

Thermal Stability of Structural One-Component Polyurethane Adhesives for Wood—Structure-Property Relationship

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ABSTRACT: The relationship between the chemical structure of commercial polyurethanes and temperature-dependent creep properties was determined in full scale tests and the results were compared with thermomechanical analysis. Comparison of mechanical performance with ¹³C-NMR spectroscopy studies elucidated important structure-property relationships, which either allow the reduction or elimination of temperature-dependent creep in one-component polyurethanes (1C-PUR) adhesives for wood. The combination of the relative content of still reactive, free —NCO groups on the polyurethane, careful selection of the degree of resin polymerization and a slower rate of reaction are the three most significant parameters that have to be controlled

to overcome the problem of temperature-dependent creep found in 1C-PUR adhesives. The results obtained indicate that adhesives presenting a combination of a higher content of still unreacted —NCO groups, a lower degree of polymerization and slower reaction rate are capable to counteract problems of high sensitivity of polyurethane to temperature-dependent creep. Two commercial polyurethanes that fulfil the latter requirements and exhibit almost no creep were identified and characterized. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5698–5707, 2006

Key words: creep; NMR; polyurethane; structure property relationship; wood adhesive

INTRODUCTION

The importance of adhesives and adhesive bonding in the forest products industry is increasingly growing.^{1,2} Apart from the established polycondensation adhesives (UF-, MUF-, PF-, and R(P)F-resins), polyurethanes (PUR) are gaining popularity for surface gluing and special bonding applications in load bearing timber structures. The most promising ones are one-component types (1C-PUR), which are simple to handle and have become popular as formaldehyde-free, transparent, fast, and cold systems, suitable for exterior and interior applications.³

Meanwhile, several 1C-PUR adhesives have been evaluated individually in numerous test programs and have received approval for exterior grade structural application for glulam and finger-jointing in several European countries.⁴ PUR adhesives exhibit excellent joint strength when tested in standard climate conditions.⁵

However, one problem associated with PUR adhesives is temperature-dependent creep, determined

recently in laboratory studies by performing thermo-mechanical analysis^{6–9} and creep-to-rupture tests.¹⁰ These studies emphasize that PUR adhesives behave dissimilar under the impact of heat than polycondensation adhesives, but they also suggest that product specific influences, in particular, their chemical composition govern the temperature stability of PUR systems and that bond line thickness is an important factor under practical considerations too. Evidence for the former was recently provided in a study where temperature-dependent creep of PUR adhesives was compared with its chemical structure as defined with NMR analysis.¹¹ The results suggest that the ratio of isocyanate to polyol affects the initial joint strength and creep behavior at temperatures up to 50°C, and that a high degree of covalent cross-linkages in the hardened adhesive network is a decisive factor for good thermal stability.

The objective of the present study was to analyze temperature-dependent creep of a series of 1C-PUR adhesives and to compare the chemical structure of the bulk adhesive with the adhesion performance of the bonded assemblies. Some of the adhesives included in our research have been specifically formulated by the producers to improve temperature performance. Thus the purpose of our study was to evaluate the effectiveness of the adapted formulations.

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EXPERIMENTAL

Seven 1C-PUR adhesives developed for structural bonding of wood (PUR A to PUR G, Table I) and, for reference, one Melamine-Urea-Formaldehyde resin (MUF H, Table I) were supplied by five companies in Germany and Switzerland. All bonded assemblies used for mechanical and TMA tests were prepared from beech wood (*Fagus sylvatica*).

For thermomechanical analysis (TMA), beech wood plies each 0.6 mm thick were conditioned at 14% equilibrium wood moisture content, and then spread with each of the seven PUR adhesives according to the manufacturer's recommended quantity of 200 g/m² and then bonded under pressure (6 kg/cm²) and at ambient temperature (25°C) for the recommended curing time (Table I). The specimens were then conditioned at ambient temperature to a constant equilibrium moisture content of 9% producing bonded joints of 50 × 40 × 1.2 mm³. These specimens were then cut to dimensions of 21 × 6 × 1.2 mm³ for testing. Triplicate specimens were tested in isothermal mode at 40, 60, and 90°C with a Mettler 40 TMA apparatus with three points bending on a span of 18 mm, exerting a dynamic force cycle of 0.1/0.5N on the specimens with each force cycle of 12 s (6s/6s). Modulus of elasticity (MOE) was calculated for each case and tested and depicted as a function of temperature and time.

Totally, 288 lap-joint test specimens were prepared for analysis of the integrity of bond lines in a heat resistance test (HRT) according to EN 14292.¹² One

half of each batch was prepared with close contact (0.1 mm), the other half with thick (0.5 mm) glue-lines. After bonding, one replica of each test sample was placed directly in standard climate (20°C/65% RH), whereas the other was heated in an oven at 80°C for 4 h after initial preconditioning of 24 h.

