50 cps. We measured 50 cps on our specific sample with an Ares liquid rheometer, using cone and plate geometry which is in line with the product specification (pMDI is known to undergo viscosity increase with time because of reaction and chain extension with adventitious water). Southern pine and oak boards were obtained from a local hardware store. Samples as purchased were planed and cut to size but not otherwise treated.

A polished surface across the area of interest on each sample was created using a Reichert-Jung Ultracut E microtome equipped with a sapphire knife at room temperature. Each sample was then mounted on a scanning electron microscope sample stub with conductive carbon paint and coated with a conductive and contrast enhancing layer of platinum. The samples were examined in a FEI Nova NanoSEM600 scanning electron microscope (S/N NPV 19/D8134) using secondary imaging at 5 or 10 keV. Observations were made, and images were recorded digitally. Average penetration depth was approximated using a wide view shot and calibrating with the scale marker. Error in estimating pene-

tration depth was approximately  $\pm 30\%$ , due to uneven penetration across the front.

Sample preparation was performed by applying an excess of pMDI to the wood surface and then wiping the wood surface of nonpenetrating pMDI after a specified time. Wood edge surfaces were protected with a low tack sealant to prevent inadvertent infiltration of the pMDI by alternative routes. The sealant was removed before tensile testing. The wood specimens were 152.4-mm long, 12.2-mm wide, and 6-mm thick. Flexural modulus measurements were obtained using a three-point bend test (ASTM D 790). The flexural modulus of a beam<sup>14</sup> is calculated by eq. (1):

$$E_b = \frac{PL^3}{4wy t^3} \quad (1)$$

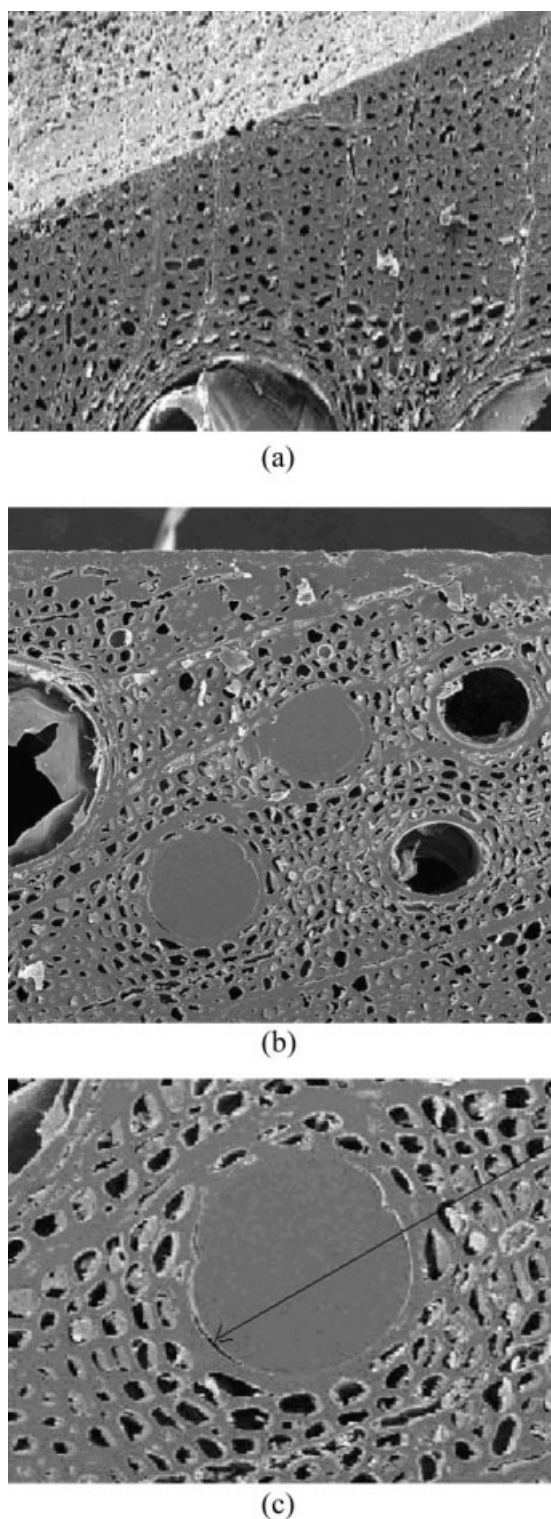
where  $E$  is the flexural modulus,  $P$  is the normal force,  $L$  is the beam length,  $w$  is the beam width,  $t$  is the thickness, and  $y$  is the strain or deflection at load point in this case.

