Structure–Property Relationships in One-Component Polyurethane Adhesives for Wood: Sensitivity to Low Moisture Content

F. Beaud,[1,2] P. Niemz,[2] A. Pizzi[1]

[1]*ENSTIB-LERMAB, University of Nancy 1, Epinal, France*
[2]*ETH, Zürich, Switzerland*

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ABSTRACT: The causes of strength loss of wood joints and their consequent delamination from one-component polyurethane adhesives used for bonding structural wood when used at a low moisture content was investigated by testing wood joint strength and elongation at rupture at different wood moisture contents and by ^{13}C-NMR spectroscopy and scanning electron microscopy of the hardened bond line. The combination of the relative proportion of the still-reactive free —NCO groups on the polyurethane, of the wise choice of degree of polymerization of the resin, and of a slower rate of reaction were the three parameters found to be important in overcoming the problem of poor or no bonding of wood at low to very low moisture contents from one-component polyurethane adhesives. The results obtained indicated that one-component polyurethane adhesives that had a combination of a higher proportion of still-unreacted —NCO groups, a lower degree of polymerization, and a slower reaction rate were capable of overcoming the problem of the high sensitivity of polyurethane gluing at low to very low wood moisture contents. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4181–4192, 2006

Key words: polyurethanes; structure-property relations; adhesives; degradation; strength; failure

INTRODUCTION

One-component polyurethane resins are starting to be used industrially to a wide extent in the preparation of wood-laminated beams and wood finger joints for structural purposes. Their use is favored because of their ease of handling during application relative to the alternate resins that are their main competitors for use in the same types of products.

One-component polyurethanes have the advantage of being able to bond timber with a higher moisture content[1,2] but require careful formulation of the resin to minimize temperature-dependant creep of the joint.[1,3–6] Although minimizing if not eliminating such a problem altogether has already been proposed and attempted,[4] the controversy on temperature-dependent creep of these adhesives is still ongoing.

However, there is a second problem with these resins, of which fewer people are aware: the joints bonded to them appear to be sensitive to delamination and fail at low moisture content.[7–10] Thus, in heated rooms in winter, where the equilibrium moisture content of timber decreases to less than 8% and often to less than 6%, the joints tend to open and fail. All polyurethane adhesive manufacturers clearly state in their data sheets that such materials should not be used for bonding if timber moisture content is below 8%.

The problem, however, is not one of bonding at low humidity, where it is logical that moisture-driven crosslinking of the residual isocyanate groups of the polyurethane would be markedly inhibited by very low moisture content of the substrate. The phenomenon is more far-reaching. It extends to the already well-hardened bond line once the moisture content of the joint, mainly of the wood substrate, drops under a certain value. Thus, even well-bonded joints with polyurethane bond lines of good performance lose strength under the low-moisture conditions indicated during service of the joint.

The aims of the present study were to quantify this problem in commercial one-component polyurethanes for wood bonding and to try to correlate such a property or lack of it with the relevant structure of the polyurethane adhesives used.

EXPERIMENTAL

The 10 one-component polyurethane adhesives tested were produced by three manufacturers, seven from two major Swiss manufacturers (manufacturers A and C, Table I) and three from a major German/Swiss manufacturer (manufacturer B, Table I). All 10 adhe-

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Correspondence to: P. Niemz or A. Pizzi.

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TABLE I
Technical Characteristics of the 10 Polyurethane Adhesives Tested as Recommended by the Manufacturers

Manufacturer	Adhesive	Resin spread (g/m^2)	Open assembly time maximal (min)	Wood moisture content w (%)	Minimum pressing time (min)	Pressure (N/mm^2)
A	1	180	5.5 (at 20°C and 65% h)	Not indicated	17 (at 20°C and 65% h)	0.6
A	2	180–200	60 (at 20°C and 65% h)	Not indicated	150 (at 20°C and 65% h)	0.6–0.8
A	3	180–200	4 (at 20°C and 65% h)	Not indicated	10 (at 20°C and 65% h)	0.6–0.8
B	4	150–230	20 ± 5 (at 20°C)	9–15	60 (at 20°C)	0.29–0.39 softwoods 0.49–0.78 hardwoods
B	5	150–230	50–70 (at 20°C)	9–15	180–240 (at 20°C)	0.29–0.39 softwoods 0.49–0.78 hardwoods
B	6	150–230	35 ± 5 (at 20°C)	9–15	120 (at 20°C)	Not indicated
C	7	150–300	60 (at 23°C, 50% h w = 10–12%)	6–18	180–360 (at 23°C, 50% h, w = 10–12%)	0.1–0.8
C	8	150–300	10 (at 23°C, 50% h w = 10–12%)	6–18	45 (at 23°C, 50% h, w = 10–12%)	0.1–0.8
C	9	150–300	6 (at 23°C, 50% h w = 10–12%)	6–18	30 (at 23°C, 50% h, w = 10–12%)	0.1–0.8
C	10	150–300	3 (at 23°C, 50% h w = 10–12%)	6–18	15 (at 23°C, 50% h, w = 10–12%)	0.1–0.8

h = Relative humidity.

sives can be used for wood and for other applications, although none are certified for wood structural applications in the several European countries that have this certification. These adhesives are more advanced evoluted, alternate formulations developed to eliminate or minimize the few structure–property problems this type of adhesives still present for structural wood applications. Of the 10 adhesives tested, seven are freely available on the market, and the other three will be in commercial use shortly.

European Norm EN 302[11] specifies that for phenolic or aminoplastic adhesives, bonded samples should be prepared using beech. In this study, EN 302 was followed for all point save the substitution of spruce (*Picea abies* Karst.) for beech, as in practice spruce is the species used most often for polyurethane wood gluing. Thus, spruce specimens 150 × 150 × 10 mm in size, as specified in European Norm EN 302-2,[12] were bonded two by two. After adhesive curing and conditioning, the specimens were cut to make five bonded specimens with dimensions of 150 × 25 × 20 mm for each test as required by the norm. Clear, defect-free specimens of spruce were used, all from the same 107-year-old log. The specimen specifications were: dry density = 0.46 ± 0.031 g/cm^3; number of annual growth rings per centimeter = 4.55 ± 1.59; average growth ring width = 2.45 ± .85 mm; average growth ring angle = 16.5° ± 8.5°. The concentration of adhesive used was 180 g/m^2 for all the adhesives. The open assembly time was strictly limited to the short time used to apply the adhesive to the substrate. Such a short open assembly time and the relatively dry atmosphere in the laboratory minimized the influence of air moisture content on adhesive hardening. For each adhesive the closed pressure time of the joints corresponded to the minimum value of the range recommended by its manufacturer (Table I).

