One-Component Polyurethane Adhesives for Green Wood Gluing: Structure and Temperature-Dependent Creep

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ABSTRACT: Creep and temperature-dependent creep, characteristic of one-component polyurethane adhesives for wet and green structural wood gluing are two different parameters. Testing of standards-approved commercial polyurethane adhesives for this purpose shows that while ambient temperature creep can be avoided or at least greatly limited according to the formulation used, this is not the case for temperature-dependent creep. The commercial adhesive formulation characteristics that minimize or enhance ambient temperature and temperature-dependent creep are identified. Basic principles on the structure of simple polyurethane adhesives influencing temperature-dependent creep are also identified and discussed. The higher the proportion of all hardened network nodes, the lower creep is likely to be at ambient temperature. Instead, due to segment movement and easier disentanglement with increasing temperature, the lower the proportion of covalently linked nodes and the greater the proportion of just physical entanglement nodes, the greater the temperature-dependent creep will be. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1231–1243, 2005

Key words: adhesives; polyurethanes; creep; structure–properties relations; green wood gluing; NMR

INTRODUCTION

Bonding of timber of high moisture content, namely "gluing wet wood," or gluing of green wood as it is sometimes called, to prepare glulam and fingerjointing became possible with the industrial introduction of honeymoon, fast-set, separate application phenol-resorcinol-formaldehyde (PRF) adhesives in the early 1980s. Honeymoon fast-set adhesives for exterior-grade structural glulam and fingerjointing have now been used industrially for about twenty years,[1–4] even for this application. From the original concept of the honeymoon fast-set system and the initial systems that were eventually industrialized[1–4] and are still extensively used commercially, several other relevant variations on the same theme were also derived and used over the years.[5–8] The use of melamine-urea-formaldehyde separate application honeymoon adhesives for the same purpose is more recent, but already commercial for a few years now.[9]

The use of one-component polyurethane adhesive systems for wet and "green" wood gluing is relatively new.[10–12] While wet wood gluing up to 90% moisture content of the timber was already achieved commercially in the early 1980s,[10,12] only more recently have single application, one-component polyurethane systems for "gluing wet wood" been formally approved and widely promoted for use in structural glulam in some European countries. The use of polyurethanes for this application has been rendered possible by the disappearance in the now unified Western European standard of the requirements of minimum percentage wood failure that were required in several older national standards. Polyurethanes often impart lower percentage wood failure than what were the older requirements, and also impart excellent joint strength.

The main characteristic of reactive polyurethanes, hence still containing reactive isocyanate groups to yield crosslinking in applications, such as those used for glulam, is that the presence of water in the timber should set off and accelerate the crosslinking, hardening reaction. In this and in their ease of handling, polyurethane systems are a very interesting proposition for bonding glulam. The main problem all polyurethanes, even crosslinked ones, present, however, is that of creep. This means that in the past even good polyurethane systems, even those well resistant to water and weather deterioration, could not be used for structural application. Considering that the majority of the applications for glulam and fingerjointing are for structural building applications, this can be a grave defect indeed. It is the existence of this problem that has effectively stopped polyurethanes, good wood adhesives, being used in glulam applications in the far

past, and perhaps their slighter higher cost. Temperature-dependent creep is a somewhat different problem, but critical to the safety of under-roofing structural timber in hot countries (under-roof temperatures in Mediterranean and other countries can reach 70°C in summer) and in the behavior of structures in fires.

The concern for creep under load, and for temperature-dependent creep, has only very recently started to be addressed[13–16] as a serious threat to the structural application for which these resins have already been approved in a few European countries. The clear existence of this threat has elicited a number of responses from the specifying authorities involved, namely either the problem has been ignored and dismissed as if it did not exist, or the problem has been addressed by reporting only results of polyurethane adhesives that present a low level of creep. Recent work, however, has clearly shown that of the few types of commercial polyurethanes approved and used in Europe for this application,[12] some present no creep, some present medium-level creep, and some present a potentially disastrous level of creep. A study of 6 variants of these[16] showed 2 in the first, 2 in the second, and 2 in the third category. The very real problem that some approved systems that are not suitable for structural wood gluing are actually used, then, exists and cannot be denied. The principle that polyurethanes can be excellent structural wood adhesives is not in doubt here. What is important is that knowledge of their structure and network is essential and is determinant to the extent of creep and temperature-dependent creep they present in this application. The correlation of structure and creep for polyurethanes for structural wood application is not available anywhere, and without this knowledge little can be done to reformulate the existing "creeping" formulations so that the problem can be eliminated or at least minimized.

This paper then deals first with trying to correlate temperature-dependent creep with the structure obtained from the analysis of a number of commercial one-component polyurethanes approved for this purpose and commercially available in the European market. Second, it deals with the laboratory combination in different proportions and hardening of three isocyanates, and three diamines/polyols. All six compounds used present structures different enough to be able to at least establish some initial, simple structure/creep correlations for temperature-dependent creep.
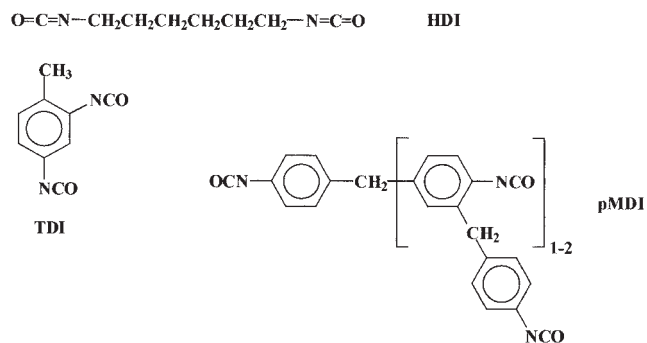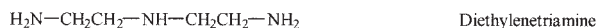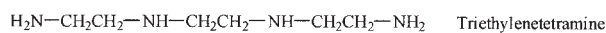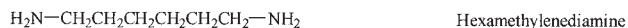
EXPERIMENTAL

Three commercial polyurethane (PU) adhesives, all of them approved either in Germany, Sweden, or France for exterior grade structural application to glulam and fingerjointing, were tested dynamically by thermomechanical analysis (TMA) on a Mettler apparatus. Of these, two were originally from Scandinavian countries and the third from a continental European country. Six samples of beechwood alone, and of two beechwood plies each 0.6 mm thick, after conditioning at 14% equilibrium wood moisture content of the wood, were spread at the manufacturer's recommended spread of 200 g/m² with each adhesive system and then bonded at ambient temperature (25°C) and under pressure (6 kg/cm²), and then conditioned at ambient temperature and to a constant equilibrium moisture content of 9% to give bonded joints of 50 × 40 × 1.2 mm. These samples were then cut to dimensions of 21 × 6× 1.2 mm for testing. Triplicate samples were also tested in isothermal mode at 40°C, 50°C, and 100°C with a Mettler 40 TMA apparatus in three points bending on a span of 18 mm exercising a dynamic force cycle of 0.1/0.5N on the specimens with each force cycle of 12 s (6s/6s). The classical mechanics relation between force and deflection $E = [L^3/(4bh^3)][\Delta F/(\Delta f)]$ allows the calculation of the Young's modulus E for each case tested, and this was done to follow the increase of modulus (MOE) as a function of temperature and time.

The liquid ^{13}C-NMR spectra of the three 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 shifts control. However, the spectra were done at 80°C due to the high viscosity of the PUR specimens. Thus, the shifts obtained at 80°C are 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.

