

Colourless formaldehyde-free urea resin adhesives for wood panels

A. Despres · A. Pizzi · C. Vu · L. Delmotte

Received: 18 April 2008 / Published online: 29 May 2009
© Springer-Verlag 2009

Abstract Amino resin precursors prepared by the addition of a new, colourless, non-volatile and non-toxic aldehyde, dimethoxyethanal (DME), to urea gave resins for boards that while able to harden were underperforming due to the lower reactivity of DME in relation to formaldehyde. Urea reacts with one and even two molecules of DME to form UDME and U(DME)₂ (called DU) but the subsequent cross-linking reaction to form bridges between two ureas, although existing as observed by CP MAS ¹³C NMR, was too slow at temperatures lower than 140 °C to be of significance for wood panel adhesives. However, addition of 20% isocyanate (pMDI) contributed to cross-linking of DU by its reaction with pMDI to also form urethane bridges, their existence being confirmed by CP-MAS ¹³C NMR. The adhesive resins so formed had excellent performance, were colourless, and produced boards that satisfied well the requirements of the relevant norms for interior panels (EN 120 and EN 312). The results were good enough to decrease the proportion of pMDI to 14% at pressing times starting to be of significance for industrial panel products. Formaldehyde emission, by perforator method was down exclusively to the formaldehyde produced by heating the wood chips.

The panel emission was sufficiently low to even satisfy the relevant F**** JIS A 5908 Japanese standard (JIS A 5908, 1994). These adhesives are colourless, as UF resins.

Farblose, formaldehydfreie Harnstoffharzkleber für Holzwerkstoffplatten

Zusammenfassung Durch Zugabe von Dimethoxyethanal (DME), einem neuen, farblosen, nicht flüchtigen und ungiftigen Aldehyd, zu Harnstoff, wurden Vorstufen von Aminoharz hergestellt. Dies ergab Harze, die zwar härteten, jedoch aufgrund der im Vergleich zu Formaldehyd geringeren Reaktivität von DME die Erwartungen nicht ganz erfüllten. Harnstoff reagiert mit einem oder auch zwei DME-Molekülen und bildet UDME und U(DME)₂ (als DU bezeichnet). Die nachfolgende Vernetzungsreaktion zur Bildung von Brücken zwischen zwei Harnstoffen war zwar, wie anhand CP-MAS ¹³C NMR gezeigt wurde, vorhanden, bei Temperaturen unter 140 °C war sie jedoch zu langsam, um die Anforderungen an Klebstoffe für Holzwerkstoffe zu erfüllen. Mittels CP-MAS ¹³C NMR konnte nachgewiesen werden, dass durch Zugabe von 20% Isocyanat (pMDI) die Vernetzung von DU durch Reaktion mit pMDI durch zusätzliche Bildung von Urethan-Brücken verbessert wurde. Die so hergestellten Harze zeigten ausgezeichnete Eigenschaften, sie waren farblos und ergaben Platten, die die Anforderungen der entsprechenden Normen für Platten im Innenbereich (EN 120 und 312) erfüllten. Die Ergebnisse waren so gut, dass der pMDI-Anteil auf 14% verringert werden konnte bei Presszeiten, die für eine industrielle Produktion noch akzeptabel sind. Die mittels Perforatormethode ermittelte Formaldehydemission hing ausschließlich von dem beim Erhitzen der Holzspäne entstandenen Formaldehyd ab. Die Plattenemission war so niedrig, dass sie sogar

A. Despres · A. Pizzi (✉)
ENSTIB-LERMAB, University of Nancy 1,
27 rue du Merle Blanc,
88000 Epinal, France
e-mail: antonio.pizzi@enstib.uhp-nancy.fr

A. Despres · C. Vu
Clariant (France), LRA, Usine de Lamotte,
Trosly-Breuil, France

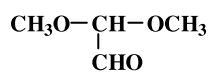
L. Delmotte
ENSCMu, Mineral Materials Laboratory,
University of Haute Alsace,
13 rue Jean Starcky,
Mulhouse, France

die Anforderungen der entsprechenden japanischen Norm F**** JIS A 5908 erfüllte. Diese Klebstoffe sind wie die UF-Harze farblos.

1 Introduction

Amino resins based on urea-formaldehyde condensation are the major binders for wood composite boards such as plywood, medium density fibreboards and particleboards. However, the main drawback of these resins is their principal component: formaldehyde. Formaldehyde is classified as dangerous to health. Approximately eleven million tons of urea-formaldehyde resins are produced and used yearly in the world, the greater proportion of these as binders for wood products. The ever decreasing formaldehyde emission limits, hence formaldehyde resin content, imposed by ever stricter standard regulations have induced considerable research not only (i) in the engineering of UF resins of ever decreasing formaldehyde content (Pizzi 1994), but also (ii) in the development of all sorts of alternative resins to urea-formaldehyde (Amaral-Labat et al. 2008, Ballerini et al. 2005, El Mansouri et al. 2007, Lei et al. 2008, Liu and Li 2007, Lorenz et al. 2006, Pizzi et al. 1995, Pichelin et al. 2006, Wescott et al. 2006, Zanetti and Pizzi 2004). One area that has not been much explored is the use of alternative, non-toxic, non-volatile aldehydes to produce urea-based resins. Alternative aldehydes have also problems: either they are coloured (furfural) (Pizzi 1983) rendering the resin unsuitable for a number of applications; or they are also toxic to some level; or they are also volatile; or they present potential problems of solubility (Mansouri and Pizzi 2006, Wang and Pizzi 1997); or they present reactive problems with urea (glyoxal) (Despres 2006).