The percentage of moisture content of the specimens used in the first series of experiments was measured after conditioning by the desiccation method according to European Norm EN 13 183-1.[13] The bonded specimens were conditioned at 20°C and 50% air relative humidity until their weight remained constant. They were then cut and tested for shear strength in tension according to European Norm EN 302-1.[14] The conditioning parameters used, drier than what is specified in the norm (20°C and 65% air relative humidity), were chosen to minimize the danger of delamination from the stress being too great as a result of the dried wood swelling to the different moisture contents used for bonding. The specimens were tested in tension on a computer-controlled Zwick 100 kN universal testing machine. The testing rate was 1.5 mm/min. The extent of the induced deformation was measured by video camera, and the stress–strain graph was calculated by an image analysis program.

The bond line of a few of the tested specimens was observed with a scanning electron microscope (FEI Quanta 600) after cathodic metallization with gold-palladium for 3 min at 160 v under 0.1 mbar of argon with an oven treatment at 60°C.

TABLE II
Average Shear Strength and Standard Error as a Function of Wood Moisture Content Percentage for Adhesives Tested

Adhesive*	1		2		3		4		5	
Moisture	τ_r (N/mm^2)	S (N/mm^2)	τ_r (N/mm^2)	S (N/mm^2)	τ_r (N/mm^2)	S (N/mm^2)	τ_r (N/mm^2)	S (N/mm^2)	τ_r (N/mm^2)	S (N/mm^2)
w = 2%	—	—	—	—	2.01	2.11	3.31	3.13	7.42	4.27
w = 4%	7.12	3.99	8.02	1.99	5.53	3.5	9.2	2.61	10.5	2.68
w = 6%	9.93	2.46	7.96	1.17	6.77	3.47	12.25	2.29	11.14	2.04
w = 8%	9.95	1.49	9.64	1.95	—	—	—	—	—	—

The liquid ^{13}C-NMR spectra of 6 of the 10 commercial polyurethane (PUR) resins used were obtained on a Brüker DSX 400 FT-NMR spectrometer. Chemical shifts were calculated relative to tetramethylsilane (TMS) at ambient temperature for NMR shift control. However, the spectra were done at 60°C because of the high viscosity of the PUR specimens. Thus, the shifts obtained at 60°C were slightly different from those that would be expected at ambient temperature. The spectra were done at 62.90 MHz for approximately 1000 transients. All the spectra were run with a relaxation delay of 5 s, and chemical shifts were accurate to 1 ppm.

RESULTS AND DISCUSSION

The characteristics and conditions of application advised by the manufacturers for the different single-component polyurethanes used are shown in Table I. As can be seen, their characteristics are quite different from each other.

The results of wood joints bonded with different one-component polyurethanes, some commercial and some experimental, all from different industrial manufacturers, when bonding wood at different percentages of moisture content, namely, 0%, 2%, 3.3%–4%, 5.4%–6%, and 8%–8.6%, are shown in Table II and Figure 1. Some of the adhesives tested performed well, that is, had more than 60% wood failure on testing. With a percentage of moisture content of 8.6%, thus higher than the 8% minimum recommended by the adhesive manufacturers, the performance of all the adhesives tested was excellent, that is, there was 100% wood failure on testing. Thus, the hardened adhesive was definitely stronger than the substrate. The situation was different for substrates with a smaller moisture content. The variability in the percentage of wood failure in general increased as moisture content of the wood decreased to bond. This can be seen from both the interval of percentage of wood failure values, shown in Figure 2 as well as from the standard deviation values for the shear strength of the joints, shown in Table II. However, even at a percentage of moisture content as low as 3.3%–4%, bonding occurred for all the adhesives tested (Table II), and the average shear strength values were quite good for all the adhesives tested except adhesive 9 and perhaps adhesive 10 (Table II and Fig. 1).

The results were quite different, however, at 0% moisture content (Fig. 2) for the percentage of wood failure and at 2% moisture content (Table II) for the joint shear strength. In both cases only adhesive 5 showed a good shear strength of the joint, although with great variability (Table II) and a good percentage wood failure (Fig. 2); remarkably, the latter did not vary at all.

These results illustrate well the problem of resistance to low air humidity of single-component polyurethane bond lines. They illustrate equally well, however, that single-component polyurethanes capable of tolerating very low substrate moisture contents already exist and can be produced, for example, resin 5 in Table II.

Adhesives 1, 2, 3, 6, 8, and 9, which performed more poorly at a low moisture content (Table II), were also tested on wood substrate at 3% and 5% moisture contents to which water was added by spraying it on the surfaces of the substrate before the adhesive was applied. As would be expected, the performance of most adhesives improved considerably relative to the results presented in Table II. These results are not reported here as they were logically expected. This experiment was only carried out to show that the poor performance of most adhesives at very low moisture content, shown in Table II, resulted from a relative lack of water, which limited the reaction and crosslinking of isocyanate groups in sufficient number. Diffusion problems and consequent early immobilization of the hardened network while forming because of the marked dryness of the substrate also appeared to contribute to the decrease performance.

Figure 1 shows the shear strength results of the wood joints bonded with the 10 polyurethane adhesives as a function of the percentage of moisture content of the wood. Five trends can be observed:

1. The strength performance of adhesives 4 and 10 depended markedly on the percentage of moisture content of the wood. Average shear strength

TABLE II *Continued*

6		7		8		9		10	
τ_r (N/mm^2)	S (N/mm^2)	τ_r (N/mm^2)	S (N/mm^2)	τ_r (N/mm^2)	S (N/mm^2)	τ_r (N/mm^2)	S (N/mm^2)	τ_r (N/mm^2)	S (N/mm^2)
—	—	5.53	4.87	—	—	—	—	2.03	3.15
10.33	1.44	9.18	1.46	9.66	2.05	1.39	2.77	5.65	1.92
10.68	1.92	10.46	1.94	10.41	1.11	9.46	2.54	9.36	1.63
10.5	1.02	—	—	9.61	1.11	9.61	1.17	—	—

decreased very markedly and almost linearly with decreases in moisture content.

2. The strength performance of adhesives 3 and 9 also depended markedly on the percentage of moisture content of the wood, but this dependence was different from that for adhesives 4 and 10 as it was far from linear.
3. The strength performance of adhesives 5 and 7 also depended markedly and nonlinearly on the percent moisture content of the wood, as with adhesives 3 and 9, but they had far higher average shear strength with a low percentage of wood moisture content. Both these two adhesives are slow-reacting types, requiring that a joint have a relatively longer clamping time.
4. The strength performance of adhesives 1 and 2 did not depend much on the percentage of moisture content of the wood.
5. The strength performance of adhesives 6 and 8 in practice did not appear to depend on the percentage of moisture content of the wood at all.