Specimens for TMA testing at 25°C, 40°C, 50°C, 75°C, and 100°C also in isothermal mode, under the same conditions used for the commercial samples, were prepared as follows: two beech veneers of dimensions 50 × 40 × 0.6 mm were spread with premixes of an isocyanate and a di-, tri-, or tetramine, and these were cured/hardened in a press, at 6 kg/cm² and 120°C temperature for 10 min. They were cured at 120°C to make sure they were fully cured before showing if they still creeped. The samples were then conditioned at ambient temperature and to a constant equilibrium moisture content of 9% to give bonded joints of 50 × 40 × 1.2 mm. These joints were then cut to dimensions of 21 × 6 × 1.2 mm for TMA testing. The relative proportions of isocyanate and amine were varied wherever possible, as indicated in the results tables and figures. Three isocyanates, namely hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), and polymeric 4,4' diphenylmethane diisocyanate, and three amines, namely hexamethylenediamine (HMD), triethylenetetramine (TET), and diethyl-

$H_2N-CH_2CH_2CH_2CH_2CH_2CH_2-NH_2$ Hexamethylenediamine

$H_2N-CH_2CH_2-NH-CH_2CH_2-NH-CH_2CH_2-NH_2$ Triethylenetetramine

$H_2N-CH_2CH_2-NH-CH_2CH_2-NH_2$ Diethylenetriamine

$O=C=N-CH_2CH_2CH_2CH_2CH_2CH_2-N=C=O$ **HDI**

TDI

pMDI

Scheme 1

enetriamine (DET), were used. Their formulas are indicated in Scheme 1. All the combinations of isocyanate/amine were tested.

RESULTS AND DISCUSSION

The ^{13}C-NMR of the three PUR samples showed that two of these, from the same manufacturer, differed slightly, while the third PUR sample, from a different manufacturer, was quite different. The NMR spectra and their details are shown in Figures 1, and 3, and the shifts[17,18] of note are reported in Table I and Scheme 2. The spectra of the two PUR in Figures 1 and 2 show peaks for pMDI-derived and TDI-derived urethane residues at 138.6 ppm (Ar C-CH$_2$- in *para* or in *meta* to a –NCO group), at 135.1 ppm (Ar C-CH$_2$- in *para* to a –NCO group), around 131 ppm (Ar C-NCO in *para* to a –CH$_2$- group), and at 119.3 ppm (Ar C *meta* to a -CH$_2$- and *ortho* to a –NCO group; as well as Ar C *ortho* to a -CH$_2$- (C17,19), and also *para* to a –NCO group). Also visible are the other aromatic carbons of the
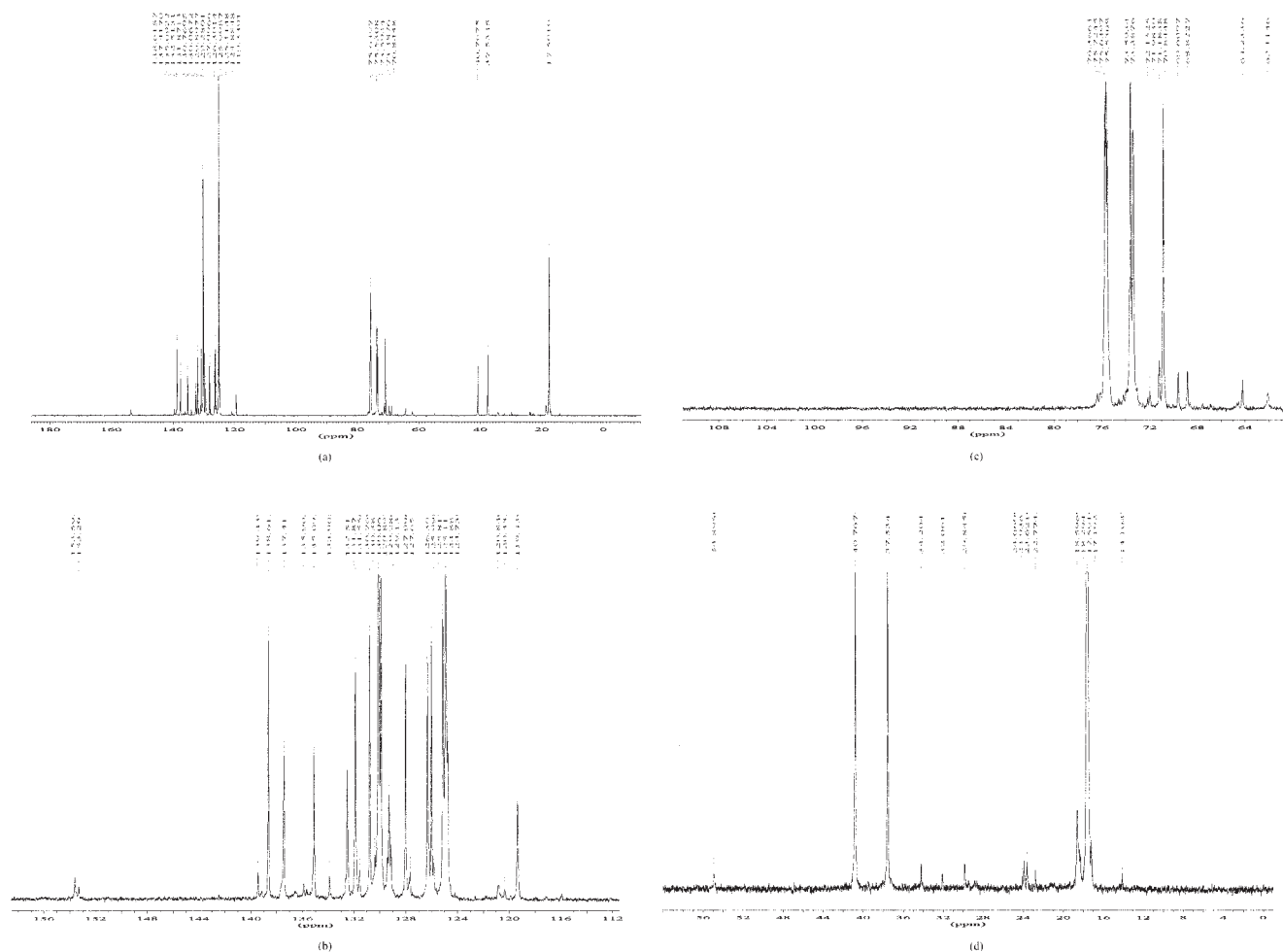