For each parameter combination (adhesive type × glue-line thickness × preheating), nine lap-joint specimens were tested in bending-shear mode as described in,¹² where a lever arm exerts a load of 214 ± 2N on the bonded area of 200 mm². The load device with the loaded specimens (Fig. 1) was placed in an oven, and the temperature was increased at a constant rate of 50°C/h, starting at 20°C increasing to a maximum temperature limit of 130°C. The test of each single sample was stopped when the lever arm reached a horizontal position due to rupture or after extreme deformation of the adhesive bonds, or when the temperature maximum was reached. The temperature at failure was recorded directly from a temperature recording device. Additionally, creep deformation of all nonruptured test specimens was evaluated. For this purpose, the bending-sheared test specimens were placed edgewise on a plane surface, one part of the assembly was pressed on the surface and any distortion was measured at the opposite end of the sample.

Liquid ¹³C-NMR spectra of all the seven PUR adhesives used were obtained on a Brüker DSX 400 FT-NMR spectrometer. Chemical shifts were calculated relative to tetramethylsilane (TMS) at ambient temperature for NMR shifts control. However, the

TABLE I
Adhesive Types and Characteristics (Data from Adhesive Companies)

Product code	Type	Manufacturer code	Viscosity mPa s	NCO content (%)	Curing time (min)	Specification/modification
A	1C-PUR	1	10,000	14.5	150	Modified formulation of an adhesive approved for load bearing timber structures according to EN 301
B	1C-PUR	1	14,000	14.5	150	Modified formulation of an adhesive approved for load bearing timber structures according to EN 301
C	1C-PUR	2	8,100	16	180–240	Approved for load bearing timber structures in fingerjoints and surface glueing according to EN 301; max. glue line thickness 0.3 mm
D	1C-PUR	2	9,200	18	120–180	Approved for load bearing timber structures in fingerjoints, surface glueing, and I-joists, according to EN 204/205 and ASTM 2559; max. glue line thickness 0.3 mm
E	1C-PUR	3	10,000	13.5	180–210	Approved for load bearing timber structures according to EN 301; max. glue line thickness 0.3 mm
F	1C-PUR	4	>15,000	14.5	180–360	Open time 60 min, D4 classified according to EN 204
G	1C-PUR	4	>15,000	13	45	Fast curing system; open time 15 min, D4 classified according to EN 204; high filling capacity for up to 1 mm glue line thickness
H	Melamine-Urea-Formaldehyde	5	ca. 4,000	–	330	Approved for load bearing timber structures according to EN 301

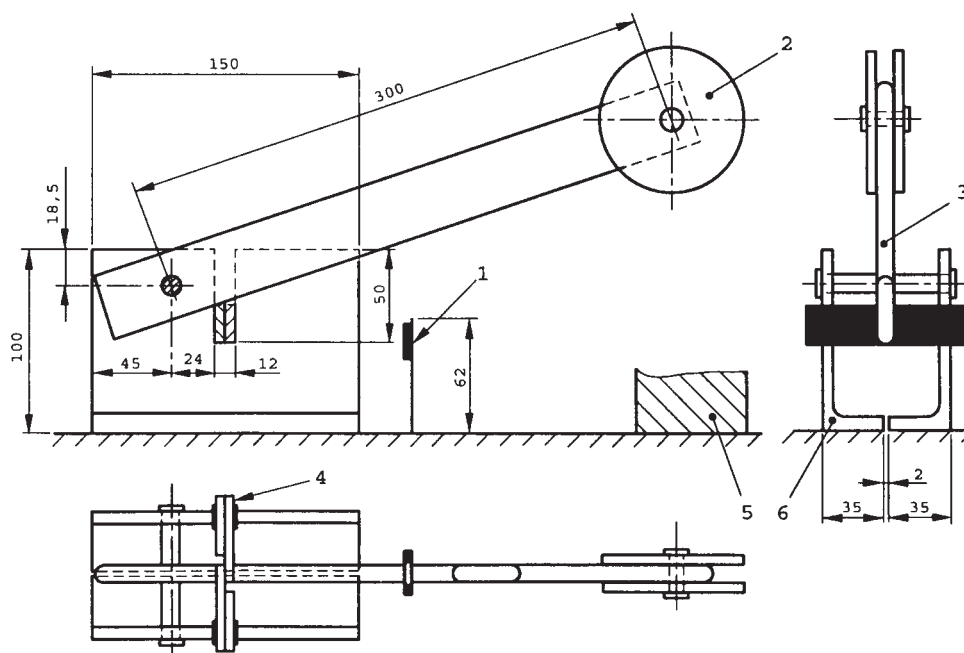


Figure 1 Scheme of load device used in heat resistance test (1: electronic switch; 2: load; 3: lever arm; 4: lap joint test specimen; 5: buffer; 6: alu frame. All measure in mm).

spectra were recorded at 60°C due to the high viscosity of the PUR specimens. Thus, the shifts obtained at 60°C are slightly different from those that would be expected at ambient temperature. The spectra were recorded at 62.90 MHz for ~ 1000 transients. All spectra were run with a relaxation delay of 5 s and chemical shifts were accurate to 1 ppm.