Notwithstanding that the behaviors of the adhesives were so different, it was interesting to analyze the results obtained for all the adhesives together. This allowed a description of the generalized trend in behavior of single-component polyurethane adhesives when used for bonding wood that has a very low moisture content. In Figure 3 such a treatment of the data shows that, in general, the shear strength of the joints bonded with one-component polyurethane adhesives decreased the lower the moisture content of the wood. In contrast, the shear strength remained constant at moisture contents of 6%, 8%, and higher. This behavior is logical given that it is mainly the reaction of the residual isocyanate groups with water that leads to crosslinking and formation of the hardened adhesive network. Second, the results in Figure 3 show that both the variability and the spread of the results increased as the percentage of moisture content of the wood decreased.

Third, determination of the dimensions of wood spans in wood structures uses the characteristic values of a material rather than its average. The level of safety required in calculating building structures is based on values obtained by calculation of the 5th percentile, $p = 5\%$. This means the weakest link taken into account is estimated by taking the weakest strength value of 95% of the samples tested. European Norm prEN

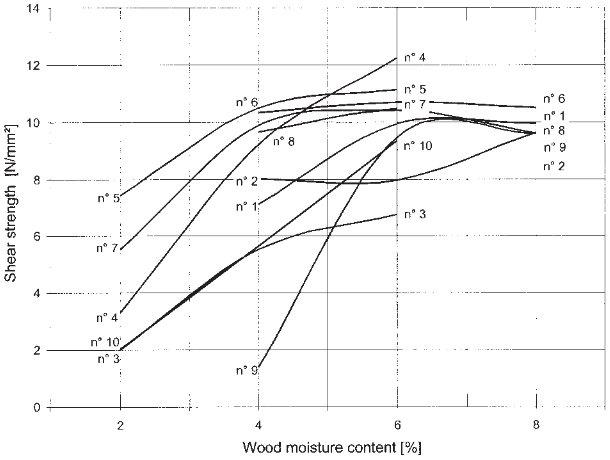


Figure 1 Average shear strength of wood joints bonded with each of the 10 one-component polyurethane adhesives tested as a function of the percentage of moisture content of the wood.

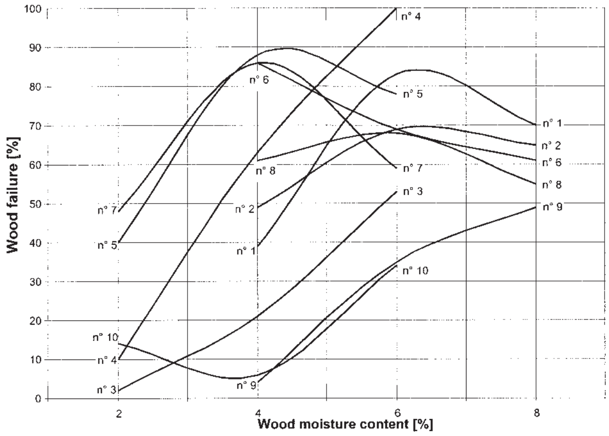


Figure 2 Average percentage of failure of wood joints bonded with each of the 10 one-component polyurethane adhesives tested as a function of the percentage of moisture content of the wood.

14358[15] describes the procedure for this calculation; it requires[8] a minimum value of 6 N/mm^2. Figure 3 shows that the 5th percentile curve is slightly lower than 8 N/mm^2 at an 8% wood moisture content, decreasing to 5 N/mm^2 at a 6% wood moisture content. Thus, the recommendations of the adhesive manufacturers that single-component polyurethanes be used at not less than 7%–8% wood moisture content are fully justified by the 5th percentile curve shown in Figure 3. This also explain why one-component polyurethanes generally present performance problems at low wood moisture contents.

The measure of the percentage of wood failure according to European Norm EN 302-2[12] is aimed at defining the durability of a hardened adhesive during accelerated aging. In this study the adhesives were tested to the limits of their capacity, and wood failure can be almost said to have been intentionally provoked for study purposes. Figure 2 shows that the lower the percentage wood moisture content, the lower the percentage wood failure. Again, variability increased the lower the percentage wood moisture content was. However, this rather general outlook does not take into account the differences between the adhesives. Thus, adhesives 3, 4, 6, and 9 showed a linear dependence on wood failure as a function of substrate moisture content. Moreover, adhesive 6 showed a decrease in wood failure as the moisture content increased. Of particular interest is adhesive 4, which showed a marked and practically linear increase in wood failure with increasing wood moisture content. Adhesives 1, 2, 5, 7, 8, and 10 instead showed nonlinear wood failure variations, generally presenting a maximum at intermediate moisture content values. These rather variable wood failure results are an indication that wood failure results do not depend only on the quality of the adhesive, with the variability induced by the wood itself playing perhaps a determining role. Observation of the tested samples showed that breaking of 24% of the samples was 0% in the wood. Breaking of 28% of the samples was 100% in the wood. The remaining samples were in between these two values.

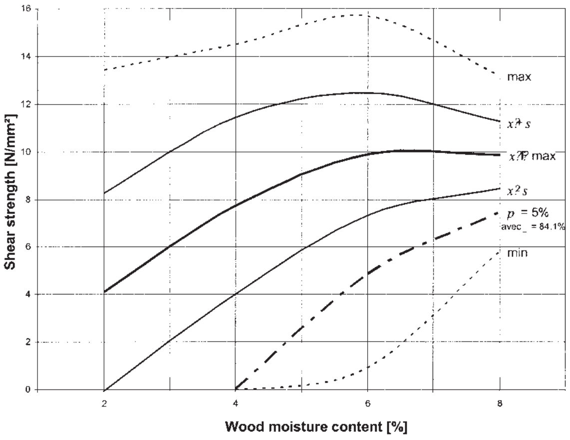


Figure 3 Average shear strength of wood joints bonded with all 10 one-component polyurethane adhesives tested, as a function of the percentage of moisture content of wood. This was compared to the 5th percentile p curve with alpha = 84.1% calculated according to European Norm prEN 14 358 for the values characteristic of structural wood. The standard error curves, $x \pm s$, are also shown.