Figure 1 ^{13}C-NMR spectrum of (a) a commercial one-component polyurethane adhesive approved by European standards for structural wet and green wood gluing (identified as PUR A in text), (b) details of the 112–158 ppm region of the spectrum, (c) details of the 60–110 ppm region of the spectrum, and (d) details of the 0–60 ppm region of the spectrum.
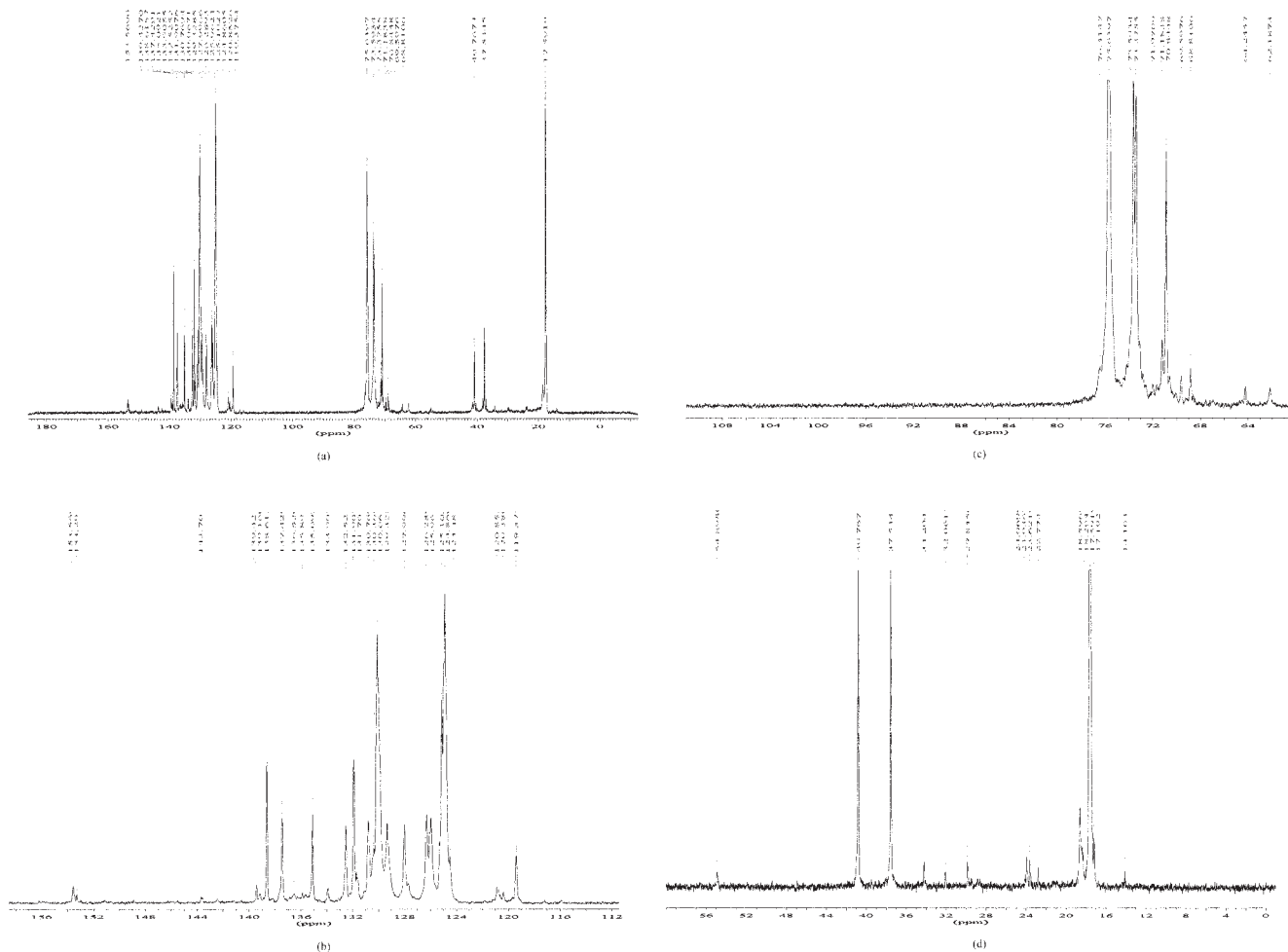
Figure 2 ^{13}C-NMR spectrum of (a) a commercial one-component polyurethane adhesive approved by European standards for structural wet and green wood gluing (identified as PUR B in text), (b) details of the 112–158 ppm region of the spectrum, (c) details of the 60–110 ppm region of the spectrum, and (d) details of the 0–60 ppm region of the spectrum.

pMDI cycle, namely 40.7 ppm (C7,14, -CH$_2$- of pMDI), 124.5 ppm (C2,6), 125.1 ppm (C10), 125.9 ppm (-N=C=O), 126.3 ppm (C9), 128.0 ppm (-N=C=O), 129.3 ppm (C13,16,20), 130.06 ppm (C3,5), 131.7–131.9 ppm (C1 and C18 when linked to an unreacted –N=C=O group), 132.5 ppm (C12), either the 133.9 ppm or the 135.1 ppm representing the C15 linked to a urethane bridge that by software calculation estimate[17] should appear at 134.5–134.6 ppm, 135.9 (C1 and C18 when linked to a urethane bridge), 138.6 ppm (C4,8), 143.7 ppm (C11), and 153.3 and 153.6 ppm (the NH-COO- carbon of the urethane bridge).

Overimposed to the pMDI pattern and partly hidden by it there is a TDI pattern at 17.6 or 18.6 ppm (Ar-CH$_3$), 130.7 ppm (aromatic C *ortho* to -CH$_3$ and *meta* to the two –NCO or urethanes), 133.9 ppm (aromatic C *ortho* to -CH$_3$, linked to one –NCO and *meta* to the second –NCO or urethane bridge), and 138.6 ppm (aromatic C *para* to -CH$_3$ and linked to one –NCO or urethane, and *meta* to the second –NCO). The signal at 128.0 is that of the –NCO of the TDI superimposed on one of the –NCO of the pMDI.

The pattern of the polyols or diamines used is relatively more complex. At 68.8 ppm, 69.5 ppm, and 70.8 ppm are present two of the carbons (-CH$_2$- and –CH-) of a polyoxypropylene from 1,2-propylene glycol, and at 17.6 or 18.6 ppm its -CH$_3$ group. The rest of the peaks of the polyols belong to free and etherified polyalcohols where a considerable proportion of secondary alcohols or ether groups are present. Thus, for example, a polyalcohol such as sorbitol [HOH$_2$C-(CHOH)$_4$CH$_2$OH] would present for the four secondary alcohol functions shifts of, respectively, 74.5, 72.9, 74.3, and 76.1 ppm, which fit within the ± 1 ppm precision of the spectra with the 73.4, 73.6, and 75.7 ppm observed experimentally. Small amounts of 1,4-butanol shown by the first –CH$_2$- of the alcohol reacted (64.2 ppm) and unreacted (62.2 ppm) can also be observed.

