

Fast Advancement and Hardening Acceleration of Low Condensation Alkaline Phenol-Formaldehyde Resins by Esters and Copolymerized Urea. II. Esters during Resin Reaction and Effect of Guanidine Salts

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ABSTRACT: Guanidine carbonate is shown to be an accelerator of phenol-formaldehyde (PF) resins that while yielding slightly slower gel times than triacetin when added to a PF resin glue mix, is also capable of giving glue-mix pot lives on the order of several days. Hence, this is long enough to be premixed with the resin long before use. Both triacetin and guanidine carbonate used as simple glue-mix additives are shown to increase the ultimate strength of the resin bond, whatever the length of the curing time used for the purpose. This is shown by thermomechanical analysis and the application to wood particleboard. Triacetin is shown to be usable during PF resin preparation rather than just being added to the glue mix, yielding better resins capable of giving higher bond values without a great acceleration of the gelling of the resin itself. The mechanisms involved in the acceleration of PF resins introduced by both compounds appears to be based on facilitating reactions of crosslinking involving carbonic acid ions present in the resin solution. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 249–259, 2000

Key words: phenol-formaldehyde resin; esters; urea; alkaline resins; guanidine salts

INTRODUCTION

Alkaline phenol-formaldehyde (PF) resins have been used for many decades as exterior wood adhesives for bonded wood products¹ and constitute by volume about a third of all the adhesives used worldwide to prepare composite wood panels. Traditionally, one of the main problems of phenolic resins has been their much slower curing time in comparison to melamine resins. Recently, however, systems have been developed to considerably accelerate the cure of alkaline PF resins when used as adhesives for wood. Among these

are the use of diisocyanates as accelerators of the PF resin,¹ the use of very high condensation level PF resins subsequently drowned in solutions of noncopolymerized urea in order to decrease their viscosity,² and systems that not only accelerate but also improve the strength performance of the resins such as the use of urea copolymerized with the phenolic resin during resin preparation^{1,3–5} to yield veritable phenol-urea-formaldehyde (PUF) resins, and also the use of carboxylic acid esters^{5–7} and anhydrides⁸ and combinations of the two latter systems.⁴ These systems have allowed the preparation of PF and PUF resins capable of curing times as fast or even faster than those traditionally associated in this field with aminoplastic resins, and this is without any loss of exterior performance. Some of these systems are

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already at the beginning of full-scale commercialization.⁹

The best of these acceleration systems (the very convenient method of adding small proportions of esters or other accelerators in the resin glue mix just before application to the wood substrate) does however suffer from a commercial drawback: the adhesive producers do not like to give a separate, easily analyzed hardener to the users who have traditionally received a single component resin ready for use. Addition of the accelerator to the resin after resin manufacture engenders too short a shelf-life of the resin, because the accelerators shorten not only the resin high temperature curing time but also its period of stability at ambient temperature.

This problem was solved according to two different approaches:

1. by finding an accelerator that, while considerably accelerating the higher temperature curing of the resin, also imparted to the resin a sufficiently long period of stability at ambient temperature, and
2. by prereacting the accelerator with the PF resin during resin manufacture.

This article deals with the solutions of the problem according to the two approaches outlined above.

EXPERIMENTAL

PF Resin Preparation

PF resins were prepared at F : P molar ratios of 1.7 and 2.5. Furthermore, PUF resins containing a 48 and 72% molar proportion of urea on phenol content were also prepared, the former with two additions of 24% molar urea each, and the second by a first addition of 24% molar urea followed by a 48% molar urea addition. For the PUF resins the initial P : F molar ratio was of 1 : 3.3. The preparation procedure used is exemplified as follows for a resin composed of a P : F molar ratio of 1 : 1.7 and containing a 24% molar proportion of urea on phenol coreacted in the resin (F : [P + U] molar ratio = 1.37); 1.0 mol of phenol is mixed with 0.35 mol NaOH as a 30% water solution and 1.2 mol of formaldehyde (as a 37% formalin solution) in a reactor equipped with mechanical stirring, heating facilities, and a reflux condenser.