With all geometric factors kept constant, the flexural modulus will scale linearly with  $P$ , the normal force.

Control and isocyanate-treated specimens were aged in a temperature-humidity controlled room (25°C/50% humidity) for 7 days. Samples cured at elevated temperatures were placed in a calibrated convection oven at 150°C for 1 h and then allowed to equilibrate under ASTM conditions for 48 h prior to testing. Flexural moduli were measured on an Instron 4202 frame running Blue Hill software. The strain rate was 2.54 mm/min. Each sample is the average of at least five specimens, and the standard deviation of the data is provided in the tables.

## RESULTS AND DISCUSSION

In a previous article,<sup>11</sup> we showed the penetration of pMDI into a pine structure using scanning electron microscopy (SEM). Although the pMDI had formed a penetration boundary front, it was clear that certain porous structures had not been filled by the pMDI, presumably because of a lack of pore continuity. Figure 1 shows this behavior even more dramatically with an oak sample. Figure 1(a) shows the structure of an oak specimen with no added pMDI. Figure 1(b,c) show a specimen in which pMDI had been allowed to penetrate the structure for 30 min before it was cured at 150°C. The low viscosity pMDI follows a path of least resistance in its penetration of the wood structure, often with surprising inhomogeneity. Interestingly, magnification of one of the vessels shows apparently inconsistent interfacial adhesion, disturbed sufficiently by the sectioning to result in some delamination.



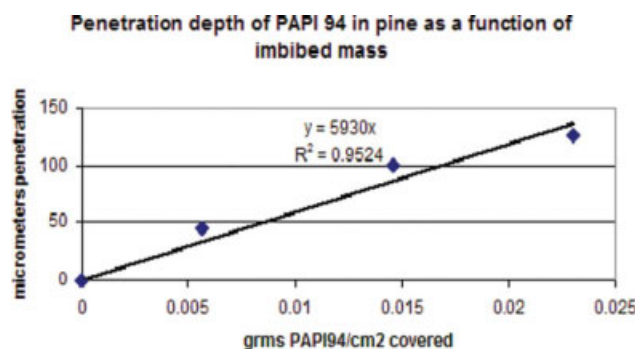
**Figure 1** (a) SEM of unmodified oak used in these experiments. (b) Oak with pMDI imbibed into the substructure for 30 min. (c) Magnification of (b). The arrow indicates region of possible delamination resulting from the sectioning process.

Treated beams were evaluated for approximate penetration depths as a function of penetration time. Figure 2 shows that penetration depth approxi-

mately follows a linear function with exposure time, though as Figure 1 reveals, the pMDI does not always form a regular front. We have observed that pine, having a somewhat more regular structure, also presents a more easily determinable penetration depth, and the present visually determined data is similar to the results obtained using a Raman scattering technique.<sup>11</sup> Error in this measurement decreases accuracy when quantifying the interaction between the wood and the isocyanate. However, as will be shown, this turns out not to be an issue.

Wood beams treated as described were tested for the effect of composite structure on flexural modulus. As composite properties may only reveal themselves at very low strains, we compiled modulus values at progressively increasing strain intervals. Table I shows that the flexural modulus was generally independent of the strain range at low strains. Clearly, the data shows some scatter with pMDI addition and cure conditions. However; given the error bars of the data, it would be difficult to suggest a convincing trend in modulus or maximum stress data. These results are consistent with previous results using double cantilever beam geometry.<sup>15</sup>

It could be argued that the pMDI addition levels in these experiments are too small to detect interphase effects; however, the very low strains probed should be most intensively sampling composite structure just beneath the wood surface, where there is the highest concentration of pMDI. Thus, it is reasonable that the current procedure should be sampling and reflecting composite structure and that comparison to noncomposite wood samples should detect differences if they are there to be seen. Furthermore, previous work has shown that even when the entirety of a wood sample is fully infiltrated with resin (usually achieved by submersion until such time as the wood does not float in the submersion medium), strength increase is on the order of



**Figure 2** Penetration of pMDI into pine as a function of imbibed mass. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE I**  
**Flexural Modulus Data for Pine and Oak pMDI Composites as a Function of Imbided pMDI and Cure Condition**