Recently, a newly conceived aldehyde that is uncoloured, water clear, non-toxic and non-volatile has been developed and produced (Clariant 2002). It is dimethoxyethanal (DME), a derivative of glyoxal.



Its only problem is its level of reactivity with urea phenols and melamine which is considerably slower than formaldehyde.

This paper deals with a study to produce urea-DME (called DU) resins where cross-linking and reactivities are

enhanced to produce adhesives suitable for particleboard and other wood panels of zero to very low formaldehyde emission, while maintaining all the other advantages of UF resins.

2 Experimental

2.1 Preparation of the dimethoxyethanal (DME) based resin

Urea-DME resin (DU) 147 g of urea (2.45 mol) was added to 849.3 g (4.9 mol) of a 60% dimethoxyethanal solution in water in a stirred reactor. The pH was adjusted and kept with 30% NaOH solution at 9–9.5. The mix was heated at 45 °C for 2 hours. The pale yellow resin was then cooled and stored at ambient temperature. DU is already prepared industrially by Clariant (France) Pty Ltd. The commercial product was sometime used as ready-made.

During the different tests, the resins were always used with a hardener: 5% solid of ammonium sulfate (30% in water).

2.2 The isocyanate used

A commercial polymeric diphenylmethane diisocyanate (pMDI) (Bayer: Desmodur VKS20) was used where indicated (Table 1).

2.3 CP-MAS ¹³C NMR

The solid state CP-MAS ¹³C NMR spectra of the hardened DU/pMDI resin systems used, of the DU resin control, and of the hardened water/pMDI product were obtained on a Bruker MSL 300 FT-NMR spectrometer at a frequency of 75.47 MHz and at a sample spin of 4.0 kHz. The pulse duration at 90 °C was 4.2 μs, contact time was 1 ms, number of transients was about 1,000, and the decoupling field was 59.5 kHz. Chemical shifts were determined relative to tetramethyl silane (TMS) used as a control.

2.4 Particleboard preparation and testing

The DU precursor resin and pMDI were premixed prior to application on the wood particles in the proportions shown in Table 1.

Table 1 Glue-mixes and dry wood proportion for one layer laboratory particle boards

Tabelle 1 Klebstoffmischungen und Trockenholzanteil für die Herstellung von einschichtigen Laborspanplatten

	Sample number and quantities of dry products (g)			
	1	2	3	4
Dry wood	1000	1000	1000	1000
Dry resin U/DME (1/2) (DU)	120		80	56
Dry hardener ((NH ₄) ₂ SO ₄)	6		4	2,8
pMDI Desmodur VKS20		22	20	14

Duplicate single layer particleboard of $350 \times 350 \times 14 \text{ mm}^3$ was made using core wood particles with 2% moisture content. The particles were taken from a board mill and were composed 50/50 (weight/weight) of hardwood/softwood species. A rotary drum blender and an automated hot press were used to make the laboratory panels. Resins were hardened by addition of 5% ammonium sulfate as a 30% water solution based on solid resin and the resin solids load on dry wood weight/weight was 10% and 7%. The hot pressing time was 42 s/mm (10 minutes) at 193 °C. Faster pressing times were also used as indicated in the tables, namely 32 s/mm (7.5 minutes), 5.5 minutes 23.5 s/mm (5 minutes) and 17 s/mm (4 minutes). Faster press times could not be implemented due to mechanical limitations of the press used. Several panels (5 panels per each case reported) ($350 \times 300 \times 14 \text{ mm}^3$) were made for each resin and each pressing condition. The target specific gravity of the panels was about 660–680 kg/m^3 . The pan-

els were tested for internal bond (IB) strength according to EN 312 (EN 312, 1995).

For each panel, the formaldehyde emitted by the panels was collected by perforator (EN 120) and the formaldehyde emitted was measured by iodometric titration and given for 6.5% moisture content. Comparative results obtained by dessicator method according to Japanese Standard JIS A 5908 were also obtained.