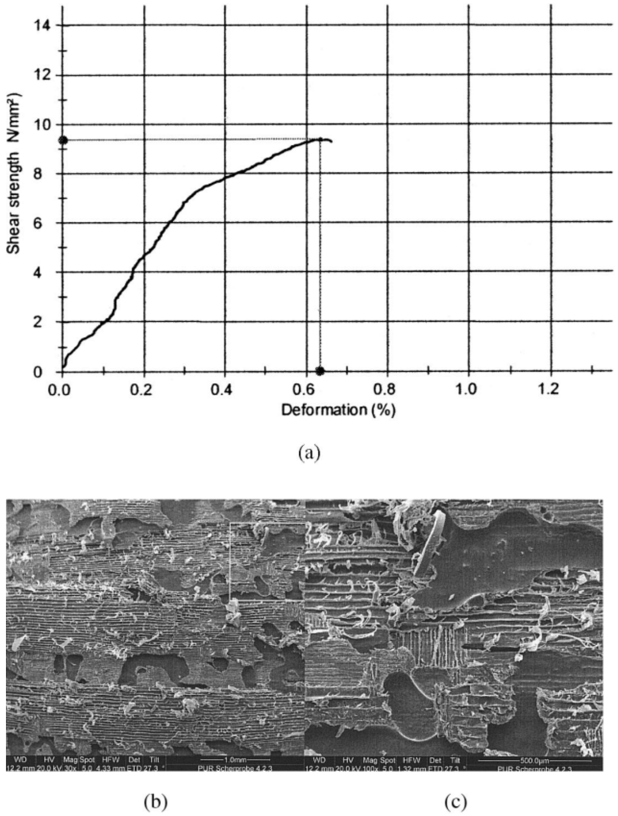
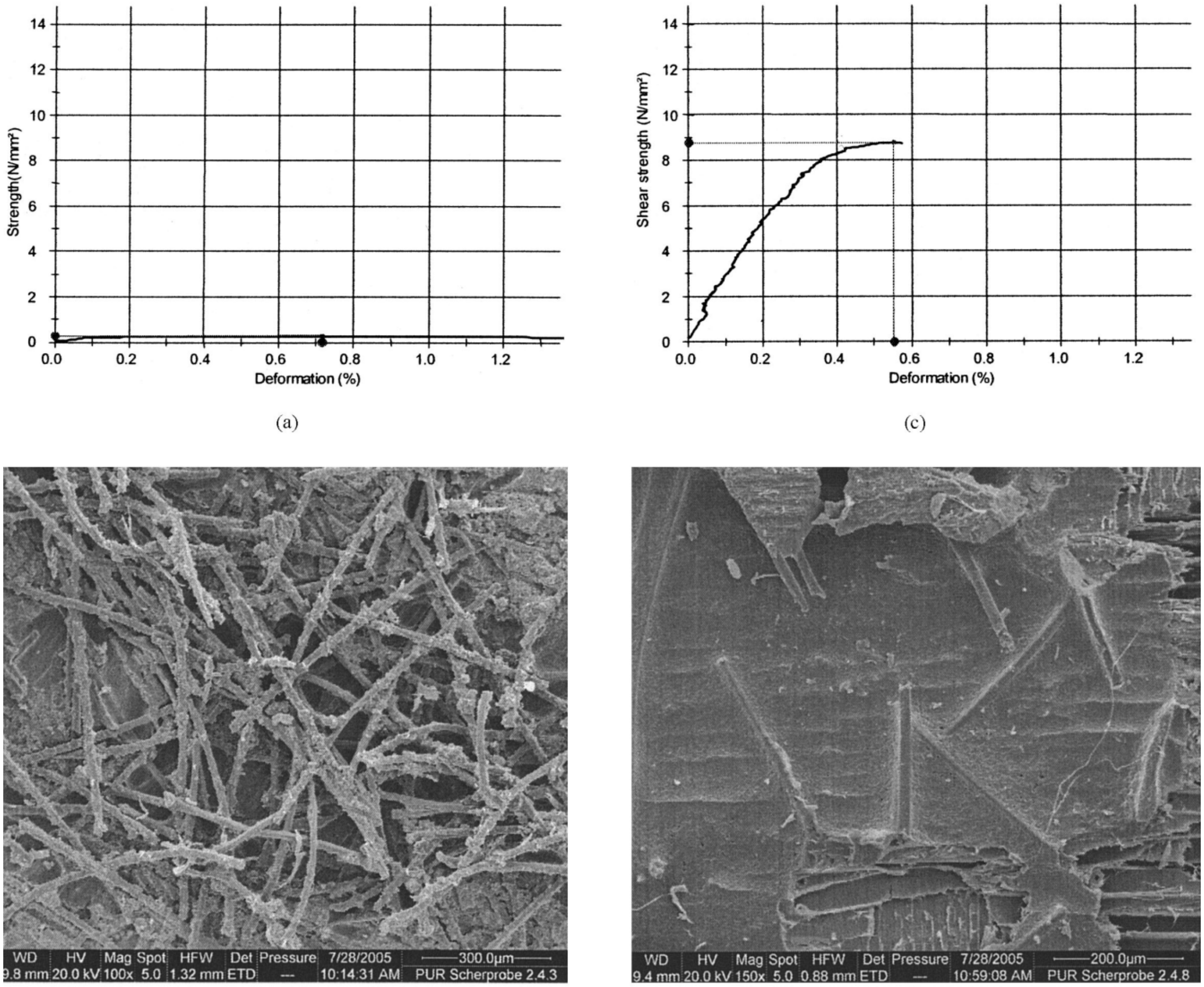


Figure 4 Joint bonded with medium reaction rate adhesive, adhesive 2: (a) curve of shear strength as a function of the percentage of joint deformation at 4% wood moisture content; (b) SEM image of the joint after testing showing that delamination occurred in the first layer of wood cells at the interface with the hardened adhesive [area enclosed in white square is magnified in (c), with the arrows indicating a ribbon of adhesive showing the print of wood structural features such as punctuations between tracheids and wood rays].

A few of the samples tested were used as examples of one or another particularity of their broken interface. Figure 4(a–c) shows the broken interface of a sample bonded with adhesive 2 at a 4% wood moisture content. Breaking occurred in the first layer of wood cells and at its interface with the adhesive. Few wood fibers had been stripped from the wood, and they remained attached to the adhesive layer, but failure was mostly a result of the peeling of the adhesive layer from the substrate. The curve of shear strength in tension as a function of deformation, in Figure 4(a), also shows some creep of the material.

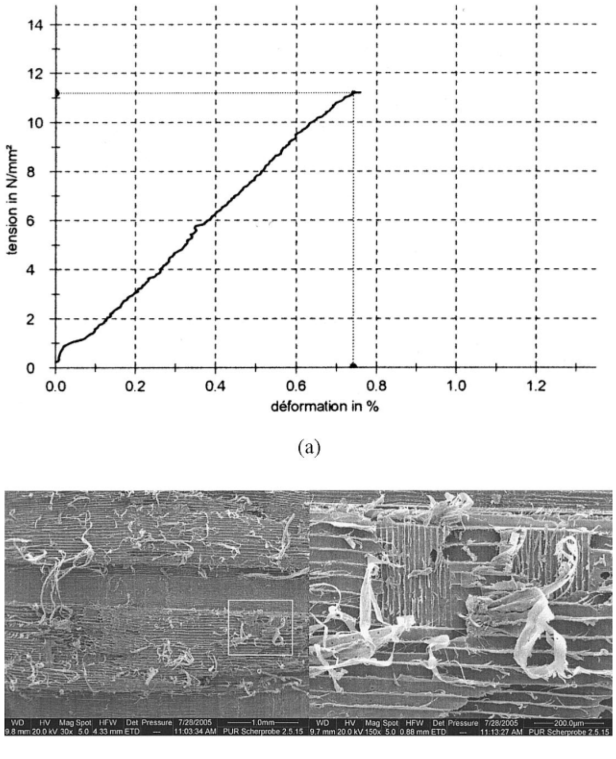


(a) (c)

(b) (d)

Figure 5 Joint bonded with adhesive 4: (a) curve of shear strength as a function of the percentage of joint deformation at 2% wood moisture content for a badly mixed adhesive; (b) SEM image of the joint in (a) after testing showing reinforcing fibers added to the adhesive by the manufacturer, which in this joint appeared starved of the bonding matrix of the adhesive; (c) curve of shear strength as a function of the percentage of joint deformation at 2% wood moisture content for a well-mixed adhesive; (d) SEM image of the joint in (c) after testing showing reinforcing fibers added to the adhesive by the manufacturer, where the fibers were drowned in a matrix of polyurethane, forming a reinforced composite.