After stirring for 10 min at 30°C, 0.24 mol of urea are added and the temperature is slowly increased to reflux (94°C) over a period of 30 min under continuous mechanical stirring and it is kept at reflux for a further 30 min. Then 0.5 mol of formaldehyde (as a 37% formalin solution) are added. The reaction mix is now at pH 11 and the reaction is continued at reflux until the resin achieves a viscosity (measured at 25°C) of between 0.5 and 0.8 Pa s. The resin is then cooled and stored. The resin characteristics are then a pH 11 and a resin solids content of $50 \pm 1\%$. For the resins in which glycerol triacetate was added during resin preparation, additions or at the beginning of the reaction or halfway during the reaction were used.

Thermomechanical Analysis (TMA)

A commercial PF resin with and without the addition of 1, 2, 3, 4, and 5% of guanidine carbonate resin solids predissolved in water was tested dynamically by TMA on a Mettler apparatus. Triplicate samples of beech wood alone and two beechwood plys each 0.6 mm thick bonded with each system for a total sample dimensions of $21 \times 6 \times 1.2$ mm were tested in nonisothermal mode at between 40 and 240°C at a heating rate of 10°C/min with a Mettler 40 TMA apparatus in 3-point bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N 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. Because the deflections Δf obtained were proved to be constant and reproducible^{10,11} and these are inversely related to the values of the modulus, it is often the values of the deflection (μm) that can be reported in the tables (IV–VII).

¹³C-NMR Spectra

The liquid ¹³C-NMR spectrum of PF resins after the addition of guanidine carbonate or prereacted during resin preparation with glycerol triacetate (triacetin) were obtained on a Brüker MSL 300 FT-NMR spectrometer. Chemical shifts were calculated relative to $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{SO}_3\text{Na}$ dissolved in D₂O for NMR shifts control.¹² 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

Table I Effect of Guanidine Salts on Gel Time at 100°C

	PF	PF + 15% Guanidine Carbonate	PF + 15% Guanidine Hydrochloride	PF + 15% Guanidine Sulfate
Gel time (min)	40	12	25	30

1 ppm. The quantitative NMR spectra indicated that the number-average molecular mass of PF resins prepared under the indicated conditions without the addition of urea was 396 while after the addition of urea the number-average molecular mass increased to 604. The yield of the actual PUF resin was 71% in relation to PF oligomers also formed and unreacted materials.

Wood Particleboard Preparation

Duplicate one layer laboratory particleboards (350 × 310 × 14 mm) were prepared by adding 9% PF or PUF resin solids content on dry wood particles pressed at a maximum pressure of 28 kg/cm² followed by a descending pressing cycle at 190–195°C and for pressing times as indicated in the results tables. All the panels had densities comprised between 0.695 and 0.704 g/mL unless otherwise indicated in the results tables. The panels, after light surface sanding, were tested for dry internal bond (I.B.) strength, for I.B. strength after 2 h boiling and 16 h drying at 105°C tested dried, and for I.B. V100 tested wet.¹³ Gel times were done in triplicate at 100°C, while viscosity results were obtained with a Brookfield viscometer at 25°C. The results obtained are shown in the tables.

DISCUSSION

The addition of the most suitable ester accelerator used for PF resins for wood bonding, glycerol triacetate (triacetin), shortens the shelf-life of the resin to only a few hours; the length of such a period generally depends on the degree of condensation of the resin and the proportion of accelerator added. The reason why triacetin is used is because it is a strong accelerator at higher temperatures while it does at least allow these few hours of use (generally 5–6 h) at ambient temperature. Most other esters are much less effective accelerators at higher temperature or they shorten the ambient temperature life of the resin

to such an extent that in practice the resin cannot be used. Triacetin works in this manner because of its lower rate of hydrolysis at ambient temperature. A variety of other esters capable of yielding a longer ambient temperature life of the resin were tried but without any success.