3 Results and discussion

The characteristic composition of the DU resin precursor of urea:DME 1:2 molar ratio can be gleaned by the liquid phase ^{13}C NMR quantitative spectrum shown in Fig. 1. In Fig. 1, the C=O groups of unreacted, monosubstituted and N,N'-disubstituted urea are clearly shown. The small free urea band indicates that DME has reacted almost quantita-

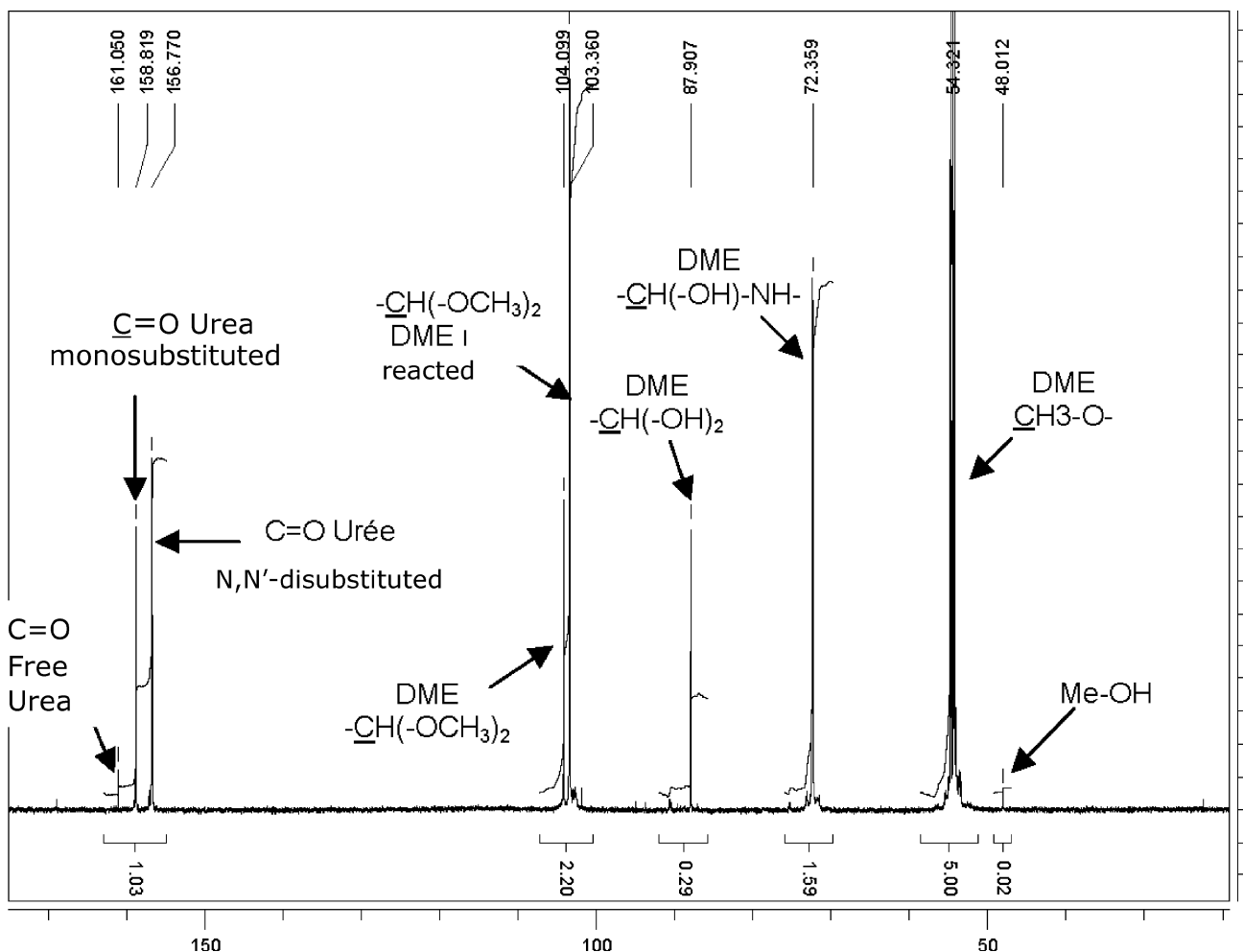


Fig. 1 ^{13}C NMR liquid phase spectrum of the DU resin precursor of urea:DME 1:2 molar ratio at 66.7% concentration in water