Of particular interest is adhesive 4 at a 2% wood moisture content, shown in Figure 5(a–e). Two distinct behaviors are observed, sometimes even in the same samples. In Figure 5(a) adhesive 4 shows very low strength for a considerable deformation at break. The optical microscope image in Figure 5(b) shows that the break surface is loaded with reinforcement fibers within the adhesive layer. At greater magnification via a scanning electron microscope [Fig. 5(b)], the presence of a considerable proportion of reinforcement fibers can be confirmed, with only traces of adhesive clinging to the surface of the fibers. This explain the poor strength of the adhesive shown in Figure 5(a). Conversely, in Figure 5(c) the diagram of strength as a function of deformation for the same adhesive 4 under the same conditions of application shows good strength at break for a smaller deformation. The explanation for this can be observed in Figure 5(d), which shows the reinforced fibers well integrated in a strong polyurethane resin matrix. Breaking occurred in the glue line at the interface with the first layer of wood cells. Adhesive 4 was the only adhesive that was heavily reinforced with fibers, and this may explain the near linearity of its behavior for both shear strength and percentage wood failure as a function of percentage wood moisture content observed in Figures 1 and 3. It was also impossible to obtain a ^{13}C-NMR spectrum of this adhesive because its viscosity



(a)

(b) (c)

Figure 6 Joint bonded with the best-performing adhesive at a low wood moisture content. Slow reaction rate adhesive, adhesive 5: (a) curve of shear strength as a function of the percentage of joint deformation at 2% wood moisture content; (b) SEM image of the joint after testing in which the high number of wood fibers lost shows that delamination occurred in the wood layers [area enclosed in white square is magnified in (c)]; (c) detail clearly showing that rupture at maximum load occurred in the wood.

was so high, from the presence of fibrous filler, that it was not possible to pour it into the NMR sampling tube: even an increase in temperature up to 60°C did not alter its viscosity enough to place it in the NMR tube.

Figure 6(a–c) shows the joint and behavior of adhesive 5 at a 2% wood moisture content. The shear strength at break was excellent at 11.2 N/mm^2 for a deformation of 0.74%. Breaking occurred exclusively in the wood without any adhesive/substrate peeling [Fig. 5(b,c)].

Adhesive 7 was particularly interesting regarding peeling. At a 6% wood moisture content, there was good maximum strength but with a very marked deformation (more than 1%). This behavior is characteristic of adhesives particularly prone to creep. Furthermore, the curve of shear strength as a function of deformation showed two slopes defining two phases of behavior. A first, more rigid phase, up to 4 N/mm^2, probably resulted from just the wood; in the second phase the material was much less rigid, up to the breaking point. Notwithstanding the good shear strength, there was never breakage in the wood. Breaking occurred in the adhesive layer at the two interfaces with the first layer of wood cells, hence, by adhesive peeling. This shows clearly how much the adhesive layer had molded the wood cells. The print on the adhesive layer of the anatomical features of the wood cells was very evident. On testing the wood had been separated very neatly from the adhesive layer without even leaving any wood fibers on its surface. It appeared that the adhesive had not wetted the wood surface; hence, the long phase of plastic deformation is likely to correspond to the progressive demolding of the adhesive from the wood cells. The indications are that the surface tension of the adhesive was too high and perhaps the average molecular weight of the polyurethane was too high, the consequences of which were poor wetting and poor transfer onto the wood surface.

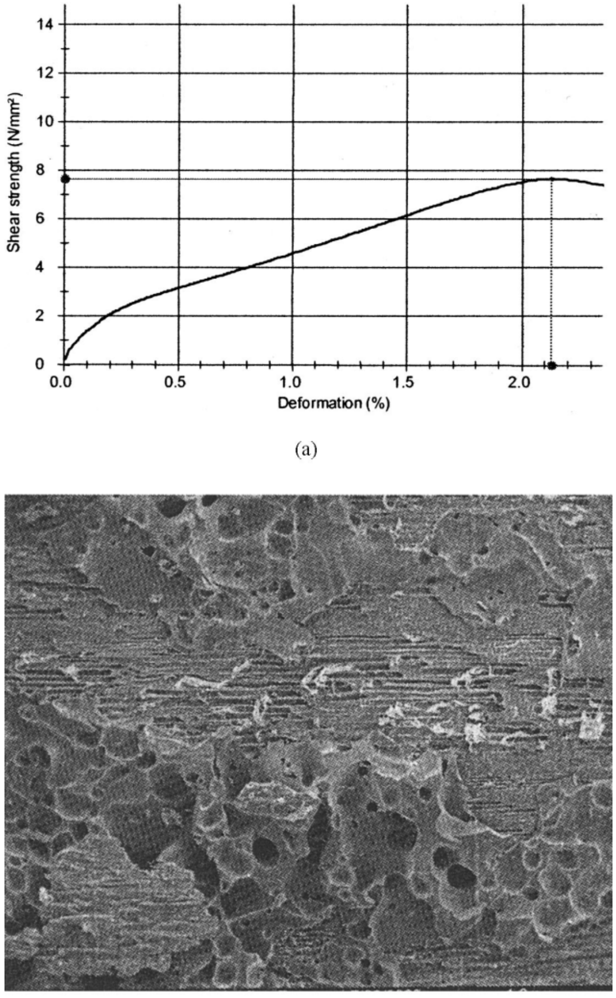
The last interesting adhesive was adhesive 10 at a 6% wood moisture content. The most noticeable characteristic in Figure 7(a) is the very high deformation, 2.1%, at breaking, notwithstanding the good shear strength obtained. This is clear evidence of creep of the bond line. The reason for this behavior is shown in Figure 7(b): a considerable number of bubbles characterizes this hardened bond line, indicating that the reaction of this adhesive is relatively fast (see Table Ia). This suggests there was considerable and relatively too fast formation of CO_2 because of the reaction of the isocyanate groups with amines, creating CO_2 bubbles during hardening. This renders the bond line markedly ductile.