Considering the above signals, Figure 1 (PUR A) shows a slightly higher proportion of TDI in the mix and of unreacted TDIs –NCO group than PUR B in Figure 2, but the total proportion of isocyanate to polyols appears to be greater in PUR A than in PUR B.
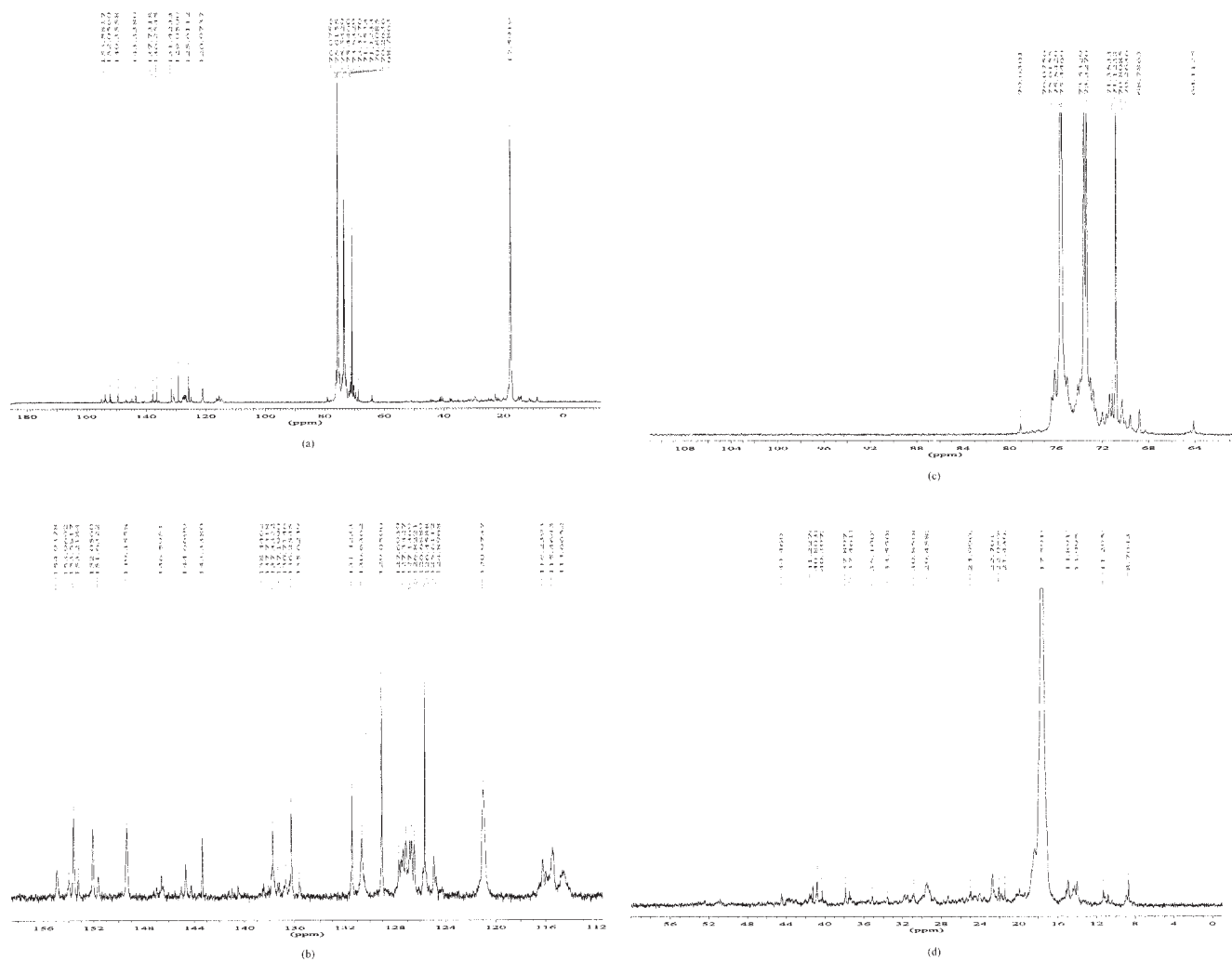
Figure 3 ^{13}C-NMR spectrum of (a) a commercial one-component polyurethane adhesive approved by European standards for structural wet and green wood gluing (identified as PUR C in text), (b) details of the 112–158 ppm region of the spectrum, (c) details of the 60–110 ppm region of the spectrum, and (d) details of the 0–60 ppm region of the spectrum.

Thus, in PUR B there are more polyols proportionally, although the differences are evident but not extreme. In Figures 4 and 5 where isothermal thermomechanical analysis (TMA) was done for beech joints bonded with PUR A (Fig. 4) and PUR B (Fig. 5) at parity of temperature, the MOE of joints bonded with PUR A are always stronger than joints bonded with PUR B, reflecting the greater proportion of isocyanate in the former. As regards temperature-dependent creep (Figs. 4 and 5), considering the 40°C and 100°C cases, PUR A is better than PUR B at, respectively, 34.6% and 40.9% MOE decrease; however, in absolute the creep is the same for the two at 1800 MPa. The differences are then rather small. The only difference that is of considerable importance is rather within which temperatures there is the biggest drop of MOE. For PUR A this is between 50°C and 100°C, while for PUR B the major drop is between 40°C and 50°C. This means that in structural applications, in the more usual range of

under-roof temperatures in hot countries, PUR A would creep less and perform better than PUR B. As regards resistance to creep at temperatures experienced during fires, there would be no difference between them.

PUR C is, instead, very different from PUR A and PUR B materials. The ^{13}C-NMR spectra in Figure 3 indicate, first of all, that the relative proportion of polyols to isocyanates is very high, much higher than in PUR A and PUR B. The proportion of isocyanate in the system is then rather low. Furthermore, the relative proportions of pMDI and TDI appear to be different: the polymer backbone appears to have mainly occurred through reaction of TDI with the polyols. A higher proportion of free –NCO groups from pMDI are present, and the pMDI has participated much less in the formation of the polyurethane polymers. To note the variety of different set-ups the –NCO group of TDI finds itself (the series of numerous small peaks

TABLE I
^{13}C NMR Shifts on Spectra in Figs 1, 2, and 3

pMDI reacted and unreacted	ppm
C1, C8, C15 when linked to –NCO	131.7–131.9
C2, C6	124.5
C3, C5	130.06
C4, C8	138.6
C7, C14	40.7
C9	126.3
C10	125.1
C11	143.7
C12	132.5
C13, C16, C20	129.3
C15 when linked to –NHCOO–	135.1
C17, C19	119.3
C18, C1 when linked to –NHCOO– TDI	135.9
Ar–C̲H$_3$	17.6
(ArC̲) (ortho –CH$_3$;meta to 2x –NCO/–NHCOO–)	130.7
(ArC̲–NCO) (ortho –CH$_3$;meta to 1x –NCO/–NHCOO–)	133.9
(ArC̲–NCO) (para –CH$_3$;meta to 1x –NCO/–NHCOO–)	138.6
–N=C=O (pMDI)	125.9
–N=C=O (pMDI and TDI)	128.0
Polyols	
–OH$_2$C(C̲HOH)$_4$CH$_2$O– major	73.4, 73.6, 75.7
HOC̲H$_2$CH$_2$CH$_2$CH$_2$OH	62.2
HOCH$_2$C̲H$_2$C̲H$_2$CH$_2$OH	29.1
–OC̲H$_2$CH$_2$CH$_2$CH$_2$O–	64.2
–OCH$_2$C̲H$_2$CH$_2$CH$_2$O–	32.0
HO–C̲H$_2$CH(CH$_3$)–OH	71.4
HO-CH$_2$C̲H(CH$_3$)–OH	72.7
HO-CH$_2$CH(C̲H$_3$)–OH	18.6

between 126.4 and 127.7 ppm in Fig. 3b) and the much greater number of carbonyl peaks present in the 144 to 155 ppm region. This latter peaks indicate a variety of biuret and allophanate bridges formed, indicating that the reaction of the isocyanate with the polyol was more advanced. (That is supported by the marked excess of polyols present.) This explains why "loose" pMDI with still reactive –NCO groups appears to have been added later to increase the relative number of
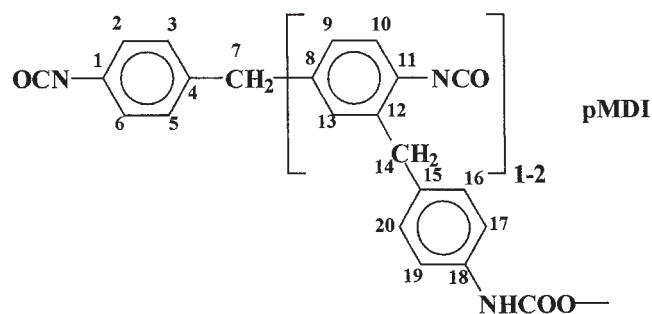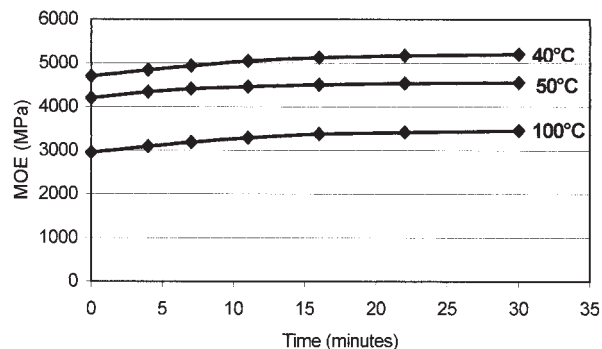
Scheme 2

Figure 4 MOE as a function of time and temperature in 40°C, 50°C, and 100°C isothermal thermomechanical analysis in bending of cured beechwood joints bonded with PUR A, a commercial one-component polyurethane adhesive for structural wet and green wood gluing.