The series of compounds, some of which were finally found to yield sufficiently rapid acceleration at higher temperatures, still coupled with increased strength of the cured resin as well as sufficiently long shelf-life at ambient temperature were the salts of guanidine. Guanidine carbonate, guanidine hydrochloride, and guanidine sulfate were tried and the PF resin gel time they yielded when added at the 15% level on resin solids are reported in Table I. Because guanidine carbonate appeared to be the best PF accelerator (because of the less acid character of the anion, indicating that both guanidine and the carbonate anion function as accelerators), we checked its accelerating capability and shelf-life at ambient temperature of the PF and PUF resins to which it had

Table II Effect on Gel Time at 100°C and Pot Life at 25°C of Proportions of Guanidine Carbonate on PF and PUF Resins of Different Molar Ratios

PF (F/P = 1.7)				
Guanidine carb.	0	5	10	15
Gel time (min)	40	20	15	12
Pot life (days)		25	15	10
PF (F/P = 2.5)				
Guanidine carb.	0	5	10	15
Gel time (min)	19	10	6	4
Pot life (h)		180	46	8
PUF (F/P = 3.3; 1st Urea = 24%, 2nd Urea = 24%)				
Guanidine carb.	0	10	17	
Gel time (s)	660	240	140	
Pot life		4 h	3 h 30	

Table III Variation of Viscosity with Time (Shelf-Life) at 20 or 30°C of Three Commercial, Advanced PF Resins with and without Different Proportions of Guanidine Carbonate Added into Glue Mix

PF Resin	Guanidine Carbonate* (%)	Temp. (°C)	Gel Time (s) at End of 25 Days	Viscosity (mPa s)						
				0 Days	4 Days	7 Days	11 Days	15 Days	18 Days	22 Days
PF 1	0	20	1,740	960	880	1,160	930	970	1,100	980
	0	30	1,740	960	990	1,200	1,300	1,220	1,520	1,460
	0.5 cryst.	20	1,710	940	880	1,140	1,040	970	1,040	1,120
	0.5 cryst.	30	1,710	940	970	1,200	1,240	1,200	1,360	1,460
	1 cryst.	20	1,680	960	940	1,120	1,040	1,080	1,040	1,080
	1 cryst.	30	1,680	960	1,060	1,160	1,300	1,460	1,520	1,520
PF 2	0	20	1,020	380	500	620	800	1,160	1,520	1,160
	0	30	1,020	380	850	1,920	9,600	—	—	—
	0.5 solut.	20	960	380	530	690	1,120	1,720	2,760	480
	0.5 solut.	30	960	380	1,320	4,800	—	—	—	—
	1 solut.	20	960	380	620	860	1,500	3,120	11,200	—
	1 solut.	30	960	380	1,540	9,280	—	—	—	—
	1 cryst.	20	840	520	710	1,000	1,940	3,480	6,640	—
	1 cryst.	30	840	520	1,900	10,400	—	—	—	—
PF 3	0	20	2,280	820	820	940	900	900	930	980
	0	30	2,280	820	900	930	1,160	1,220	1,320	1,440
	0.5 solut.	20	2,250	620	700	740	760	750	760	780
	0.5 solut.	30	2,250	620	740	800	840	860	930	960
	1 solut.	20	2,250	540	600	650	650	670	670	700
	1 solut.	30	2,250	540	630	660	740	720	730	750

solut., solution of guanidine in 33% water; cryst., guanidine added in crystalline form.

* % on resin solids.

been added in different proportions. In bulk industrial practice, a shelf-life of 6–10 days is already acceptable. The results obtained (Table II) indicate that for lower molar ratio PF resins (P : F = 1 : 1.7), shelf-lives more than suitable for industrial applications while conserving still much faster gel times of the PF resins could be obtained up to additions as high as 15% guanidine carbonate on resin solids. For the higher molar ratio PF resin (P : F = 1 : 2.5) instead the results of gel time and shelf-life indicate that only proportions of guanidine carbonate of up to 5% on resin solids are within the limits wanted. The two PF resins in Table II are low condensation PF resins. However, by preparing a higher condensation resin by copolymerization with high amounts of urea^{3,5} (PUF resin), the gel times obtained are very fast indeed but the shelf-life reverts to being too short (Table II).