RESULTS AND DISCUSSION

Results of TMA analysis performed at 40, 60 and 90°C are shown in Figure 2. Comparison of the stiffness recorded in isothermal mode allows the first assessment of temperature-dependent creep of the adhesives in a cured bondline. For PUR A, mean stiffness decreased by 12% and 8%, respectively, with increasing temperatures, thus the resin shows no drastic but a measurable thermal creep. For PUR B, temperature-dependent creep is minimal up to 60°C, but average stiffness is reduced by 15% when tested at 90°C, when compared with that of the 60°C results. All isothermal stiffness curves of PUR C and PUR D are running at the same level, thus both resins practically show no temperature-dependent creep in TMA. PUR C is rated as the adhesive with the highest initial stiffness. PUR E at 40°C has the second highest MOE level, but shows temperature-dependent creep mainly when temperatures reach 60°C, whereas stiffness reduction is under proportional when passing at higher temperatures. When compared with all other adhesives, both PUR F and PUR G have a low initial stiffness at 40°C, and show

a proportional loss in MOE when temperature is raised up to 60 and 90°C, respectively.

HRT results are summarized in Table II. In general, the performance of the adhesives was improved when compared with the results reported in our first analysis.⁹ However, and in good agreement with the TMA results reported earlier, a different performance of the adhesives in regard to temperature-creep was identified in the mechanical tests. With the exception of PUR F and PUR G, all adhesives showed a good performance with no rupture and bending creep deformation less than 1 mm for specimens with close-contact joints. The minor relative creep resistance of PUR F and PUR G is expressed as failure of two specimens of PUR F and eight specimens of PUR G. It is interesting to note that, in these cases, rupture was recorded at relatively high temperatures ($> 120^\circ\text{C}$). Thus, although, TMA revealed that creep commences at a temperature range around 60°C, in close-contact joints, bond lines retain their load capacity even at higher temperatures. Comparison of PUR and MUF results reveals no significant difference in the creep deformation of the investigated specimens. When bond line thickness was increased to 0.5 mm, the effect of temperature creep on the PUR adhesives became more evident. Of the specimens tested without preheating, two batches PUR A50 and PUR G50 failed completely, the majority at temperatures between 60 and 100°C. The nonruptured specimens of all other batches had significantly higher creep deformation, with the exception of PUR D and the reference MUF adhesive, which showed

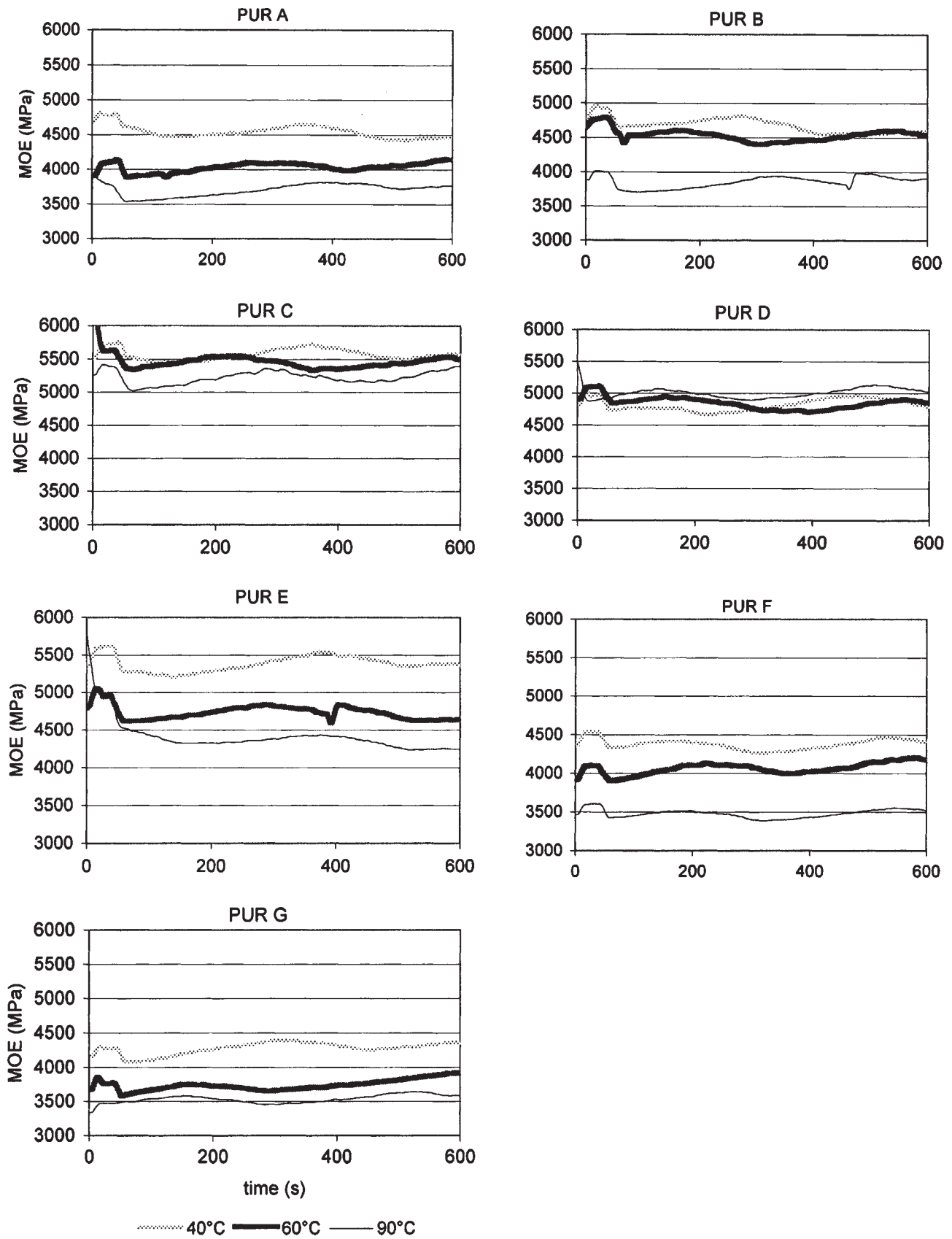


Figure 2 TMA recorded in isothermal mode at temperatures of 40, 60 and 90°C.