Sample	pMDI content (g/cm <sup>2</sup> )	Seg modulus 0.1%–0.25% (MPa)	Seg modulus 0.255%–0.55% (MPa)	Max flexural stress (MPa)	Flex strain at max stress (%)
Pine	0	6860 ± 376	6580 ± 217	61 ± 6.8	1.4 ± 0.2
Oak	0	8781 ± 0.022	8590 ± 577	99 ± 8.8	1.7 ± 0.2
Pine	0.006	7895 ± 1273	7430 ± 0.025	62 ± 2.6	1.4 ± 0.17
Oak	0.002	8996 ± 524	8586 ± 342	94 ± 4.8	1.6 ± 0.13
Pine	0.015	7953 ± 1662	7480 ± 1326	61 ± 3.6	1.2 ± 0.27
Oak	0.0036	9136 ± 117	8896 ± 154	99 ± 2.8	1.7 ± 0.11
Pine	0.024	6635 ± 785	6566 ± 813	62 ± 5.8	1.3 ± 0.23
Pine 150°C	0	7867 ± 1370	7513 ± 1151	79 ± 13.5	1.6 ± 0.44
Oak 150°C	0	8380 ± 828	8645 ± 368	98 ± 8.3	1.4 ± 0.1
Pine 150°C	0.0073	7099 ± 1600	7238 ± 1606	72 ± 24	1.2 ± 0.3
Oak 150°C	0.0014	8963 ± 0.08	9139 ± 0.00	94 ± 7.6	1.2 ± 0.07
Pine 150°C	0.0146	9009 ± 1987	9406 ± 1998	95.6 ± 22	1.4 ± 0.13
Oak 150°C	0.0038	8740 ± 536	9045 ± 617	98.3 ± 11	1.3 ± 0.11
Pine 150°C	0.0211	8244 ± 1707	8774 ± 1345	92.4 ± 8.6	1.3 ± 0.05

20%, suggesting minor influence of resin on the stress-bearing structure.<sup>16,17</sup>

The relationship of isocyanate and wood phases can be further probed if the results of flexural modulus measurements are compared to composite model results in which no phase continuity is assumed or ones in which co-continuity of the phases is assumed.<sup>18</sup> Two models that allow us to see how close the current results are to one or the other assumption are the modified Kerner equation and the Davies equation.<sup>19</sup> The Kerner equation can be employed for simple systems in which reinforcement is achieved by bonding of a spherical noncontinuous filler phase to a different major phase. The Davies equation is more often applied to composite reinforcement obtained by a filler phase having strong bonding between two co-continuous phases. Thus, the data will be well modeled by the Kerner equation in the event of local interactions between the pMDI and the wood, whereas a strong and long-range relationship between the phases will be more closely modeled by the Davies equation. A scenario intermediate between these two extremes will likely fall between the model derived modulus values.

Evaluation of the model equations requires some empirical inputs and some simplifying approximations which should not significantly affect the final results. Table II provides the initial inputs.

To evaluate each of the two models, a three-step process was used:

1. The modulus of the solid part of the wood was extracted from the wood modulus (as determined by the test on the unfilled specimens) by assuming that the wood was a composite material with air (modulus = 0) as a filler.

2. A modulus was predicted for the glue-filled wood using the solid wood modulus obtained above with a PAPI (polyurea) filler modulus.
3. The flex modulus of the wood with surface layers of glue-filled pores was computed using standard equations for bending of laminated beams.

The Kerner equation, which models two phase composites describing spherical inclusions bonded randomly to a majority phase, is shown below, using air as the filler in a matrix of solid wood polymer. In the equation,  $E_{\text{air}}$  is the modulus of air,  $E_w$  is the modulus of wood,  $E_{\text{sw}}$  is the modulus of the solid wood, and  $\phi_{\text{sw}}$  and  $\phi_{\text{air}}$  are the volume fractions of solid wood and air, respectively.

$$E_w = \frac{E_{\text{sw}}E_{\text{air}} + A(E_{\text{sw}}\phi_{\text{sw}} + E_{\text{air}}\phi_{\text{air}})}{A + E_{\text{sw}}\phi_{\text{air}} + E_{\text{air}}\phi_{\text{sw}}} \quad (2)$$

$$A = E_{\text{sw}} \frac{(7 - 5\nu_{\text{sw}})}{(8 - 10\nu_{\text{sw}})} \quad (3)$$