Figures 8–13 show the ^{13}C-NMR spectra of the single-component polyurethane adhesives 2, 5–8, and 10.

How to interpret the different groups in the spectra shown in Figures 8 and 9 is provided on the spectra themselves. Before describing in detail the different peak assignments, it is interesting to discuss the differences and similarities between the different spectra. The peaks of the spectra of adhesives 5 and 7 (Figs. 9 and 11) and 8 (Fig. 12) are sharp, an indication that the polymerization of these two resins was relatively low. This indicates that in principle these two resins should be slower setting. This was confirmed by the manufacturers' data shown in Table I, with resins 5 and 7 effectively being the slowest setting of all the adhesives tested (180–240 and 180–360 min, respectively). It is well known that the slower the setting of the resin, if sufficient time for curing is left, the stronger is the hardened network formed.[16–18] This is because of the minimization of the early immobilization of the network, leading to the increased crosslinking obtained. This explains why these two resins performed better, as observed in Figures 1 and 2 and Table II. This explanation does not apply to resin 8, a fast-setting resin (Table I), although it also has relatively high viscosity.

Adhesives 2 (Fig. 8) and 6 (Fig. 10) instead showed much broader NMR peaks, indicating resins more polymerized than resins 5 and 7. Hence, these resins should be faster but not excessively faster setting than resins 5 and 7. This appears to be the case according to the manufacturers' data, shown in Table I, which states that the curing time required is 150 min for resin 2 and 120 min for resin 6.

Resin 10 (Fig. 13) was the fastest setting of all the resins tested, requiring only 15 min pressing for curing (Table I). It was also very thick, so much so that acetone had to be used as a solvent to be able to introduce it into the NMR quartz tube. Its greater thickness and its lack of thickening agents indicated greater polymerization. Again, the NMR spectrum peaks were broad, indicating a higher average degree of polymerization, and the strength performance was relatively lower, indicating less crosslinking. Also shown in Figure 7 is the high level of creep of the bond line, as shown by the high deformation at rupture. Because the rate of setting of this resin was so fast, the lower performance and higher level of creep were the result of consequent early immobilization of the network and lower crosslinking. The same very rapid reaction caused the localized excessive production of CO_2 bubbles in the glue line, which further contributed to greater creep.



(a)

(b)

Figure 7 Joint bonded with fast reaction rate adhesive, adhesive 10: (a) curve of shear strength as a function of the percentage of joint deformation at 6% wood moisture content; (b) SEM image of the joint after testing showing that delamination had occurred both in adhesive itself and at the interface with the first layers of wood. Note the evident bubbles presumably from localized gas emission as a result of too high a reaction rate.

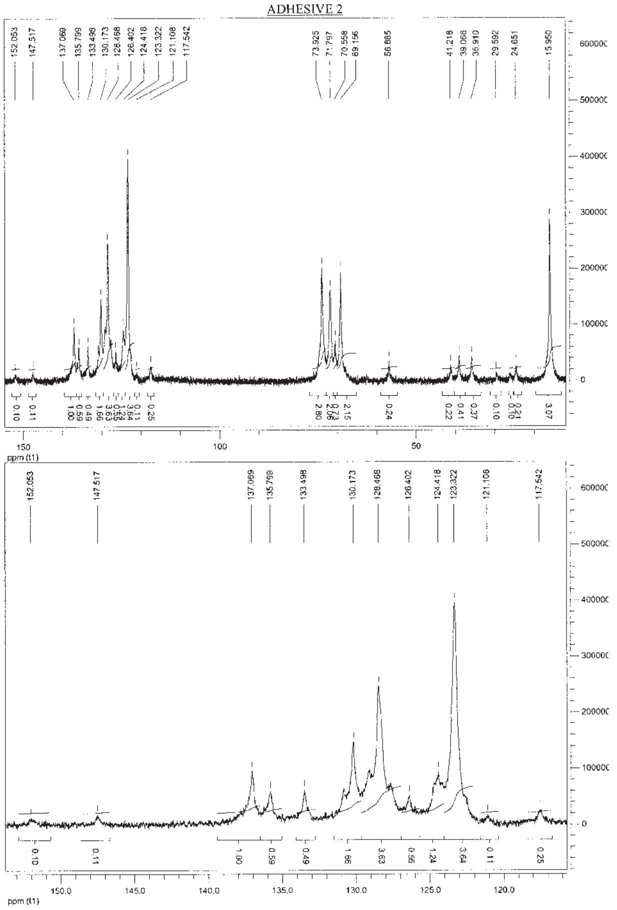


Figure 8 (a) ^{13}C-NMR spectrum of adhesive 2 in liquid form; (b) detail of the 115–155 ppm region of the spectrum.

It appears then that the same parameter, rate of curing related to the level of polymerization of the resins, is one of the main parameters influencing the strength performance of these resins. The slower the cure rate and the lower the average degree of polymerization of a resin, as exemplified by the relative narrowness of the NMR peaks, the better was its strength performance. This trend was valid for resins 2, 5, 6, 7, and 10. This is an important trend given that these resins were produced by three manufacturers. Unlike these resins, resin 8 appeared to only partly show this trend. It had the same trend in narrowness

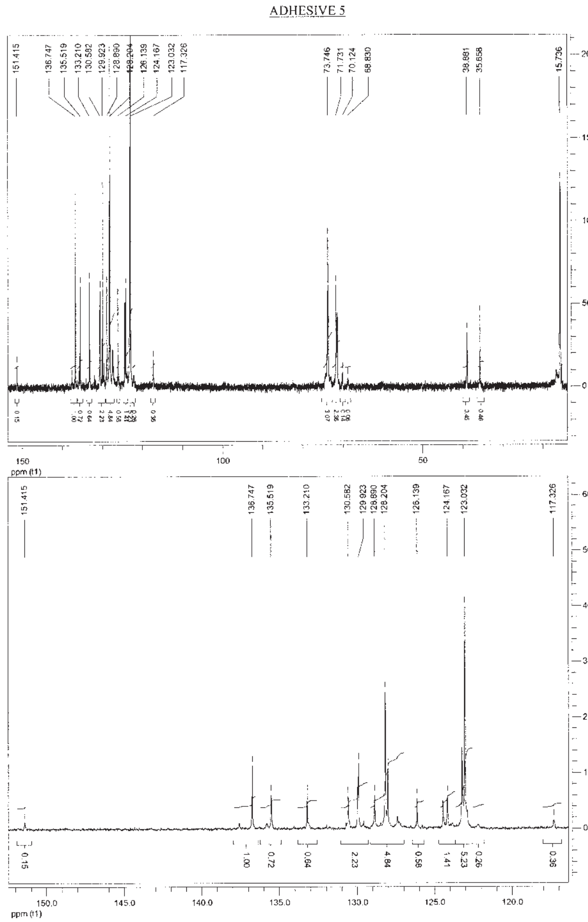


Figure 9 (a) ^{13}C-NMR spectrum of adhesive 5 in liquid form; (b) detail of the 115–155 ppm region of the spectrum.

of the NMR peaks corresponding to good strength performance (Fig. 13), but its much faster rate of curing distinguished it from resins 5 and 7. Its performance, then, was the result of the influence of some other parameter.