TABLE II
Results of Heat Resistance Testing (Code: 1. Digit A–H: Adhesive, 2. Digit 1/5 Glueline
Thickness 0.1 mm/0.5 mm; 3. Digit 0/1: without/with Preheating)

Batch no.	Specimens failed (out of 9)	Min. rupture temperature (°C)	Max. rupture temperature (°C)	Average creep of survived specimens (mm)	Batch no.	Specimens failed (out of 9)	Min. rupture temperature (°C)	Max. rupture temperature (°C)	Average creep of survived specimens (mm)
A10	0	–	–	0.5	A50	9	71	99	–
B10	0	–	–	0.6	B50	0	–	–	2.9
C10	0	–	–	0.7	C50	0	–	–	3
D10	0	–	–	0.4	D50	0	–	–	0.9
E10	0	–	–	0.5	E50	0	–	–	1.8
F10	2	122	122	0.7	F50	0	–	–	3.6
G10	8	126	127	0.4	G50	9	33	103	–
H10	0	–	–	0.4	H50	0	–	–	0.6
A11	0	–	–	0.5	A51	3	125	126	2.7
B11	0	–	–	0.7	B51	3	118	126	2.5
C11	0	–	–	0.5	C51	0	–	–	2
D11	0	–	–	0.3	D51	0	–	–	0.9
E11	0	–	–	0.7	E51	6	104	107	3.4
F11	0	–	–	0.7	F51	0	–	–	2.6
G11	0	–	–	0.7	G51	9	73	118	–
H11	0	–	–	0.5	H51	0	–	–	0.6

practically no creep even in gap joints. On average, microscopic analysis of the sheared surfaces identified 70 to 80% cohesive adhesive failures. As formerly reported,⁹ particularly gap-joint bond lines have a honey-combed structure with numerous CO₂ bubbles. Shear forces are thus not acting on a homogenous adhesive layer, but are concentrated on the flanges between the bubbles, where the bondline failed when internal strength and stiffness are reduced due to thermal creep. Figure 3(a) shows the failed surface of a gap joint, and Figure 3(b) illustrates the creep deformation of a bond line after HRT.

The effect of postcuring of the adhesives improved the performance of PUR A, as only three ruptured specimens failed at higher temperatures, but had negative effects on specimens of PUR B and E, where three, six specimens were ruptured, respectively. Because equally creep deformation of the preheated specimens showed no consistent trend toward reduced values in HRT, it can be concluded that contrary to the behavior of epoxy adhesives,¹³ postcuring of bond lines at a temperature of 80°C for 4 h in 1 day after bonding is not an effective method for improving the quality of 1C-PUR adhesive bonds. Obviously, crosslinking and the structural

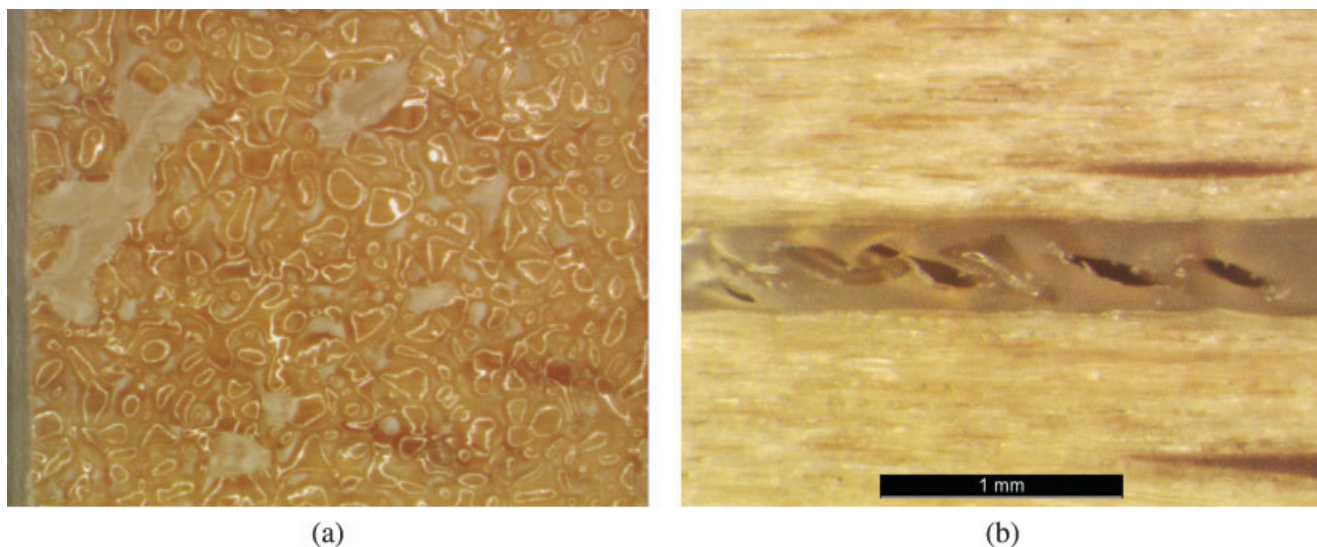


Figure 3 (a) Reflected light micrograph of a gap-joint failure surface. The high amount of CO₂ bubbles is clearly visible. At the light colored areas the bond failed at the wood-adhesive interface (A50-12). (b) Transverse section of a gap joint after HRT. Temperature-creep deformed the shape of the CO₂ bubbles to ellipsis (A50-12). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