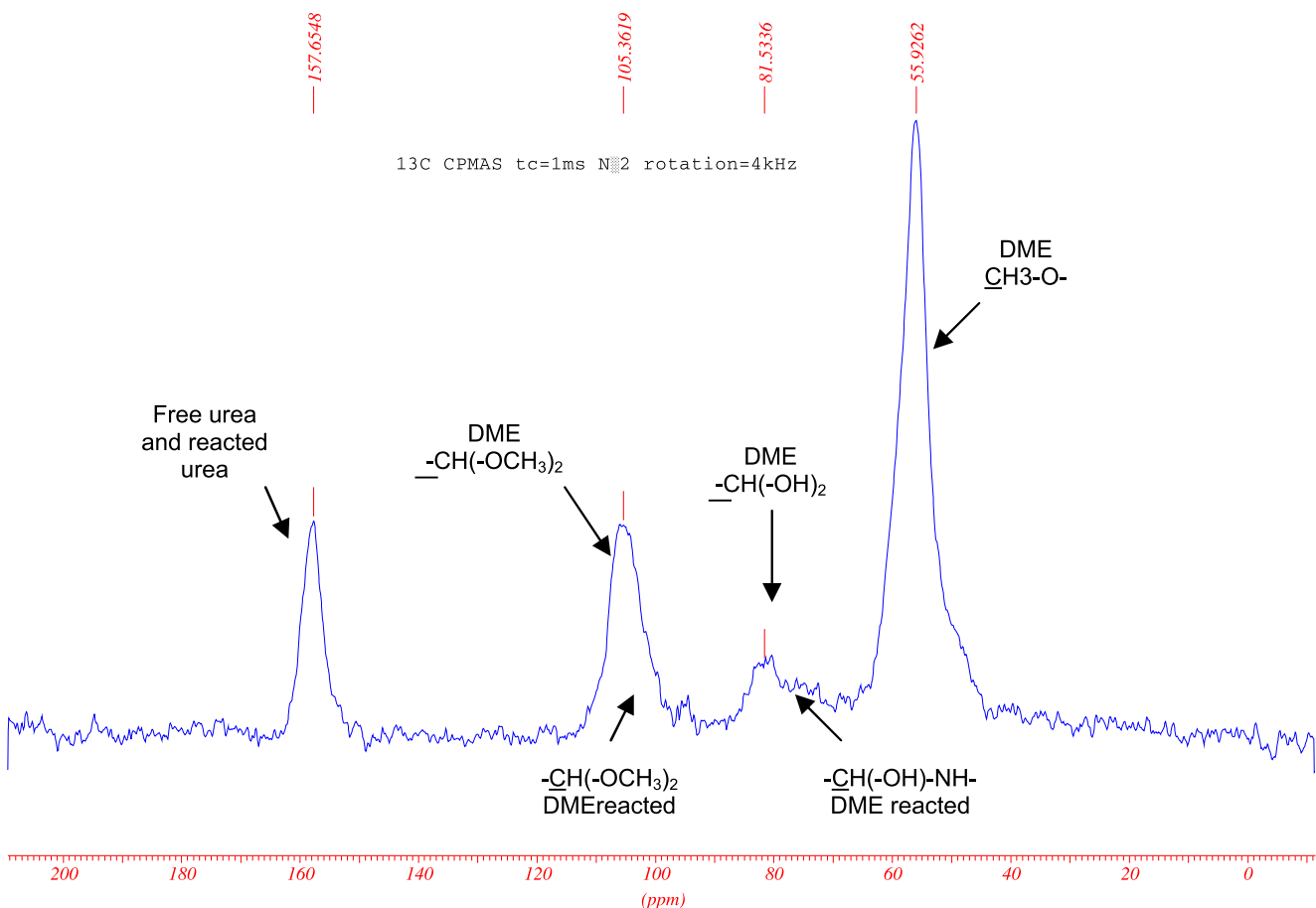
Abb. 1 ^{13}C NMR Flüssigphasenspektrum der DU-Harz Vorstufe mit einem Molverhältnis von 1:2 (Harnstoff:DME) bei einer Konzentration von 66,7% in Wasser

Table 2 Results of laboratory panels bonded with the glue mixes given in Table 1**Tabelle 2** Ergebnisse der mit den in Tabelle 1 aufgeführten Klebstoffmischungen verklebten Laborplatten

Sample number	Resin load (%)	Pressing time (min)	Specific gravity (kg/m ³)	Internal bond (MPa)
1. DU alone	12	10 min	627 (springback)	0.02 MPa
2. pMDI alone	2.2	10 min	624 (springback)	0.16 MPa
3. DU + 20% pMDI	10	10 min	691	0.71 MPa
4. DU + 20% pMDI	7	10 min	687	0.54 MPa

Table 3 Formaldehyde emission of DU + pMDI 14 mm thick panels. E1 = 6.5 mg/100 g, E0 = 2 mg/100 g, F**** ≤ 0.3 mg/l**Tabelle 3** Formaldehydemission von 14 mm dicken mit DU + pMDI verklebten Platten. E1 = 6,5mg/100 g, E0 = 2 mg/100 g, F**** ≤ 0,3mg/l

Panel	Resin load (%)	Pressing time (minutes)	Internal bond strength (MPa)	Formaldehyde emission perforator (mg HCHO/100 g)	Formaldehyde emission dessicator (mg/l)
DU + 20% pMDI	7%	10	0.53	0.5	0.11
DU + 20% pMDI	7%	7.5	0.48	1.1	0.21
DU + 20% pMDI Three-layer (16 mm)	7% core, 12% surface	10	0.40	0.6	0.10
DU + 20% pMDI	7%	5.5	0.36	0.8	0.15
DU + 20% pMDI	10%	4	0.42	0.8	0.16
DU + 20% pMDI	9%	4	0.42	0.7	0.13

**Fig. 2** Control solid state CP-MAS ¹³C NMR spectrum of the DU resin hardened at 103 °C**Abb. 2** Festkörper-CP-MAS ¹³C NMR Referenzspektrum von bei 103 °C gehärtetem DU-Harz

tively with urea. The integration of the C=O group signals of the three ureas allows to calculate the relative proportions of unreacted, monosubstituted and N,N'-disubstituted urea in DU. These are respectively 2.4%, 29.3% and 68.3%. Thus, DU is composed of traces of free urea and the two species at a ratio of approximately 1:2.