The same study was carried out with a few, high condensation level, commercial PF resins. The majority of them showed the same trend observed for the PUF resin in Table II. A few of

them and one in particular, a pure commercial PF resin (P : F = 1 : 2.3), for particleboard did not show any strong increase in viscosity over a period of 21 days at ambient temperature on the addition of 1% guanidine carbonate on resin solids, while still showing a faster gel time at 100°C (Table III). For this reason the resin was tested on beech wood joints by TMA by first adding amounts of guanidine carbonate between 0 and 20% on resin solids, and when it was realized that no improvement in the maximum value of the elastic modulus resulted for percentages of guanidine carbonate higher than 5%, the study was repeated at 1% intervals in the range of 0–5% guanidine carbonate on resin solids (Fig. 1). The increase of modulus on curing and the maximum values of the modulus obtained are shown in Figure 1. From Figure 1 it appears that the maximum value of the elastic modulus of the joint increases when increasing the addition of guanidine carbonate, and the 5% addition case presents a value of the modulus that is 30% higher than

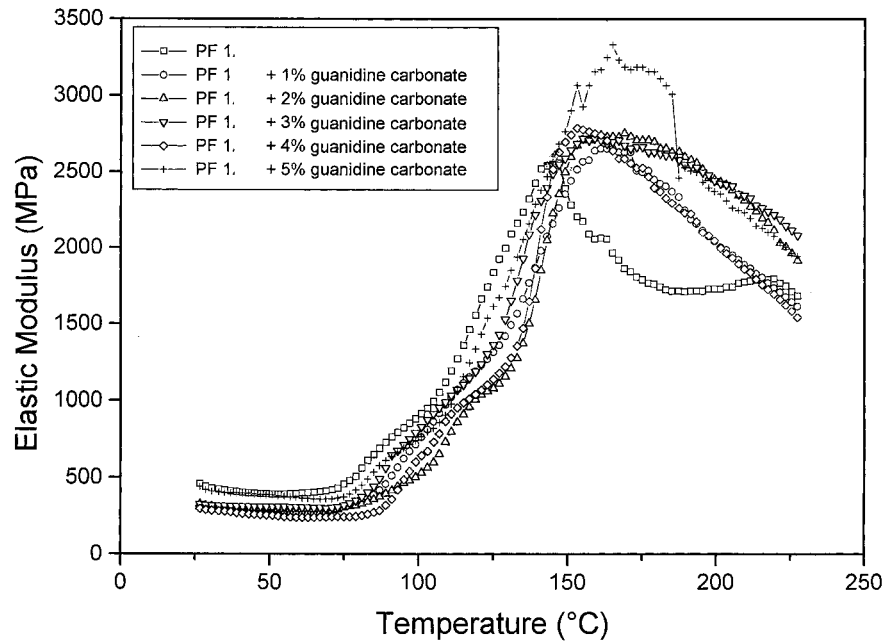


Figure 1 The variation of the elastic modulus as a function of temperature of a commercial, advanced PF resin (PF1) with and without different amounts of guanidine carbonate added in the glue mix (constant rate of heating of 10°C/min).

that presented by the same resin without any addition.

To obtain proof that better performance could be obtained for PF resins to which guanidine carbonate had been added to the resin, several wood particleboards were made with both the low condensation PF resins (of molar ratio P : F = 1 : 1.7 and P : F = 1 : 2.5) and the PUF resin of Table II, as well as with the high condensation resin of Table III and Figure 1. The results obtained, compared to relevant standards, are shown in Table IV. These results indicate that the addition of

guanidine carbonate improves the internal bond (IB) strength of the wood particleboard both when dry and after 2-h immersion in boiling water, the latter result indicating that addition of this accelerator improves long-term exterior durability of the panel. It is worthwhile to note that for the 1 : 2.5 low condensation PF resin even at 15% accelerator addition, a pot life of 8 h is still obtained but that the wet IB strength is almost double that obtained with the other boards, and this even at a lower density (which would negatively affect the result). Guanidine carbonate is then an additive

Table IV Wood Particleboard Results for PF Resins with and without Guanidine Carbonate Pressed at 190°C for 21.4 s/mm

	Dry IB (MPa)	Density (g/mL)	Wet IB (MPa)	Density (g/mL)
PF (2.5)	0.87	0.713	0.26	0.664
PF (2.5) + 15% Guanidine carbonate	0.97	0.726	0.43	0.635
PF (1.7)	0.67	0.736	0.20	0.658
PF (1.7) + 15% Guanidine carbonate	0.91	0.724	0.27	0.660
PUF (3.3)	0.73	0.771	0.21	0.682
PUF (3.3) + 15% Guanidine carbonate	0.84	0.766	0.26	0.690
Commercial PF 1 (2.3)	0.80	0.721	0.21	0.693
Commercial PF 1 (2.3) + 1% Guanidine carbonate	0.91	0.719	0.32	0.690