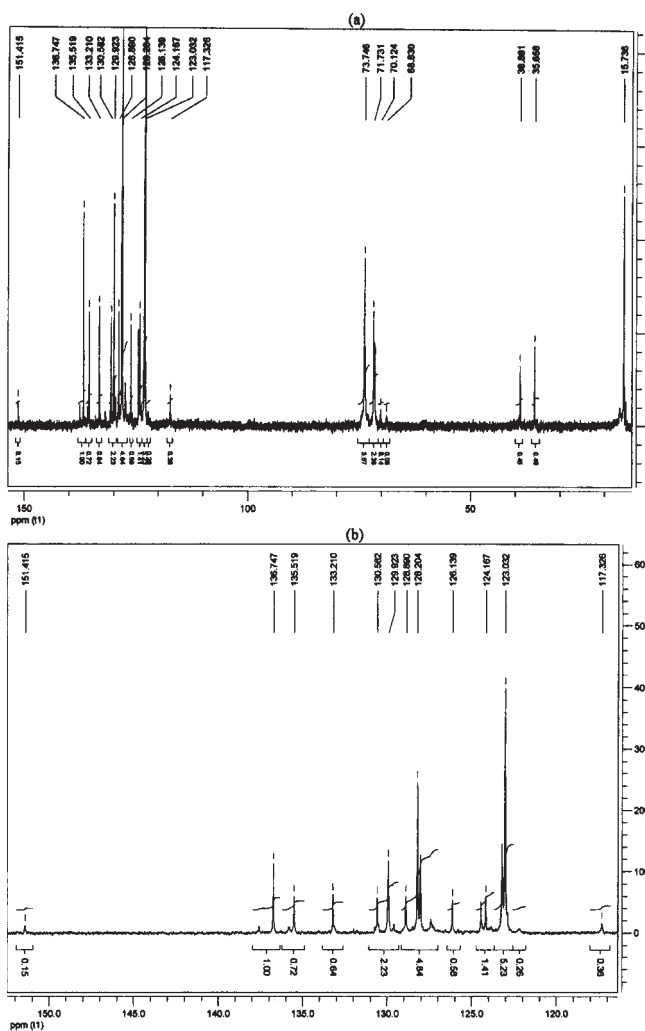


Figure 4 (a) ¹³C NMR spectrum of adhesive C in liquid form. (b) Detail of the 115–155 ppm region of the spectra.

network that develops in PUR is influenced more strongly by chemical bonding conditions (e.g., number of positively reactive —NCO and ratio that effectively react on curing) than by physical conditions.

Analysis and comparison of the ¹³C-NMR spectra of the seven adhesives revealed that the chemical composition of the basic resins on which PUR A and B, PUR C and D, and PUR F and G are based is identical, i.e., they are evenly prepared by the same chemical company. The three adhesive pairs, however, are prepared by three different adhesive companies (Table I). This means that the preparation of 1C-PUR adhesives for wood bonding is resulting in the production of similar resins as the different adhesive manufacturers try to reformulate and refine their base resin to optimize performance.

The general analysis of the ¹³C-NMR spectra of the seven 1C-PUR adhesives was based on the sharpness of the spectra peaks. PUR C (Fig. 4), PUR D, PUR F, and PUR G (Fig. 5) indicate that all adhesives have

narrow peaks. This indicates that the level of polymerization of these resins is relatively low and principally these resins should set slower. This assumption is confirmed by the manufacturers' data for PUR C, D, and F, but not for PUR G (Table I). It is well-known that a slower setting of the resin, if sufficient time and ambient conditions for curing is available, results in a stronger and harder network.^{14,15} This is due to the minimization of early immobilization of the network, and hence to the increased crosslinking obtained. This explains why PUR C and D show good results, and F shows acceptable performance in HRT of the closed contact joints. In Figure 2, however, the TMA analysis distinguishes between the performance of PUR C and D, which practically do not show any temperature-dependent creep, and whereas PUR F does exhibit temperature-dependent creep. When comparing this data with the HRT results, it must be noted that TMA analysis exaggerates differences, rendering it easier to see even slight difference that might exist. Second, the differences indicate that during practical application very little or no difference can be noted in the performance of PUR F when bonded in closed contact joints, but if it had to be used under more extreme temperature conditions a reduction in performance may be expected, which definitely is not the case for PUR D, where a reduction in performance will rarely be noticed. These same reasons do not appear to be applicable to PUR G as this resin sets faster (45 min, Table I) although it has also a relatively high viscosity.