These equations can be inverted to extract the modulus of the solid wood by setting  $E_{\text{air}} = 0$ ,  $\nu_{\text{sw}} = 0.4$  and simplifying. The result is

**TABLE II**  
**Material Properties Used for Evaluation of the Two-Phase Composite Models Used in This Work**

Inputs	Symbol	Values	Units
Polyurea modulus	$E_u$	4000	MPa
Density PAPI	$d_p$	1	g/cm <sup>3</sup>
Porosity wood	$\phi_w$	0.5	
Wood thickness	$t_w$	0.7	cm
Wood core thickness	$t_c$		cm
Poisson ratio solid wood	$\nu_{\text{sw}}$	0.4	

$$E_{sw} = E_w \times \frac{(\varphi_{sw} + 1.25)}{1.25(1 - \varphi_{sw})} \quad (4)$$

Once the solid wood modulus is known, the wood–polyurea composite modulus can be predicted by again applying the Kerner equation.

$$E_{wck} = \frac{E_{sw}E_u + (A(E_{sw}\varphi_{sw} + E_u\varphi_u))}{A + E_{sw}\varphi_u + E_u\varphi_{sw}} \quad (5)$$

In this equation,  $E_u$  is the modulus of polyurea,  $E_{sw}$  is the modulus of solid wood,  $E_{wck}$  is the modulus of the wood–polyurea composite, and  $\varphi_{sw}$  and  $\varphi_u$  are the volume fractions of solid wood and polyurea, respectively.

The composite flex modulus of the beam geometry, including an unfilled core section, is given by eq. (6):

$$E_{fck} = \frac{E_w t_c^3 + (E_{wck}(t_w^3 - t_c^3))}{t_w^3} \quad (6)$$

where the  $t$  values compensate for the partial filling of the wood with pMDI into a composite and unfilled wood core ( $t_w$  represents the total beam thickness;  $t_c$  is the thickness of the unfilled core).

The Davies equation assumes a somewhat simpler form, invoked commonly for systems that achieve co-continuous network structures, and is well applied to composites with phases that are of similar modulus. In this formalism (using the same variable labels as before),

$$E_w = (\varphi_{sw}E_{sw}^{1/5} + \varphi_{air}E_{air}^{1/5})^5 \quad (7)$$

This equation can be solved as before to give an equation for the modulus of the wood solid matrix:

$$E_{sw} = \frac{E_w}{\varphi_{sw}^5} \quad (8)$$

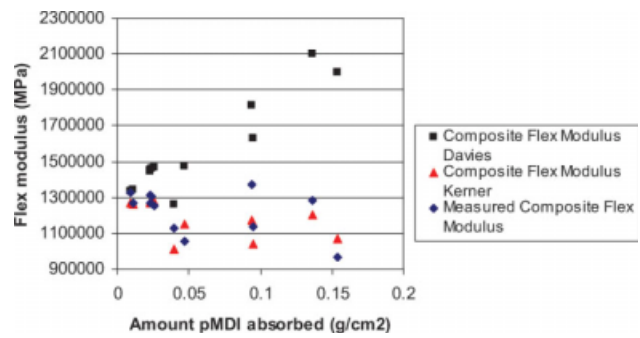
The resulting filled composite modulus would then be

$$E_{wcd} = (\varphi_u E_u^{1/5} + \varphi_{sw} E_{sw}^{1/5})^5 \quad (9)$$

And finally, the flex modulus is

$$E_{fcd} = \frac{E_w t_c^3 + (E_{wcd}(t_w^3 - t_c^3))}{t_w^3} \quad (10)$$

The calculated results from eqs. (6) and (10) compared to the measured flex modulus values are shown in Figure 3. These results show the flexural moduli to be well predicted by the Kerner two-phase composite equations, implying a discontinuous spherical composite topography. While the urea composite phase should be, and clearly is, spherical, it should not be isolated and should represent a co-continuous reinforcement. The wood structure is



**Figure 3** Comparison of measured and calculated flexural modulus values. Measured values are well predicted by the Kerner equation. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com)]

well known to be foam-like, with interconnecting and co-continuous phases. Figure 1 and previous images<sup>11</sup> illustrate this structure. However, the composite modeling unambiguously supports an isolated composite structure, implicitly describing the wood–urea composite as insignificantly different from a wood–air composite. The results suggest that the urea phase is poorly bonded to the wood phase, and even at low strains, there is significant slippage between the phases.