This calculation indicates that part of the DME has not reacted and remains free, because if all had reacted only one urea C=O band would have been left, namely that at 156.8 ppm. The proportion of DME which has not reacted can be accurately calculated by the ratio of the 87.9 and 72.4 ppm peaks representing the carbon of the aldehyde (in the form of glycol) respectively unreacted or reacted once only. This indicates that approximately 15% of the DME is still free in DU. Last, the band indicating the formation of an alkyl methine (–CHR–) bridge due to the reaction of the aldehyde with two ureas to form a dimer, which should

occur at 49–50 ppm, is absent. This indicates that the reactivity of the DME aldehyde group is so low that only the addition phase to urea occurs, but not the consequent condensation reaction.

The lack of condensation and polycondensation, due to the low reactivity of the hydroxy alkyl methine group formed after the initial addition of DME onto the urea is the reason why the internal bond (IB) strength results of particleboard bonded with DU alone were so bad (cf. Tables 1 and 2, first line). It is for this reason that it was necessary to use an alternate cross-linking reaction, not based on the low reactivity with urea of the DU hydroxy alkyl methine group. The cross-linking reaction chosen was that characteristic of adhesives methylol groups with an isocyanate to form urethane bridges (Pizzi and Walton 1992, Pizzi et al. 1993, Pizzi 1994, Despres et al. 2006, Wieland et al. 2006).

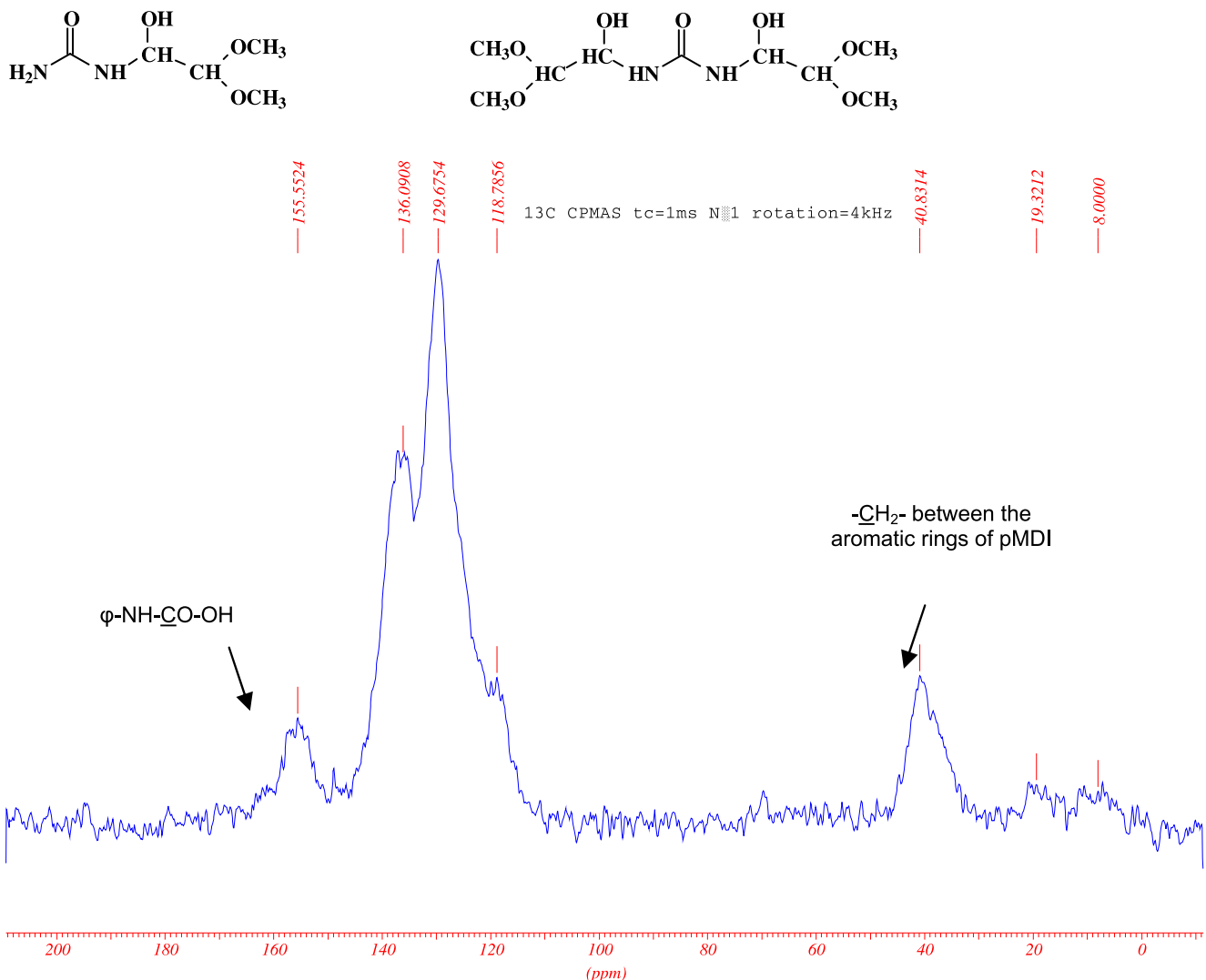


Fig. 3 Solid state CP-MAS ^{13}C NMR spectrum of the hardened product obtained by the reaction of pMDI with water at 103 °C