In contrast, PUR A (Fig. 6), B, and E (Fig. 7) present much broader NMR peaks, indicating resins that are more polymerized than the first group. If a higher degree of polymerization correlates with a higher viscosity, such a relationship is only supported for PUR C and D, which have lower viscos-

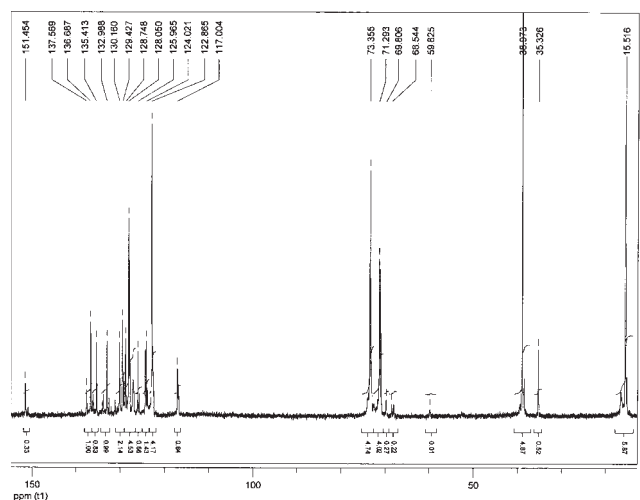


Figure 5 ¹³C NMR spectrum of adhesive G in liquid form.

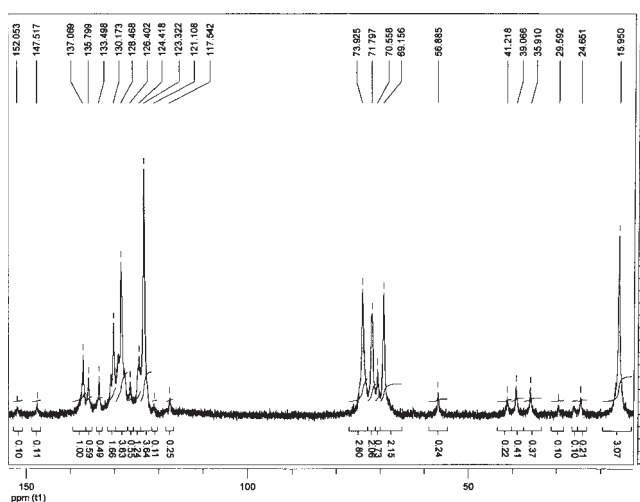


Figure 6 ^{13}C NMR spectrum of adhesive A in liquid form.

ities (8100 and 9200 mPa s when compared with 10,000 to 14,000 mPa s; Table I). Obviously, the thicker consistency of PUR F and G has to be attributed to the presence of some silica-based filler. In regard to the degree of polymerization, PUR A, B, and E should set faster, but not excessively faster than PUR C and D. Again this relationship is not supported consistently by the manufacturers' data on curing time in Table I.

Another parameter of importance for the structural performance of the PUR adhesives is the relative content of free, reactive $-\text{NCO}$ groups still present in the resins. They are 14.5%, 16%, 14.5%, and 13%, respectively, of total resin according to the values provided by the manufacturers (Table I), and 27.3%, 30.0%, 27%, and 24.3% of the isocyanate part as calculated from the NMR spectra, for PUR A and B, C, F, and G, respectively. Out of this group, PUR C showed the best performance, and had the highest percentage of still active isocyanate groups (30%). Furthermore, as PUR C has more residual $-\text{NCO}$ groups than PUR F and G, this correlates with its lower level of temperature-dependent creep as determined by TMA (Fig. 2). The same trend is evident for PUR A and B, which have a lower percentage of $-\text{NCO}$ groups than resin C and the same as resin F. This results in a higher level of creep than PUR C and a similar level of temperature-dependent creep than PUR F. This is also supported by both the relative TMA results shown in Figure 2 and, with some variations, the HRT results (Table II). However, there are evidently other parameters, which influence this trend, as PUR A, B, and F have practically the same percentage of residual $-\text{NCO}$ groups, but PUR F has a slightly weaker creep performance than PUR A and B.

Thus, it may be concluded that not one parameter alone, but a combination of residual $-\text{NCO}$ groups with the degree of polymerization (DP) and the rate

of curing governs the final tendency in behavior of 1C-PUR adhesives. Higher $-\text{NCO}$ content coupled with lower DP and a relatively slower rate of curing appear to give the best results, hence a lower temperature-dependent creep. The behavior of PUR C and D is particularly encouraging and it can be clearly stated that in the case of these resins temperature-dependent creep has been so minimized that it can be considered as eliminated for all practical applications. The NMR spectra of PUR D revealed to be exactly the same resin as C. The higher rate of curing (curing time 120–180 min) is compensated by the highest $-\text{NCO}$ content of all adhesives studied (18%, Table I) leading to the best performance in the heat resistance test with creep deformation as low as for the MUF resin. By contrast, PUR G confirms the parameter combination as well. The narrow NMR peaks obtained follow a similar trend as PUR C and D, which should correspond to a good strength performance but its much faster rate of curing distinguishes it from these adhesives and from PUR F. This faster curing rate of PUR G corresponds to an inferior creep performance in HRT with considerable higher failures than all other resins (Table II), a trend clearly confirmed by the TMA tests. Even at the lower temperatures, the MOE value is the lowest one of all the resins tested. Its lack of performance appears to be due to the influence of $-\text{NCO}$ content. PUR G has the lowest percentage of $-\text{NCO}$ groups, limited crosslinks, and an enhanced temperature-dependent creep.