–NCO groups and improve final crosslinking during glue-line hardening. Not to have done so might have given a glue-line too flexible, and possibly too prone to creep.

Figures 6 and 7 show the different behavior of this polyurethane in a joint. A decrease of mechanical resistance in a nonisothermal experiment is shown in Figure 6, where the original MOE decreases by 47% in passing from 30 to 90°C. The isothermal experiments in Figure 7, comparable to those for PUR A and PUR B in Figures 4 and 5, indicate a decrease of 1400 MPa and of 44% of the original strength for PUR C, with the greater decrease between 50°C and 100°C and a relatively smaller decrease between 40°C and 50°C. This behavior is more similar to PUR A than PUR B, but in principle worse than both, except for lower temperature creep where PUR C is better than PUR B. However, the similarity between PUR A and PUR C ends here. In
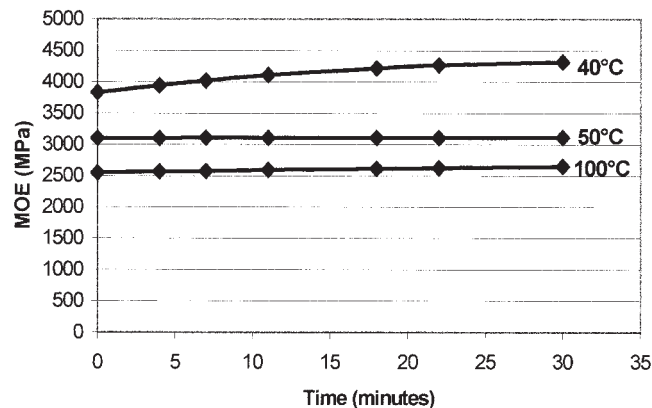
Figure 5 MOE as a function of time and temperature in 40°C, 50°C, and 100°C isothermal thermomechanical analysis in bending of cured beechwood joints bonded with PUR B, a commercial one-component polyurethane adhesive for structural wet and green wood gluing.
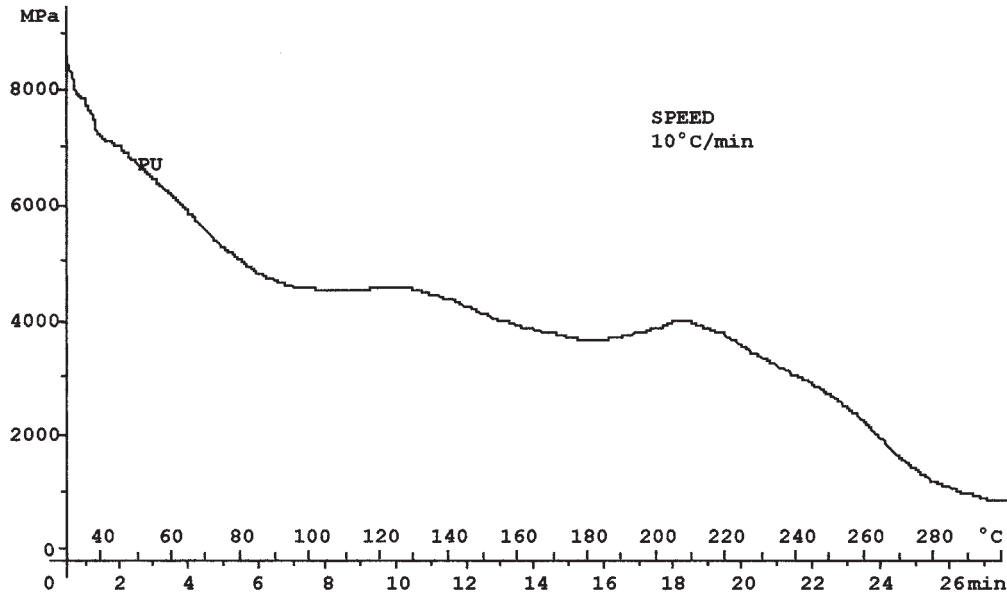
Figure 6 MOE as a function of time and temperature in nonisothermal thermomechanical analysis at a constant 10°/min heating rate, in bending, of a cured beechwood joint bonded with PUR C, a commercial one-component polyurethane adhesive for structural wet and green wood gluing.

Figure 7 one can notice the initial decrease in MOE at 40°C before the MOE starts to increase again. This is a case of time-dependent, classical-type creep, due either to lack of complete curing unless heat is supplied and a certain temperature reached (a grave fault for a material that has to cure at ambient temperature in service). This is indicative of a second crosslinking reaction, a late crosslinking reaction occurring or more likely only going to completion later. It is most likely to be the slower reaction of the pMDI added afterwards to increase the reactivity of the total adhesive system. It indicates that this reaction, and this adhesive formulation, may be more random and hence less reliable. This formulation then presents both classical-type creep as well as temperature-dependent creep.
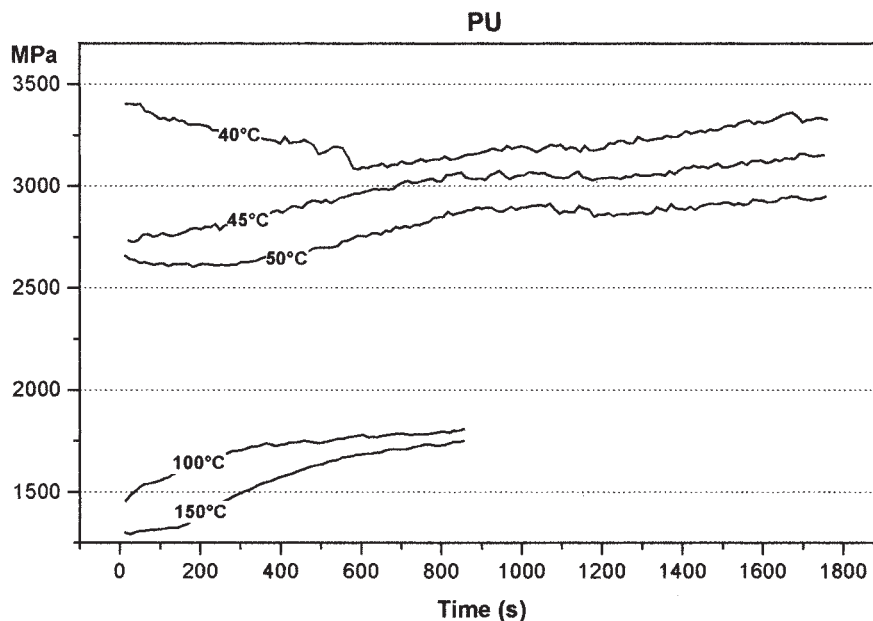
Figure 7 MOE as a function of time and temperature in 40°C, 45°C, 50°C, 100°C, and 150°C isothermal thermomechanical analysis in bending of cured beechwood joints bonded with PUR C, a commercial one-component polyurethane adhesive for structural wet and green wood gluing.
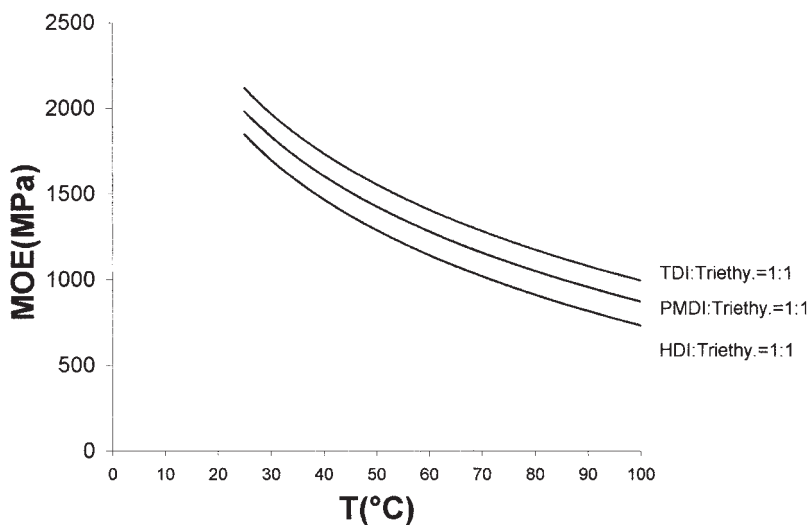
Figure 8 Variation of MOE as a function of temperature in isothermal thermomechanical analysis in bending of cured beechwood joints bonded with polyurethanes obtained from triethylenetetramine (TET) reacted with TDI, pMDI, and HDI isocyanates.