Abb. 3 Festkörper CP-MAS ^{13}C NMR-Spektrum des gehärteten Produkts, das durch Reaktion von pMDI mit Wasser bei 103 °C erhalten wurde

The results in Table 2, based on the glue-mixes shown in Table 1, indicate that urethane bridges cross-linking does give good boards. It confirms that it is not the pMDI reacting by itself that yields such good results: pMDI alone, in the same proportion on dry wood as used in the DU + pMDI mix gives a poor result. Table 2 shows that results satisfying the relevant European Norm EN 312 for interior grade particleboard can be obtained with a resin solids content down to 7% on dry wood when using relatively long press times. The influence of decreasing the pressing time on the IB strength was then studied and the results obtained are shown in Table 3. Pressing times as short as 4 minutes were obtained at a comparatively low temperature of 193 °C. This indicates that in the temperature ranges (approx 220 °C) usually employed to-day in particleboard pressing it appears possible to achieve industrially significant pressing times with such adhesive formulations. Of greater interest are the low formaldehyde emission values obtained by the perforator method (EN 120 1995), reported in Table 3. These are limited only to the formaldehyde generated by heat-

Table 4 Results of one layer laboratory particleboard when decreasing the relative proportion of pMDI in relation to DU

Table 4 Ergebnisse der einschichtigen Laborspanplatten, wenn der relative pMDI-Anteil im Verhältnis zu DU reduziert wurde

Formulation	Specific gravity (kg/m ³)	IB strength (MPa)
80% DU + 20% pMDI	710	0.66
83% DU + 17% pMDI	714	0.48
86% DU + 14% pMDI	715	0.45

ing the wood without any contribution of the resin. It is clear that such perforator values indicate that such colourless resins are capable of satisfying even more severe standards, such as the F**** JIS A 5908 (JIS A 5908, 1994), as indicated in Table 3, as regards formaldehyde emission. In Table 4, the results obtained by decreasing the relative proportion of pMDI in relation to DU are shown. Internal bond strength results still satisfying EN 312 are still obtained when using a lower proportion of 14% pMDI in the formulation. Furthermore, it must also be pointed out that