PUR E is the most unusual polyurethane of the seven adhesives (Fig. 7). It has broad NMR peaks indicating a fairly high level of polymerization of the resin. It has a good joint performance with little creep-deformation of close-contact joints, but thick gluelines show considerable creep (Table II). The setting time of 180–210 min advised by the manufac-

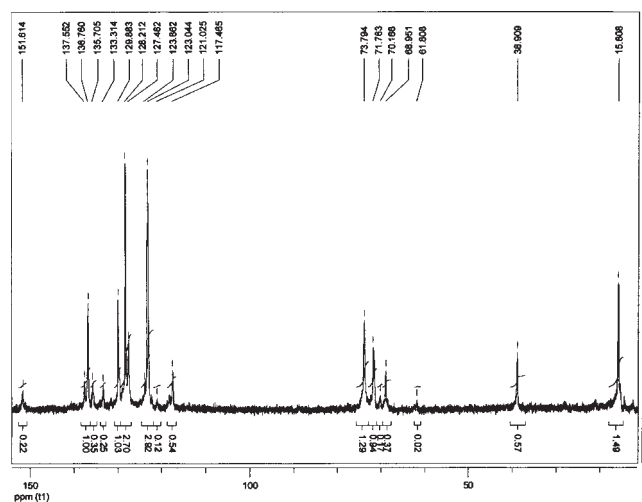


Figure 7 ^{13}C NMR spectrum of adhesive E in liquid form.

turer is long, and exceeds that of PUR D but is shorter than PUR C and F, and this is possibly the reason why it is less affected by temperature-dependent creep. It must be stressed that PUR E is more highly polymerized than PUR C and D, so the slower setting could be due to a different variety of reasons than in resin C, e.g., a higher inhibition of diffusion at the start of crosslinking due to the higher molecular mass of the polymer chains. The lower percentage —NCO content is definitely due to the more advanced state of the resin as crosslinking levels are obviously not affected as suggested by the fairly good performance of the close-contact joints and the absence of creep. Thus, two factors leading to lower temperature-dependent creep are apparent, namely slower setting, irrespective of its cause, and more importantly, a relatively lower free —NCO groups ratio implying that the resin is already fairly advanced and precrosslinked. The third factor, a low level of polymerization is absent and could be the cause of the residual creep observed under some more drastic conditions (thick glue lines).

On the basis of the structural formula presented in Figure 8, and the identification of the shifts of the NMR signals (Table III) some additional considerations of the chemical formulation of the adhesives are made. PUR A (Fig. 6) contains more of linear 1,3 propylene glycol than all the other polyurethanes, where only traces of 1,3 propylene glycol appear to be present. All the other polyurethanes examined by NMR contain 1,2 propylene glycol at approximately the same ratio, with much less, in some cases, only traces of 1,3-propylene glycol. PUR A contains, as all the other adhesives, a much higher ratio of isocyanate groups of the diphenylmethane-diisocyanate (MDI) than of the toluene-diisocyanate (TDI) type. It is not possible to determine with exact certainty the ratio of TDI from the spectra because most of its characteristic peaks have similar shifts and overlap other signals. Some adhesives may actually contain no TDI groups or TDI at all. This view is supported, for example, by the absence of TDI's —CH₃ signal at 17.6 ppm. Interestingly, in these polyurethane adhesives there appears to be more C10-type carbons and much less C9-type carbons. On the basis of the structural formula in Figure 8(b), the only possible explanation for this is that the repeating units of the pMDI are different with *m* and *n* structures present in the polyurethane skeleton.

PUR C (Fig. 4) appears to contain a slightly higher ratio of pMDI than in the case of PUR F and definitely higher than PUR G (Fig. 5), and the TDI ratio appears to be very low, or not present at all. All other differences are minor. As these resins are produced by different adhesive companies, it appears that research has enabled different industrial manufacturers to establish a similar type of formulation with a superior technical performance at a comparable price.

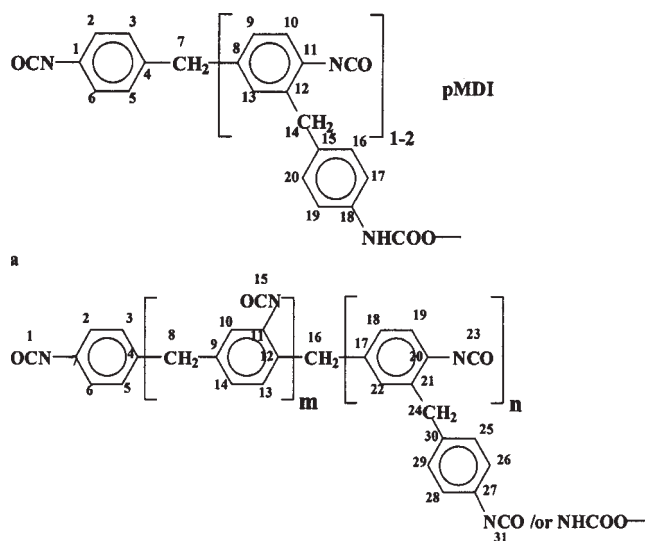


Figure 8 (a, b) Structural formula of two possible polyurethane skeletons.