Table V Gel Times and Pot Lives of PUF Resin and IB Strength Results of Wood Particleboard Bonded with It at 21.4 and 8.5 s/mm

PUF (F/P = 3.3; 1st Urea = 24%, 2nd Urea = 48%)			
Guanidine carbonate (%)	0	5	15
Gel time (s)	660	300	210
Pot life (days)	> 24	3.5	1.5
Press time 21.4 s/mm			
Dry IB strength (MPa)	1.03	1.05	1.14
Board density (g/mL)	0.771	0.752	0.766
IB strength 2-h boil (MPa)	0.21	0.23	0.26
Board density (g/mL)	0.682	0.674	0.690
Press time 8.5 s/mm			
Dry IB strength (MPa)			0.64
Board density (g/mL)			0.682
IB strength 2-h boil (MPa)			0.24
Board density (g/mL)			0.723

that can be used with a certain flexibility to upgrade the performance of the resin and of the board bonded with it.

In the case of the PUF resins it is however interesting to note from Table V that increasing the amount of the second addition of urea in the resin, thus increasing the amount of urea that is not copolymerized in the resin, also slows down the reaction. The PUF becomes then more suitable for industrial application as can be seen from the pot lives obtained and the results both at long pressing time and at short pressing time of wood particleboard bonded with such resin systems (Table V).

The second approach taken was of adding triacetin directly to the PF resin during preparation of the resin. The results obtained with this ap-

proach are presented in Table VI and show that the addition of triacetin advances the resin to high levels of condensation much more rapidly and resins of a higher level of condensation yield much higher IB results of the wood particleboards bonded with them. It is interesting in this context to compare the performance of the high level of condensation commercial PF resin in Table III, a resin obtained at a reaction time of 7 h, with the results of the resins in Table IV, the high grade of condensation of which was obtained in less than 1 h. The latter ones yield much better IB results than the former, notwithstanding that the improvement of gel time in Table IV is small and that the gel time of the commercial resin in Table III is actually shorter, an additional indication, under different conditions, of the fact already re-

Table VI Wood Particleboard Results for PF Resins with and without Coreaction with Triacetin during Resin Preparation Pressed at 190°C for 21.4 s/mm

	Gel Time (min)	Dry IB Strength (MPa)	Wet IB Strength (MPa)	Viscosity at 20°C (MPa)	Solid Content (%)
P/F = 1 : 1.7	40	0.2	—	450	48.6
P/F/T = 1 : 1.7 : 0.05, 5% triacetin added at beginning	35	0.62	0.16	327	48.0
P/F/T = 1 : 1.7 : 0.05, 5% triacetin added in midreaction	36	1.10	0.45	324	51.7
P/F/T = 1 : 1.7 : 0.025, 2.5% triacetin added in midreaction	39	1.13	0.43	296	50.8
P/F/T = 1 : 1.7 : 0.075, 7.5% triacetin added in midreaction			Separated from water after 8 h		
P/F/T = 1 : 1.7 : 0.1, 10% triacetin added in midreaction			Separated from water after 0.5 h		
P/F = 1 : 2.5	20	0.86	0.26	386	44.2
P/F/T = 1 : 2.5 : 0.025, 2.5% triacetin added in midreaction	17	1.02	0.32	320	46.9
P/F/T = 1 : 2.5 : 0.05, 5% triacetin added in midreaction	17	1.14	0.38	413	47.6