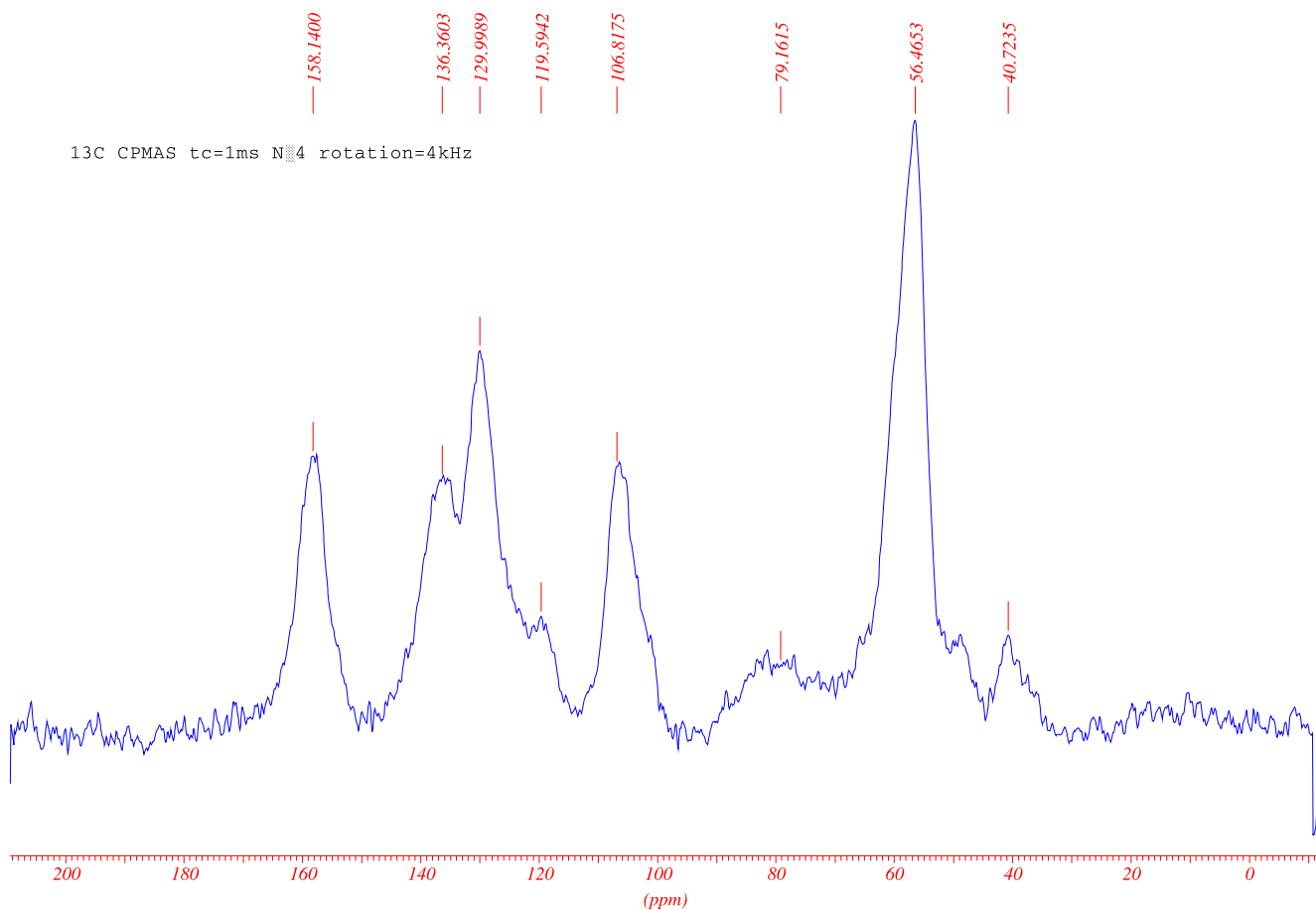


Fig. 4 Control solid state CP-MAS ¹³C NMR spectrum of the hardened product obtained by the reaction at 103 °C of a pMDI with DU resin in water

Abb. 4 Festkörper-CP-MAS ¹³C NMR Referenzspektrum des gehärteten Produkts, das bei 103 °C durch Reaktion von pMDI mit DU-Harz in Wasser erhalten wurde

the formulations described can be mixed in any proportion with urea-formaldehyde resins, to have hybrid cases, the cases reported here being the ones where no formaldehyde at all has been used.

It is necessary to understand the reaction of DU with an isocyanate to understand the results shown in the tables. The solid state CP-MAS ^{13}C NMR spectrum of the DU resin, the pMDI and the mix of both of them, all hardened in the oven at 103° , are shown in Figs. 2, 3 and 4. In Fig. 2, the 157.6 ppm band belongs to the carbonyl of substituted, cross-linked ureas in the hardened network. The 105.3 ppm band belongs to the carbon onto which the methoxy group of DME reacted with urea is linked but still free of the network. The bands at 55.9 ppm and at 81.5 ppm belong to the free methoxy group, and the glycol form of the aldehyde group of unreacted DME. Last, the 76 ppm band belongs to the aldehyde group of DME that has only reacted with a single urea. Two bands that do not occur in the spectrum of unreacted DME are noticeable in Fig. 2. These at 68 and 95 ppm are small but of interest. The 68 ppm band belongs to the carbon of the aldehyde that has reacted twice with urea and thus forming a bridge between two ureas. The 95 ppm band belongs to the carbon to which a methoxy group is attached for DME molecules that have reacted twice with urea. The very low integrated area of these last two peaks indicates that while the reaction of cross-linking based only on the reaction of DME and urea can occur, its extent is very low indeed. This also explains why DU alone does not give good board results. A higher temperature, namely 140°C was shown by FT-IR (Despres 2006) to be necessary to increase the relative proportion of this condensation.

The pMDI was hardened in presence of a considerable amount of water and under continuous mechanical agitation. The CP-MAS ^{13}C NMR spectrum of pMDI hardened in presence of water is shown in Fig. 3. The first noticeable point is that the band characteristic of unreacted isocyanate groups at 123–125 ppm is just reduced to an almost non perceptible shoulder, confirming the high proportion of this group that has reacted. High proportions of unreacted isocyanate would have caused this band to be of intensity comparable to that of the dominant 129.7 ppm band (belonging to the symmetrical C2 and C6 of the aromatic rings in relation to the $-\text{CH}_2-$ link of the diphenylmethane). Furthermore, both are broad bands centred at 155.6 ppm but having a range from 150 to 163 ppm, and a band at 118.8 ppm appears which does not occur in liquid pMDI. All this indicates that the isocyanate has reacted with water as (i) the broad band at 150–163 ppm is indicative of the existence of three different C=O groups. These are the carboxyl groups of carbamic acid expected at 155.9 ppm, the C=O of polyurea groups of the type $\text{Ar}-\text{NH}-\text{CO}-\text{NH}-\text{Ar}$ expected at 152.4 ppm, and $\text{Ar}-\text{NH}-\text{CO}-\text{N}(-\text{Ar})-\text{CO}-\text{NH}-\text{Ar}$. This shows

that there is a high proportion of polyureas and carbamic acid groups imbedded in the network. Furthermore, this is supported by the appearance of the 118–119 ppm band, as the aromatic C3 and C5 of polyureas and carbamic acid occur at 119.1 ppm and 118.8 ppm, respectively, as does the 136 ppm peak of the C4 of carbamic acid. It does not appear that any biuret is present as its characteristic bands at 115.7 (C3 and C5) and 146 ppm (C4) are absent.

The CP-MAS ^{13}C NMR spectrum of the mix of DU and pMDI is shown in Fig. 4. Comparing this spectrum with those in Figs. 2 and 3 of the two reagents hardened independently, there is only one major difference: the appearance of a band at 48 ppm. This is the band of the reaction bridge formed between the isocyanate and the DU, namely the shift of the $-\text{CH}-$ of the urethane formed by reaction of the $-\text{CRH}-\text{OH}$ of the DU with the isocyanate group. The reaction is then the same as the one occurring between pMDI and formaldehyde-based resins (Pizzi and Walton 1992, Pizzi et al. 1993, Pizzi 1994, Despres et al. 2006, Wieland et al. 2006).