In conclusion, from the three commercial polyurethanes for wet and green wood gluing, the initial findings that can be drawn are:

i. Within limits, a higher or lower proportion of isocyanate to polyol does not affect total temperature-dependent creep. However, a higher proportion of isocyanate does give higher initial joint strength and lower creep at lower temperatures, namely up to 50°C, of the hardened glueline and consequently of the bonded joint. This is possibly due to greater crosslinking.

ii. Excessively high proportions of polyol, and excessively low proportions of isocyanate, involved in the formation of the polyurethane backbone may yield glue-lines and joints of lower initial strength. The later addition of further, not prereacted isocyanate to supply a sufficiently higher number of –NCO groups to ensure adequate levels of crosslinking does achieve the results wanted, but much more slowly. There is then, possibly, under certain application conditions, a certain possible randomness to the results that can be obtained according to the level of curing, namely, if the system is fully cured or did not have a chance to do so. If the system is fully cured, results from comparable to slightly worse than what is obtained with the systems in (i) can be obtained. If the system is not fully cured (it needs a trigger temperature or heat supplied to do so) then ambient temperature, classical-type creep becomes evident also.

The two types of commercial PUR systems tested correspond to two different concepts of adhesives for green wood gluing: (i) one is based on polyurethanes in which isocyanate and polyol are in approximately equivalent proportions and relatively rich in residual reactive –NCO groups on the skeletal chain of the polyurethane itself, while the other (ii) corresponds to a polyurethane chain with little or no residual –NCO groups due to the excess in polyol, supplemented by the final separate addition of reactive isocyanate almost functioning as a separate hardener as it is little or not linked to the main polyurethane chain. It is the polyol abundance in hydroxy groups that will achieve crosslinking with the latter –NCO groups during application. Both systems have been shown to work well, but both systems present temperature-dependent creep, while of the ones tested it is mainly the second type that presents temperature-independent creep also.

The second approach to understanding what the structural parameters are that influence creep and temperature-dependent creep in wet and green wood gluing was to compose the different polyurethanes by combining three structurally different isocyanates, namely pMDI, TDI, and hexamethylene diisocyanate (HDI), with different proportions of three structurally different amines, namely hexamethylenediamine (HMD), triethylenetetramine (TET), and diethylenetriamine (DET) (see Scheme 1). A curing temperature was used with these laboratory compositions just to make sure they are fully cured before demonstrating they still creep.

Figures 8 and 9 report the curves obtained by thermomechanical analysis of the variation of the MOE of a beech wood joint bonded and cured with simple polyurethane adhesives of different composition when submitted to a constant force. In Figure 8, with
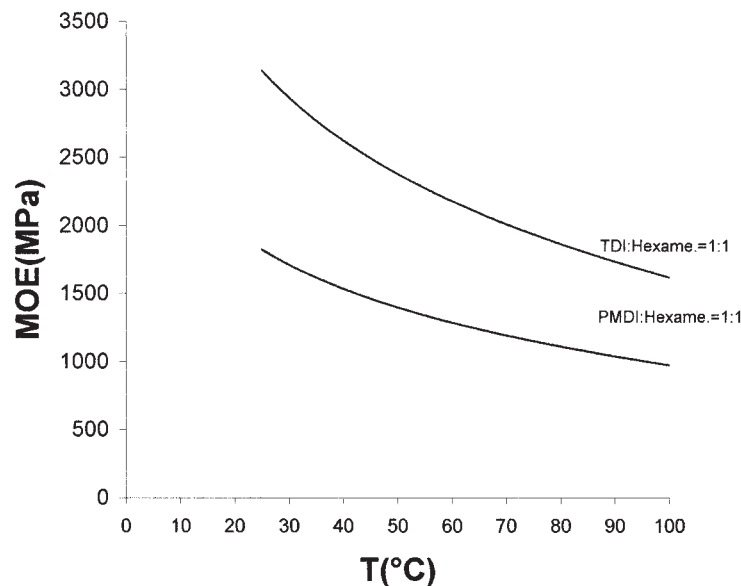
Figure 9 Variation of MOE as a function of temperature in isothermal thermomechanical analysis in bending of cured beechwood joints bonded with polyurethanes obtained from hexamethylenediamine (HMD) reacted with TDI and pMDI isocyanates.

the same TET amine and at the same proportions by weight of isocyanate : amine, two effects can be seen: (a) all three polyurethanes present temperature-dependent creep, MOE decreasing from around 2000 MPa at 25°C down to 800–1000 MPa at 100°C; and (b) the level of crosslinking, hence the higher MOE at parity of all other conditions, is higher for TDI, followed by pMDI, and lowest for HDI. This result is expected, as in TDI the distance between the different isocyanate groups is less than in pMDI; at equal weight, also, the molar proportion of TDI in relation to the amine is higher than for pMDI. HDI gives the lower result because the floppy, elastic hexamethylene chain introduces a greater level of flexibility and yield. It is remarkable, however, that the trend of temperature-dependent creep is the same for all three cases. The coefficient of correlation is good for all three cases, as reported in Table II with the relevant regression equations. The same TDI and pMDI trend is observed in Figure 9. Again, TDI gives the curve of higher MOE. The difference between the MOE of the TDI and pMDI cases is even more marked. The greater difference is due to the use in this case (Fig. 9) of the floppier of the three amines, HMD. However, the much lower pMDI curve appears to present lower rates of change with temperature, hence less temperature-dependent creep.

This means then that all polyurethanes present temperature-dependent creep. In general, isocyanates in the structure of which the segment between two isocyanate groups is shorter, or more rigid, present better strength, due possibly to greater crosslinking, hence TDI>pMDI>HDI (Figs. 8 and 9). The temperature-dependent creep can be more marked when the orig-inal strength of a joint is much higher, whenever very floppy linear segments are involved in the PUR structure (Fig. 8).