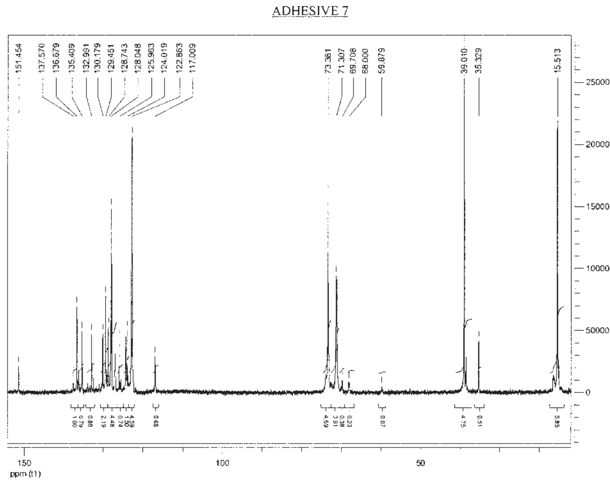


Figure 11 ^{13}C-NMR spectrum of adhesive 7 in liquid form.

Another interesting general observation about Figures 8–13, the spectra being quantitative, is the relative proportion of free, reactive —NCO groups still present in these resins, which were 27%, 30.0%, 25.3%, 27%, 24.3%, and 23.4% for resins 2, 5, 6, 7, 8, and 10, respectively. Resin 5, the best performing of the resins, had the highest percentage of still active isocyanate groups (30%). Furthermore, resin 5 having more residual —NCO groups than resin 7 was in agreement with the lower deformation at break (Figs. 9 and 11); hence, resin 5 showed lower creep than resin 7. The same trend was evident between resins 2 and 6: resin 2 had a higher percentage of —NCO groups than resin 6 and, as consequence, a lower level of creep. The same trend was related to resin 10, which had the lowest percentage of —NCO groups. However, other parameters evidently influenced this trend, as resins 2 and 7 had the same percentage of residual —NCO groups, but resin 7 had higher creep than resin 2. This difference can be explained by the level of polymer-

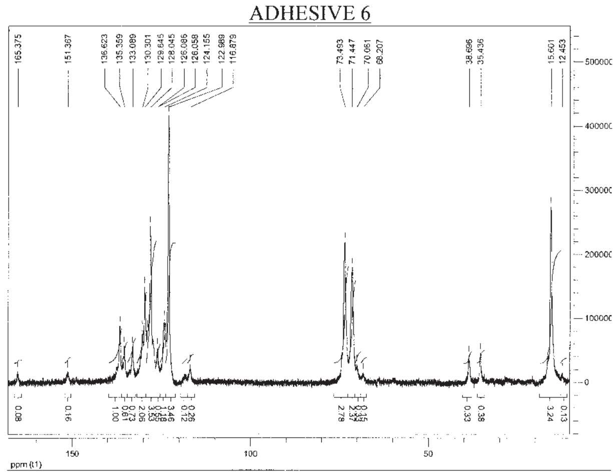


Figure 10 ^{13}C-NMR spectrum of adhesive 6 in liquid form.

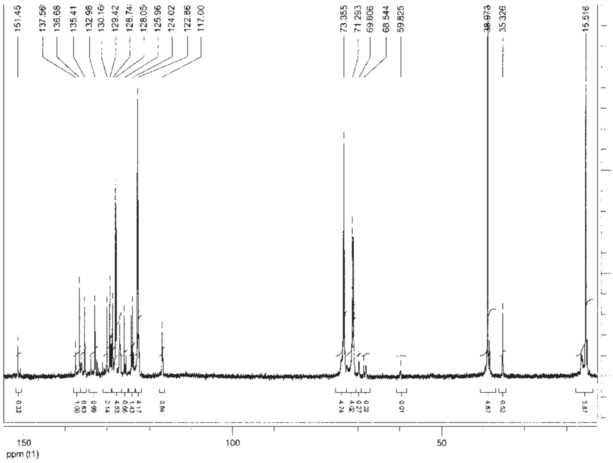


Figure 12 ^{13}C-NMR spectrum of adhesive 8 in liquid form.

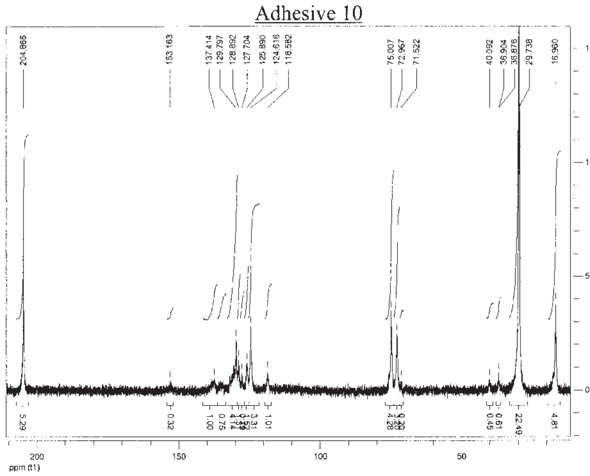
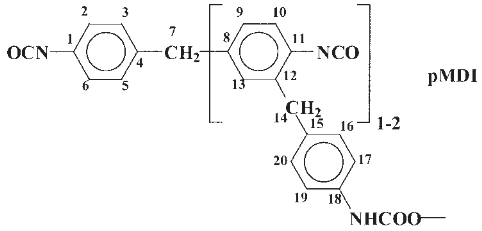


Figure 13 ^{13}C-NMR spectrum of adhesive 10 in liquid form.

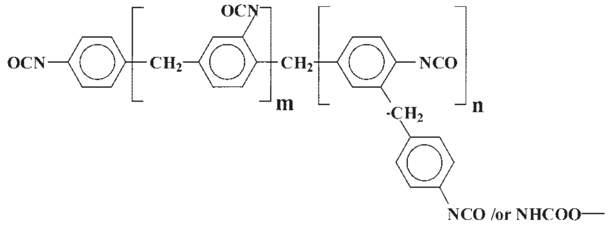
ization of resin 2 in relation to that in resin 7. Thus, it is the combination of residual —NCO groups with degree of polymerization (DP) and rate of curing that produces the final behavior of single-component polyurethanes. Higher —NCO content coupled with lower DP and a relatively slower rate of curing appear to give the best results.