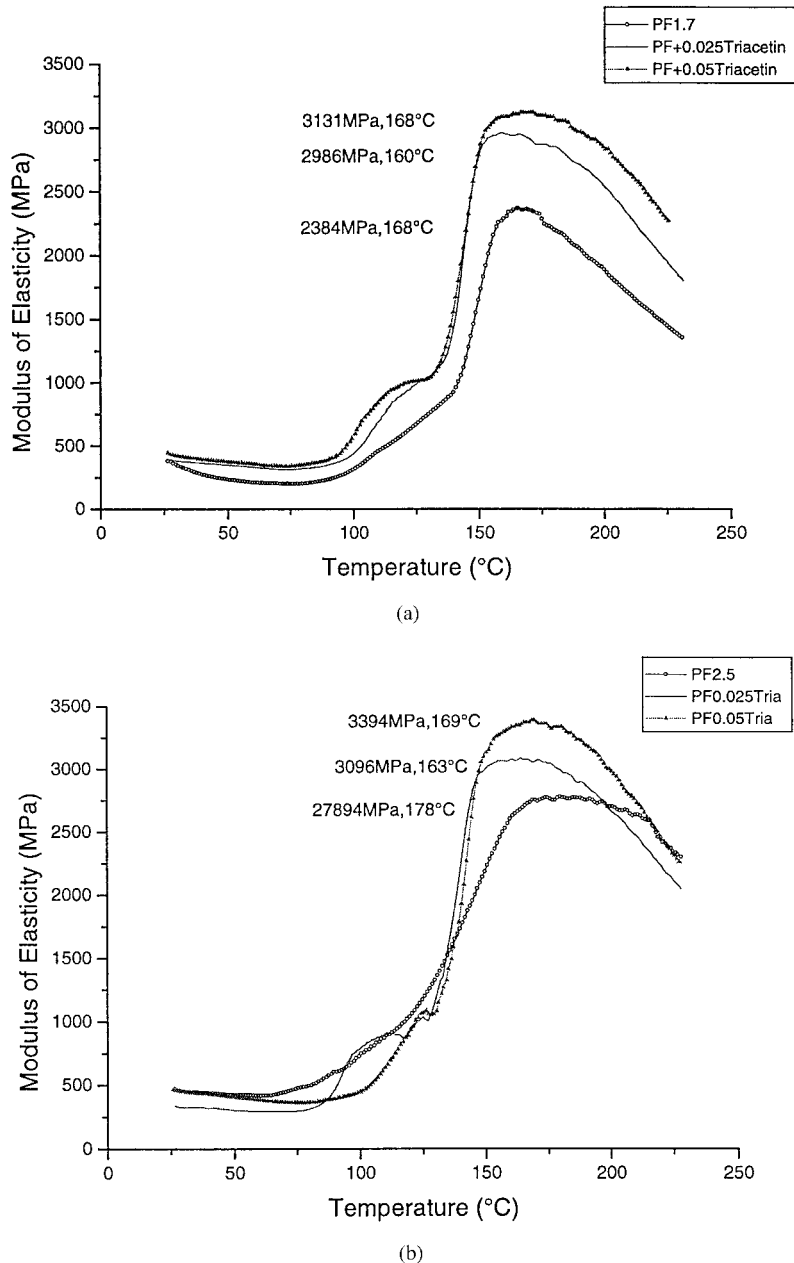


Figure 2 The variation of the elastic modulus as a function of temperature of PF resins with and without different amounts of triacetin coreacted during resin preparation (constant rate of heating of 10°C/min). PF resin of P : F = (a) 1 : 1.7 and (b) 1 : 2.5.

ported¹⁴ that triacetin appears to introduce additional crosslinking reactions in PF resin systems. Even the fact that the lower molar ratio resins (in Table IV the P : F = 1 : 1.7) give the better wet IB results again indicates that this must be the case. These results are confirmed by the TMA of these resins on a beech wood joint shown in Figure 2. The results in Table IV also indicate that when

added directly during resin preparation no more than 5% on resin solids can be added, with 2.5% yielding almost equally good results, and that addition during the course of resin preparation yields good results while addition at the beginning of resin preparation yields much poorer results. This is a further indication that triacetin is more effective in the condensation stage of the

Table VII Influence of Press Time on IB Strength Results of Particleboard of PF Resins with and without Addition in Glue Mix of Guanidine Carbonate

	Press Time (s/mm)	Dry IB Strength (MPa)	Wet IB Strength (MPa)	Gel Time (min)	Pot Life (h)
P/F = 1 : 2.5	17	0.67	Open	19	
P/F/T = (1 : 2.5 : 0.025) + 15% guanidine carbonate	10.7	0.84	0.49	4	8
P/F/T = (1 : 2.5 : 0.025) + 15% guanidine carbonate	8.5	0.45	0.19	4	8
P/F = 1 : 1.7	30	0.67	0.20	40	
P/F/T = (1 : 1.7 : 0.025) + 15% guanidine carbonate	17	1.10	0.42	12	240

resin rather than on the initial formaldehyde attack step onto the phenol to form hydroxybenzyl alcohols. Additions of triacetin in proportions greater than 5% advances the resin to such a level of condensation that it precipitates out of water in a very short time.