The effect of the proportion of polyol present can be very complex indeed. In Figures 10 and 11 at parity of isocyanate (TDI), a potentially more rigid polyamine or polyol (DET because with three reactive sites, against only two for HMD) yields better strength and slightly greater temperature-dependent creep the higher is the proportion of polyol, although the differences are not excessive (Fig. 10). Hence, increasing the proportion of polyamine or polyol with more reactive sites increases or favors tridimensional crosslinking, hence strength, but does not unduly influence temperature-dependent creep. With more floppy polyamines or polyols with only two reactive sites (HMD here) (Fig. 11), the lower the proportion of polyol, the higher the strength as crosslinking is maximized, and the higher is the temperature-dependent creep simply because the original strength of the joint is much higher. Conversely, a higher proportion of floppy, two-sites polyol produces much lower strength and much lower temperature-dependent creep. It appears then that temperature-dependent creep is an intrinsic characteristic of polyurethanes that can be minimized by decreasing the maximum strength of a joint, whatever its composition. This might be acceptable in some situations but generally is negative. Both the cases in Figures 10 and 11 were obtained from isocyanate : polyol parity to excess of polyols. The cases in which one passes from isocyanate : polyol parity to defect of polyol yield better strength and greater temperature-dependent creep the higher is the proportion of

TABLE II
Regression Curves of Experimental Temperature-Dependent Creep Results Obtained by Isothermal Thermomechanical Analysis Connecting the Value of the MOE Obtained with the Temperature Used for the Deflection According to the Equation MOE (MPa) = A ln T(°C) + B

Case	Proportion	A	B	r^a	max MOE 25°C (MPa)	min MOE 100°C (MPa)
TDI : HMD	1 : 1	−1096.2	6667.4	0.95	3000	1550
	0.7 : 1	−335.1	2360.1	0.73	1500	850
	0.5 : 1	−386.3	2588.1	0.60	1650	1000
TDI : DET	1 : 1	−531.6	2526.7	0.98	800	110
	0.7 : 1	−624.0	3165.9	0.98	1150	340
	0.5 : 1	−551.6	2675.1	0.99	910	205
	0.3 : 1	−698.3	3380.9	0.97	1220	260
TDI : TET	1 : 1	−809.6	4727.3	0.99	2200	1000
PMDI : TET	1 : 1	−800.2	4557.7	0.94	2100	1000
PMDI : HMD	6 : 1	−139.3	832.5	0.66	375	-
	4 : 1	−155.7	988.3	0.89	475	305
	2 : 1	−204.8	1183.5	0.94	540	280
	1 : 1	−611.6	3790.9	0.78	2000	900
PMDI : DET	6 : 1	−95.4	1010.5	0.39	680	450
	4 : 1	−306.6	1789.2	0.86	910	450
	2 : 1	−114.9	1047.1	0.93	650	500
	1 : 1	−607.7	3647.5	0.68	1700	500
HDI : TET	1 : 1	−803.02	4431.3	0.98	1875	700
HDI : HMD	1 : 1	73.78	518.9	0.36	700	920

[a] Coefficient of correlation.

polyol; two such cases, with two different polyols, are shown in Figures 12 and 13.

As regards the effect of the type polyol, this is also of importance. In Figure 14 TDI/HMD gives higher strength than TDI/TET. This might appear strange as TET should potentially introduce better crosslinking; hence, the reverse of what is shown in the figure should be true. However, in the case of Figure 14, the proportion of TDI is not enough to react with all the potential reactive sites of TET, and TET reacting on

average with only two sites becomes even more floppy than HMD (a chain of 11 atoms between the two reactive/reacted amines for TET, instead of 6 in the case of HMD).

Creep and temperature-dependent creep in polyurethane networks are then due to the relative proportions of covalently-linked and just physical entanglement nodes in the hardened network. The longer the average segments of polymer between covalently-linked nodes in the network, the higher will be the
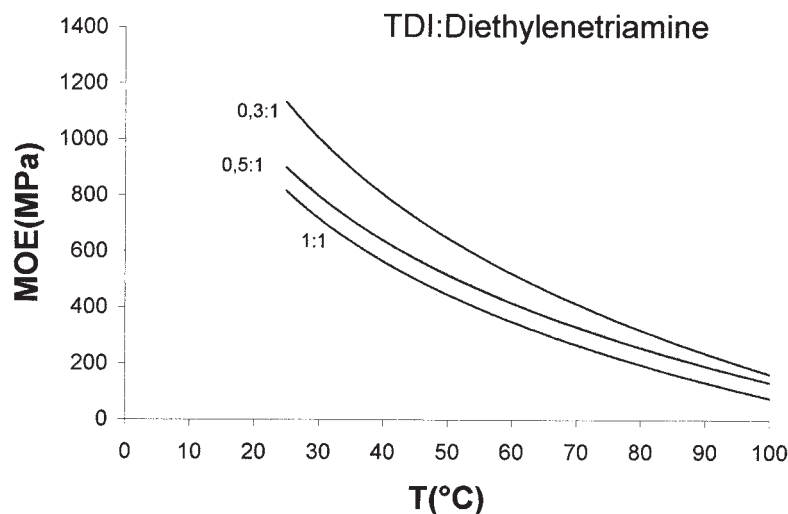

Figure 10 Variation of MOE as a function of temperature in isothermal thermomechanical analysis in bending of cured beechwood joints bonded with polyurethanes obtained from varying the relative proportions by weight of amine and isocyanate. Case of dithylenetriamine (DET) reacted with TDI isocyanates.
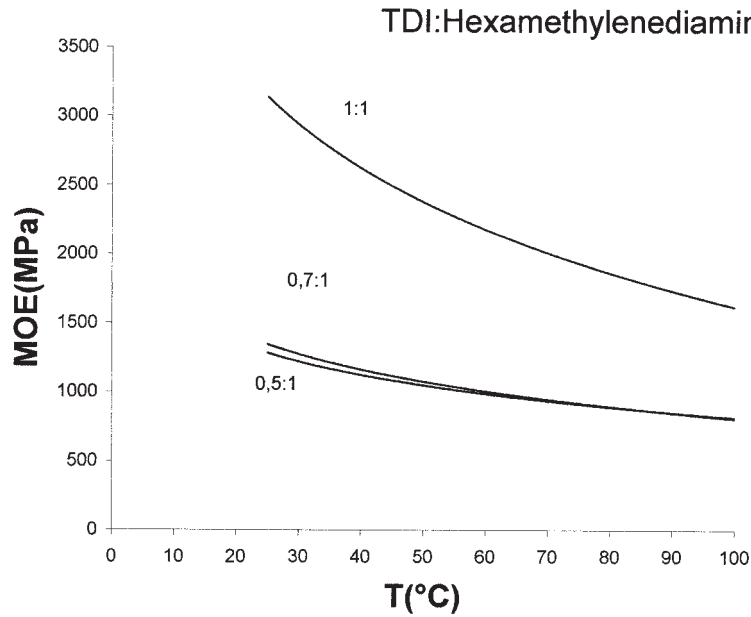
Figure 11 Variation of MOE as a function of temperature in isothermal thermomechanical analysis in bending of cured beechwood joints bonded with polyurethanes obtained from varying the relative proportions by weight of amine and isocyanate. Case of hexamethylenediamine (HMD) reacted with TDI isocyanates.

relative proportion of physical entanglement nodes in the network. The higher the proportion of all nodes, the lower creep is likely to be at ambient temperature. However, due to segment movement and easier disentanglement with increasing temperature, the lower the proportion of covalently-linked nodes, the greater the temperature-dependent creep will be. The higher the proportion of covalently-linked nodes in relation to just physical entanglement, the lower the temperature-dependent creep is.