4 Conclusion

In conclusion, the reaction of 20% isocyanate (pMDI) with DU, a urea-DME resin precursor containing no formaldehyde, and where the aldehyde used is non toxic and non-volatile, allows the preparation of particleboards of excellent properties and this at acceptably fast board pressing times. The panels prepared have very weak formaldehyde emission, only the proportion emitted in heating the wood chips and no formaldehyde emitted from the adhesive as no formaldehyde was used. The panel properties then fulfill the F**** requirement according to Japanese standard JIS A 5908. The use of water-emulsified pMDI still gives good results but lower than what was obtained with non-emulsified pMDI (not reported here) (Despres 2006). It must also be pointed out that the formulations described can be mixed in any proportion with urea-formaldehyde resins, the cases reported here being the ones where no formaldehyde at all has been used.

References

- Amaral-Labat GA, Pizzi A, Goncalves AR, Celzard A, Rigolet S (2008) Environment-friendly soy flour-based resins without formaldehyde. *J Appl Polymer Sci* 108:624–632
- Ballerini A, Despres A, Pizzi A (2005) Non-toxic, zero-emission tannin-glyoxal adhesives for wood panels. *Holz Roh- Werkst* 63:477–478
- Clariant (France) (2002) Highlink DM: A non toxic agent to produce formaldehyde-free aminoplast cross-linkers. Brochure

- Despres A (2006) Mise au point de nouvelles résines aminoplastes écologiques à base de diméthoxyéthanal et sans formaldéhyde pour application en tant que colles pour panneaux de particules. PhD thesis, ENSTIB, University Henri Poincaré – Nancy 1, Epinal, France
- Despres A, Pizzi A, Delmotte L (2006) ^{13}C NMR investigation of the reaction in water of UF resins with blocked emulsified isocyanates. *J Appl Polymer Sci* 99:589–596
- El Mansouri N-E, Pizzi A, Salvadó J (2007) Lignin-based wood panel adhesives without formaldehyde. *Holz Roh- Werkst* 65: 65–70
- European Norm EN 120 (1995) Wood-based panels. Determination of formaldehyde content. Perforator extraction method
- European Norm EN 312 (1995) Wood particleboard – Specifications
- Japanese Standards Association (JIS) JIS A 5908 (1994). Particleboards, Tokyo, Japan
- Lei H, Pizzi A, Du G (2008) Environment-friendly, mixed tannin/lignin wood resins. *J Appl Polymer Sci* 107:203–209
- Liu Y, Li K (2007) Development and characterization of adhesives from soy protein for bonding wood. *Int J Adhesion Adhes* 27:59–63
- Lorenz L, Frihart CR, Wescott JM (2006) Analysis of soy flour/phenol-formaldehyde adhesives for bonding wood. *Proceedings Wood Adhesives 2005*, Forest Products Society, Madison, Wisconsin, pp 501–506
- Mansouri HM, Pizzi A (2006) Urea-formaldehyde-propionaldehyde physical gelation resins for improved swelling in water. *J Appl Polymer Sci* 102:5131–5136
- Pichelin F, Nakatani M, Pizzi A, Wieland S, Despres A, Rigolet S (2006) Thick wood panels bonded industrially with formaldehyde free tannin adhesives. *Forest Prod J* 56:31–36
- Pizzi A (1983) *Wood adhesives: chemistry and technology*. M. Dekker, New York
- Pizzi A (1994) *Advanced wood adhesives technology*. M. Dekker, New York
- Pizzi A, Meikleham N, Dombo D, Roll W (1995) Autocondensation-based, zero-emission, tannin adhesives for particleboard. *Holz Roh- Werkst* 53:201–204
- Pizzi A, Valenzuela J, Westermeyer C (1993) Non-emulsifiables, water-based, diisocyanate adhesives for exterior plywood, Part 2: industrial application. *Holzforschung* 47:69–72
- Pizzi A, Walton T (1992) Non-emulsifiable, water-based diisocyanate adhesives for exterior plywood, Part 1. *Holzforschung* 46:541–547
- Wang S, Pizzi A (1997) Succinaldehyde-induced water resistance improvements of UF wood adhesives. *Holz Roh- Werkst* 55:9–12
- Wescott JM, Traska A, Frihart CR, Lorenz L (2006) Durable soy-based adhesive dispersions. *Proceedings Wood Adhesives 2005*, Forest Products Society, Madison, Wisconsin, pp. 263–370
- Wieland S, Pizzi A, Hill S, Grigsby W, Pichelin F (2006) The reaction in water of UF resins with isocyanates at short curing times: a ^{13}C NMR investigation. *J Appl Polymer Sci* 100:1624–1632
- Zanetti M, Pizzi A (2004) Dependence on the adhesive formulation of the upgrading of MUF particleboard adhesives and decrease of melamine content by buffer and additives. *Holz Roh- Werkst* 62:445–451