The polyols used show four different alcohols or esters bonds in the region 68 to 74 ppm. In general, there is a polyalcohol polyol similar to a sugar or to sorbitol of the type —OH₂C(CHOH)₄CH₂O—, the peaks of which are 73–74 ppm and the 1,2 and 1,3 propylene glycols. With the exception of PUR A, for all the other adhesives, the 1,2 glycol is the second most important and only 1,3 glycol occurs in traces. In PUR A, the mix of the two propylene glycols is in higher ratio than the —OH₂C(CHOH)₄CH₂O—, differently from all others polyurethanes. Small amounts of 1,4-butanol, generally present in this types of resin, shown by the first —CH₂— of the alcohol reacted (64.2 ppm) and unreacted (62.2 ppm) are not present here.

As regards the methylene bridges C7 and C14 between the aromatic rings of pMDI, these are generally at 38–39 ppm for the para-para —CH₂— bridge between aromatic rings of pMDI (Table III), and at 35–36 ppm for the ortho-para —CH₂— bridge between aromatic rings of pMDI. These appear in all the adhesives. PUR A (Fig. 6), however, is again different from the rest, as it presents the very rare peak for ortho-ortho —CH₂— bridges between aromatic rings at 41–42 ppm.¹⁶ Finally, the peak around 15–16 ppm is the CH₂ carbon of the grouping —NHCOO—CH₂CH₂—. The lack of —CH₃ signals at around 18–19 ppm indicates that in the experimental formulations TDI does not appear to be present.

CONCLUSIONS

Our analysis reveals that creep performance of 1C-PUR adhesives was improved when fundamental chemical principles had been taken into consideration by the

TABLE III
¹³C-NMR General Shifts for the Seven 1-C PUR Adhesives Tested

	ppm
pMDI, reacted, and unreacted	
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—CH ₃	17.6
(ArC) (ortho —CH ₃ ; meta to 2x —NCO/—NHCOO—)	130.1–130.7
(ArC—NCO) (ortho —CH ₃ ; meta to 1x —NCO/—NHCOO—)	133.9
(ArC—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 ₂ C(CHOH) ₄ CH ₂ O— major	73.4–73.8
HOCH ₂ CH ₂ CH ₂ CH ₂ OH	(62.2)
HOCH ₂ CH ₂ CH ₂ CH ₂ OH	29.1
—OCH ₂ CH ₂ CH ₂ CH ₂ O—	(64.2)
—OCH ₂ CH ₂ CH ₂ CH ₂ O—	(32.0)
HO—CH ₂ CH(CH ₃)—OH and —O—CH ₂ CH(CH ₃)—O— ^a	71.3–71.8
HO—CH ₂ CH(CH ₃)—OH ^a	72.7
HO—CH ₂ CH ₂ CH ₂ OH and —O—CH ₂ CH ₂ CH ₂ —O— ^b	68.0–69.2
HO—CH ₂ CH ₂ CH ₂ OH and —O—CH ₂ CH ₂ CH ₂ —O— ^b	69.7–70.5
HO—CH ₂ CH(CH ₃)—OH and —O—CH ₂ CH(CH ₃)—O— ^a	18.6
—NHCOO—CH ₂ CH ₂ —	15.5–16.0

^a 1,2-propylene glycol linked and unlinked.

^b 1,3-propylene glycol linked and unlinked.

industrial formulators. The comparison of mechanical performance with the ¹³C-NMR spectroscopy findings indicate that the combination of three parameters is decisive for the temperature stability of 1C-PUR wood adhesives: (i) the relative proportion of still reactive, free —NCO groups in the polyurethane, (ii) the degree of polymerization of the resin, and (iii) the rate of reaction. The results obtained show that adhesives presenting a combination of a higher proportion of still unreacted —NCO groups, lower degree of polymerization and slower reaction rate are capable to counteract the problem of high sensitivity of polyurethane to temperature-dependent creep. Appropriate chemical formulation of an adhesive turned out to be an effective means to reduce thermal-creep to tolerable values, comparable to those of polycondensation adhesives, whereas post curing of preset bond lines was ineffective.

Results of gap joint (0.5 mm) testing show that creep is a serious problem with common polyur-

ethanes if glue line thickness cannot be reduced to close-contact conditions. Six out of seven adhesives showed visible deformations of the lap-shear specimens after heat resistance tests. Microscopic analysis provides evidence that the higher amount of CO₂ bubbles formed in the curing process in gap joints is closely related to an increased failure rate in thick gluelines. This intensifies the effect of the structural weakening of the bulk adhesive due to segment movement and easier disentanglement with increasing temperature. In close-contact joints, the gluelines have fewer defects because fewer gas bubbles are formed, although the relative amount of adhesive is lower and the adhesive undergoes a similar softening process. This is one of the reasons that maximum bond line thickness for all approved structural 1C-PUR adhesives is so far limited to 0.3 mm. Glulam manufacturers are strictly advised to take all appropriate measures to meet this threshold, inde-

pendent of the climatic situation in which the structural components are intended to be used.

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