In Table II are indicated also other cases besides those shown in the figures. All the cases considered in Figures 8 to 14 are those where the coefficient of correlation r is good enough to establish some repeatable trends. However, the cases in which the coefficient of correlation r is not good enough, have not
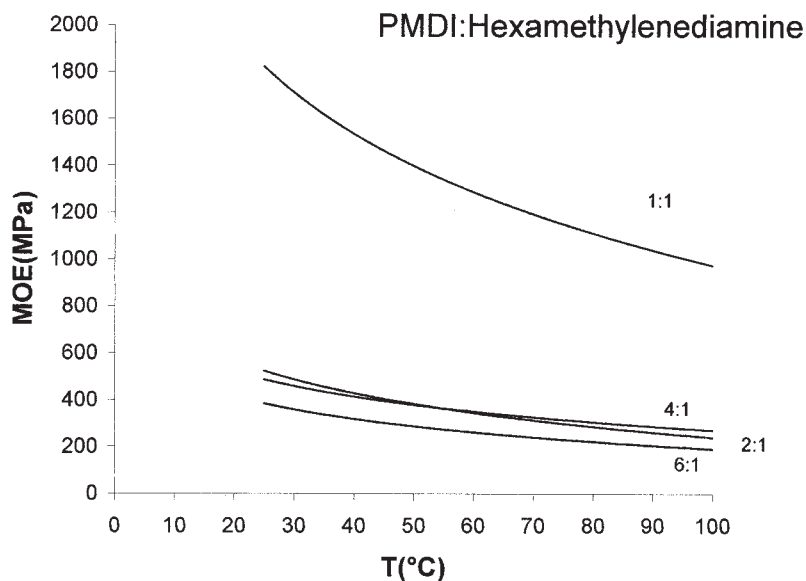

Figure 12 Variation of MOE as a function of temperature in isothermal thermomechanical analysis in bending of cured beechwood joints bonded with polyurethanes obtained from varying the relative proportions by weight of amine and isocyanate. Case of hexamethylenediamine (HMD) reacted with pMDI isocyanates.
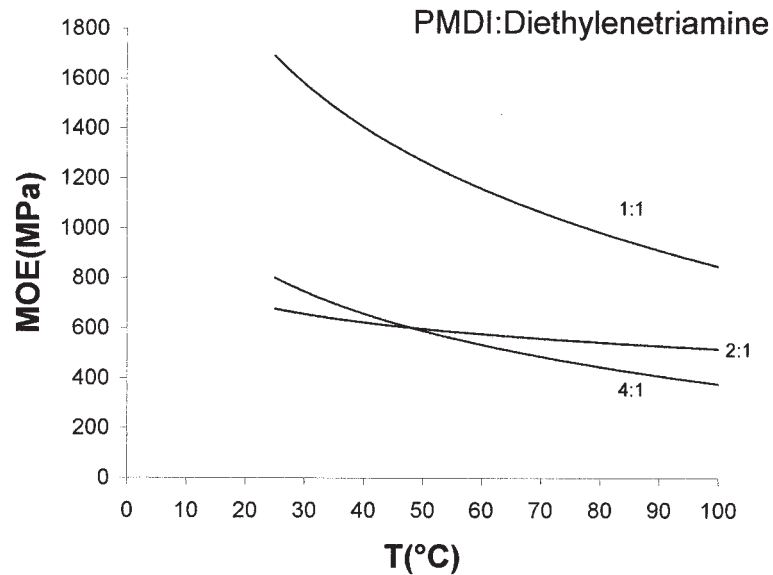
Figure 13 Variation of MOE as a function of temperature in isothermal thermomechanical analysis in bending of cured beechwood joints bonded with polyurethanes obtained from varying the relative proportions by weight of amine and isocyanate. Case of dithylenetriamine (DET) reacted with pMDI isocyanates.

been considered as they cannot really contribute to establishing proper trends between structure, creep, and performance.

CONCLUSIONS

The conclusions that can be drawn from these results about industrial one-component polyurethane adhesives for green and wet wood gluing are:

1. Within limits, a higher or lower proportion of isocyanate to polyol does not affect total temperature-dependent creep. However, a higher proportion of isocyanate does give higher initial joint strength and lower creep at lower temperatures, namely up to 50°C, of the hardened glue-line and consequently of the bonded joint. This is possibly due to greater crosslinking.
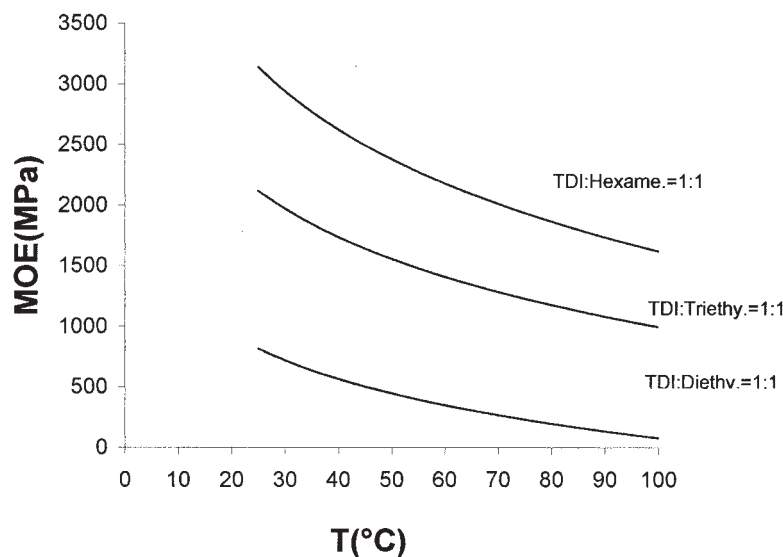

Figure 14 Variation of MOE as a function of temperature in isothermal thermomechanical analysis in bending of cured beechwood joints bonded with polyurethanes obtained by varying the type of amine. Case of TDI isocyanate with hexamethylenediamine (HMD) and triethylenetetramine (TET).

2. Excessively high proportions of polyol and excessively low proportions of isocyanate involved in the formation of the polyurethane backbone may yield glue-lines and joints of lower initial strength.

From more defined laboratory synthesis of polyurethanes for the same application:

1. All polyurethanes studied present temperature-dependent creep, and this is one of their intrinsic characteristics.
2. In general, isocyanates in the structure of which the segment between two isocyanate groups is shorter, or more rigid, present better strength, due possibly to greater crosslinking, hence TDI>pMDI>HDI.
3. In general, the floppier and the higher the number of degrees of freedom introduced in the network by the polyol, the lower is the strength and the lower is the creep.
4. The temperature-dependent creep can be more marked when the original strength of a joint is much higher whenever very floppy linear segments are involved in the PUR structure.
5. From isocyanate : polyol weight parity to excess of polyols, increasing the proportion of polyamine or polyol with more reactive sites increases or favors tridimensional crosslinking, hence improves strength, but does not unduly influence temperature-dependent creep.
6. From isocyanate : polyol weight parity to excess of polyols, in the case of more floppy polyamines or polyols with only two reactive sites (HMD here), the lower the proportion of polyol, the higher is the strength as crosslinking is maximized, and the higher is the temperature-dependent creep simply because the original strength of the joint is much higher.
7. From isocyanate : polyol weight parity to a deficiency of polyol, better strength and greater temperature-dependent creep are obtained the higher is the proportion of polyol.

Finally, the higher the proportion of all hardened network nodes, the lower creep is likely to be at ambient temperature. Instead, due to segment movement and easier disentanglement with increasing temperature, the lower the proportion of covalently-linked nodes and the greater the proportion of just physical entanglement nodes, the greater will the temperature-dependent creep be.

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