These results do not by themselves preclude the existence of a covalent bonded interphase between wood and a polyurea.<sup>9</sup> However, they do suggest, as previous NMR work has suggested, that its role in wood composite formation may be minimal.<sup>8</sup> The results furthermore validate a view that the most efficient use of pMDI in wood bonding is in that method which most widely and uniformly coats the wood surface with a minimum of wood penetration.<sup>11,15,20</sup>

## CONCLUSION

This article presents data measuring the flexural modulus of beams made of pine and oak in composite with pMDI. The results were measured as a function of strain in the linear elastic range and as a function of volume fraction pMDI within the composite. The measured flexural moduli were then compared to the calculated values using two-phase composite models. The measured values were well predicted by a Kerner model, in which the polyurea phase is implicitly spherical and isolated. The data was not well predicted by a Davies model, which presupposes that the phases are co-continuous, even though this model is demonstrably relevant to the wood–polyurea composite morphology. The mismatch between model results and correct physical description is interpreted to mean that the polyurea phase has weak interactions with the wood

carbohydrate structure. The results also provide additional support to the hypothesis that the most effective use of pMDI when making wood composites is in that method which most enhances surface coverage and mitigates penetration below the surface.

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## References

1. Wegner, T. H. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1989; Vol. 17, p 843.
2. Sellers, T. *Handbook of Adhesives Technology*; Pizzi, A.; Mittal, K. L., Eds.; Marcel Dekker: New York, 1994; p 599.
3. Elwell, M.; Ryan, A. J.; Grunbauer, H.; Van Lieshout, H.; Lidy, W. *Plast Rub Compos Process Appl* 1995, 23, p 265–276.
4. Zhou, X.; Frazier, C. E. *Int J Adhes Adhesives* 2001, 21, 259.
5. Martin, D. J.; Mejis, G. F.; Ginitallake, P. A.; McCarthy, S. J.; Rewick, G. M. *J Appl Polym Sci* 1997, 64, 803.
6. Marchinko, J. J.; Newman, W. H.; Phanopoulous, C. *ICI Polyurethanes*, ICI Group Publications 516; Leiden, The Netherlands, 1996.
7. Jensen, E. S.; Gatenholm, P.; Seletti, C. *Die Angew Makromol Chem* 1992, 200, 77.
8. Sudipito, D.; Malmberg, M. J.; Frazier, C. E. *Int J Adhes Adhesives* 2007, 27, 250.
9. Pizzi, A. *Advanced Wood Adhesives Technology*; Marcel Dekker: New York, 1994.
10. Johns, W. E. Pizzi, A., Ed. In *The Chemical Bonding of Wood in Wood Adhesives: Chemistry and Technology*; Pizzi, A., Ed.; Marcel Dekker: New York, 1989; Vol. 2, p 79–80.
11. Sonnenschein, M. F.; Wendt, B. L.; Sonnenschein, G. F. *J Appl Polym Sci* 2005, 98, 449.
12. Sonnenschein, M. F.; Wendt, B. L. *Wood Sci Technol* 2005, 39, 27.
13. Shaler, S. M.; Blankenhorn, P. R. *Wood Fiber Sci* 1990, 22, 246.
14. Pocius, A. V. *Adhesion and Adhesives Technology*; Hanser: Munich, 1997; p 29.
15. Conrad, M.; Smith, G. D.; Fernlund, G. *Int J Adhes Adhesives* 2003, 23, 39.
16. Moustafa, A. B.; Kandil, E. E.; Hady, B. A.; Ghanem, N. A. *Die Angew Makromol Chem* 1977, 65, 121.
17. Ors, Y.; Atar, M.; Keskin, H. *Int J Adhes Adhesives* 2004, 24, 287.
18. Halpin, J. C.; Kardos, J. L. *Polym Eng Sci* 1976, 16, 344.
19. Wakabayashi, K.; Register, R. *Polymer* 2005, 46, 8838.
20. Frisch, K. C.; Rumao, L. P.; Pizzi, A. In *Wood Adhesives*; Pizzi, A., Ed.; Marcel Dekker: New York, 1983; p 289.