The last general observation is that the chemical composition of the polyurethane resin on which resins 7 and 5 are based was the same. They were not prepared by the same manufacturer. The same was true for resins 2, 5, and 6, which had the same basic polymer, bar a different degree of polymerization, despite these resins being prepared by different manufacturers. This means that the preparation of one-component polyurethanes for wood bonding is converging toward similar resins as different manufacturers try to reformulate and refine their base resin to optimize performance.

A few more considerations can be made about the structural formula (Scheme 1) that identifies the shifts of the NMR signals shown in Table III.



Adhesive 2 contained more linear 1,3-propylene glycol than all the other polyurethanes, which had only traces of 1,3-propylene glycol. The five other polyurethanes examined by NMR all had 1,2-propylene glycol in approximately the same proportion, with much less, in some cases just traces, of 1,3-propylene glycol. Adhesive 2, as did all the other adhesives, showed a much higher proportion of isocyanate groups of the MDI type than of the TDI type. It was not possible to determine the proportion of TDI from the spectra because most of its characteristic peaks have similar shifts and overlap other signals. Some adhesives may actually have no TDI groups or TDI at all. This view is supported, for example, by the absence of the —CH_3 signal of TDI at 17.6 ppm. Of interest is that in these polyurethane adhesives there appeared to be more C10-type carbons and many fewer C9-type carbons. Looking at the key formula above, the only possible explanation for this is that the repeating units of the pMDI were different, with *m* and *n* structures present in the polyurethane skeleton.



Adhesive 5 showed a slightly higher proportion of pMDI than did adhesives 7 and 8, and TDI was either present in a very small proportion or completely absent. Other than that, the differences were minor. As these resins were produced by different manufacturers, it appears that research led them to establish for this type of product and this type of application some strictly valid equilibriums between technical performance and costs—hence, the similarity of the formulations.

The polyols used showed four different alcohol or ester bonds in the 68–74 ppm region. In general, there was a polyalcohol polyol similar to a sugar or to a sorbitol of the —$OH_2C(\underline{C}HOH)_4CH_2O$— type, the peaks of which were 73–74 ppm, and 1,2- and 1,3-propylene glycols. In all the adhesives except adhesive 2, 1,2-glycol was the second most important, and only trace amounts of 1,3-glycol were present. In adhesive 2, unlike in all the other polyurethanes, the mix of the two propylene glycols made up a larger proportion than the —$OH_2C(\underline{C}HOH)_4CH_2O$—. Small amounts of 1,4-butanol, generally present in this type of resin and shown by the first —CH_2— of the alcohol reacted (64.2 ppm) and unreacted (62.2 ppm), were not present here.

The methylene bridges C7 and C14 between the aromatic rings of pMDI were generally at 38–39 ppm for the *para–para* —CH_2— bridge between the aromatic rings of PMDI (Table IV) and at 35—36 ppm for the *ortho–para* —CH_2— bridge between the aromatic rings of PMDI. These appeared in all the adhesives. Adhesive 2 (Fig. 8), however, again was different from the rest, as it showed a very rare peak, at 41–42 ppm,

TABLE III
^{13}C-NMR General Shifts for the Six One-Component Polyurethane Adhesives Tested

pMDI reacted and unreacted	ppm
C1, C8, C15 when linked to —NCO (without other ring substitutions)	131.7–131.9
C2, C6	124.0–124.4
C3, C5	129.4–130.1
C4, C8	136.5–137.6
C9	125.9–126.4
C10	122.8–123.3
C11(according to ring substitution pattern)	143.7–147.5
C12	132.9–133.5
C13, C16, C20	128.0–128.7
C17, C19 (*ortho* free sites)	116.9–117.5
C18, C15, C1 when linked to –NHCOO—	135.3–135.8
C15, C4 unlinked (*para* free sites)	118.2
C7, C14 (Ar—CH_2—Ar)	
ortho–ortho	41.2
para–para	38.6–39.1
ortho–para	35.3–35.9
C=O of—NHCOO—	151.3–152.1
TDI	
Ar-$\underline{C}H_3$	17.6
(Ar$\underline{C}$) (*ortho*—CH_3; *meta* to 2x—NCO/—NHCOO—)	130.1–130.7
(Ar$\underline{C}$—NCO) (*ortho*—CH_3; *meta* to 1x—NCO/—NHCOO—)	133.9
(Ar$\underline{C}$—NCO) (*para*—CH_3; *meta* to 1x—NCO/—NHCOO—)	136.7–138.6
—N=C=O (pMDI)	122.8–123.3
—N=C=O (pMDI and TDI)	128.0–128.8
Polyols	
—$OH_2C(\underline{C}HOH)_4CH_2O$—major	73.4–73.8
$HO\underline{C}H_2CH_2CH_2\underline{C}H_2OH$	(62.2)
$HOCH_2\underline{C}H_2\underline{C}H_2CH_2OH$	29.1
—$O\underline{C}H_2CH_2CH_2\underline{C}H_2O$—	(64.2)
—$OCH_2\underline{C}H_2\underline{C}H_2CH_2O$—	(32.0)
HO—$\underline{C}H_2CH(CH_3)$—OH and —O—$\underline{C}H_2CH(CH_3)$—O—[a]	71.3–71.8
HO—$CH_2\underline{C}H(CH_3)$—OH[a]	72.7
HO—$\underline{C}H_2CH_2CH_2OH$ and —O—$\underline{C}H_2CH_2\underline{C}H_2$—O—[b]	68.0–69.2
HO—$CH_2\underline{C}H_2CH_2OH$ and —O—$CH_2\underline{C}H_2CH_2$—O—[b]	69.7–70.5
HO—$CH_2CH(\underline{C}H_3)$—OH and —O—$CH_2CH(\underline{C}H_3)$—O—[a]	18.6
–NHCOO—$CH_2\underline{C}H_2$—	15.5–16.0

[a] 1,2-Propylene glycol linked and unlinked.
[b] 1,3-Propylene glycol linked and unlinked.

for *ortho–ortho* —CH_2— bridges between the aromatic rings.[19]

Finally, the peak around 15–16 ppm was the CH_2 carbon of the —NHCOO—$CH_2\underline{C}H_2$— group. The lack of —CH_3 signals at about 18–19 ppm indicates that TDI was apparently not present in the experimental formulations.

CONCLUSIONS

In conclusion, it appears that the combination of the relative proportion of still-reactive free —NCO groups, the wise choice of degree of polymerization, and of a slower rate of reaction were the three important parameters for overcoming the problems of one-component polyurethane bonding wood with a low to very low moisture content. The results obtained show that the combination of a higher proportion of —NCO groups, a lower DP, and a slower reaction rate is capable of overcoming the problem of high sensitivity of polyurethane gluing at low to very low wood moisture content. This does not mean that other equally good combinations of these parameters could not be found that would produce a similar result. It must be pointed out that none of the adhesives tested, although available commercially and now recommended for use in wood bonding by the manufacturers also, is one of the five adhesives at present certified for wood structural application in the several European countries that have this certification.

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