The resins obtained by the addition of triacetin during resin preparation and accelerated with lower amounts of guanidine carbonate (or even triacetin itself) added just in the glue mix were also tested by preparing wood particleboard at much faster pressing times to prove that fast pressing times were indeed possible. The results shown in Table VII indicate clearly that PF resins

advanced in this manner are capable of giving much better IB results than the faster pure PF resins, and this even at much lower molar ratios than actually used in commercial PF resins for this application. The achievement of a pressing time of 8.5 s/mm panel thickness at 190°C indicates the capability of these resins to yield press times faster than 7 s/mm at the higher temperatures (210–220°C) used today in more modern industrial plants.

Of interest is to try to determine what occurred during resin preparation on both the addition of triacetin added during resin preparation, as well as on the addition of guanidine at the end of the

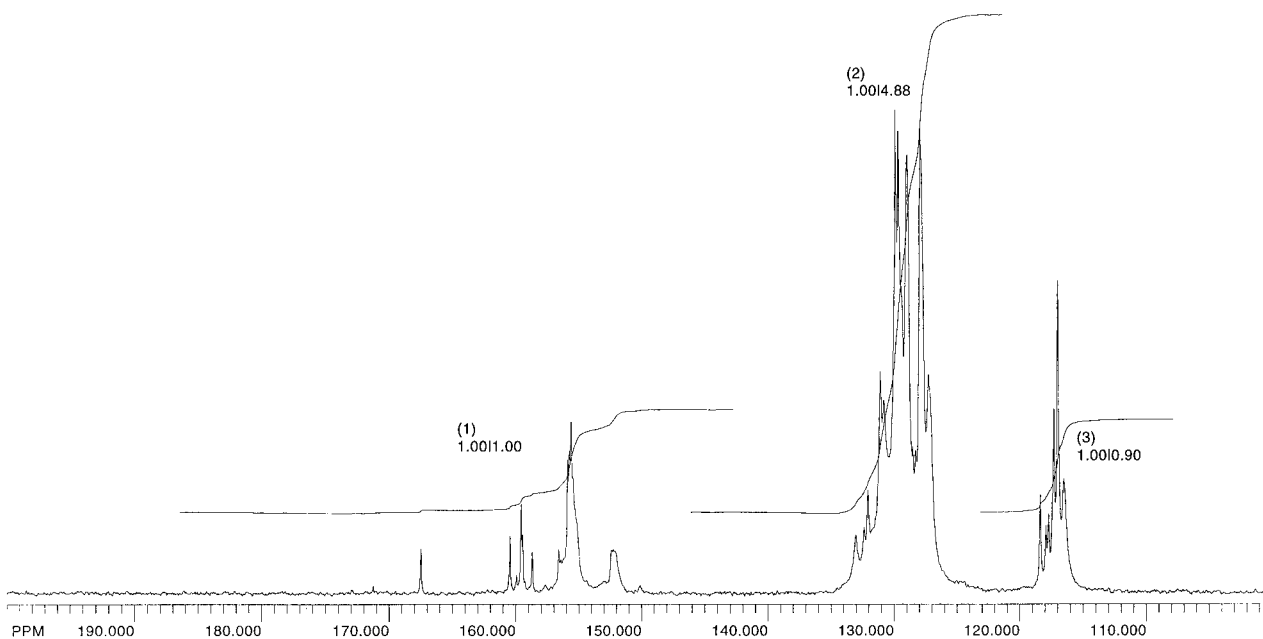


Figure 3 The detail of the 110–170 ppm region of the ^{13}C -NMR spectrum of a liquid PF resin with 10% guanidine carbonate.

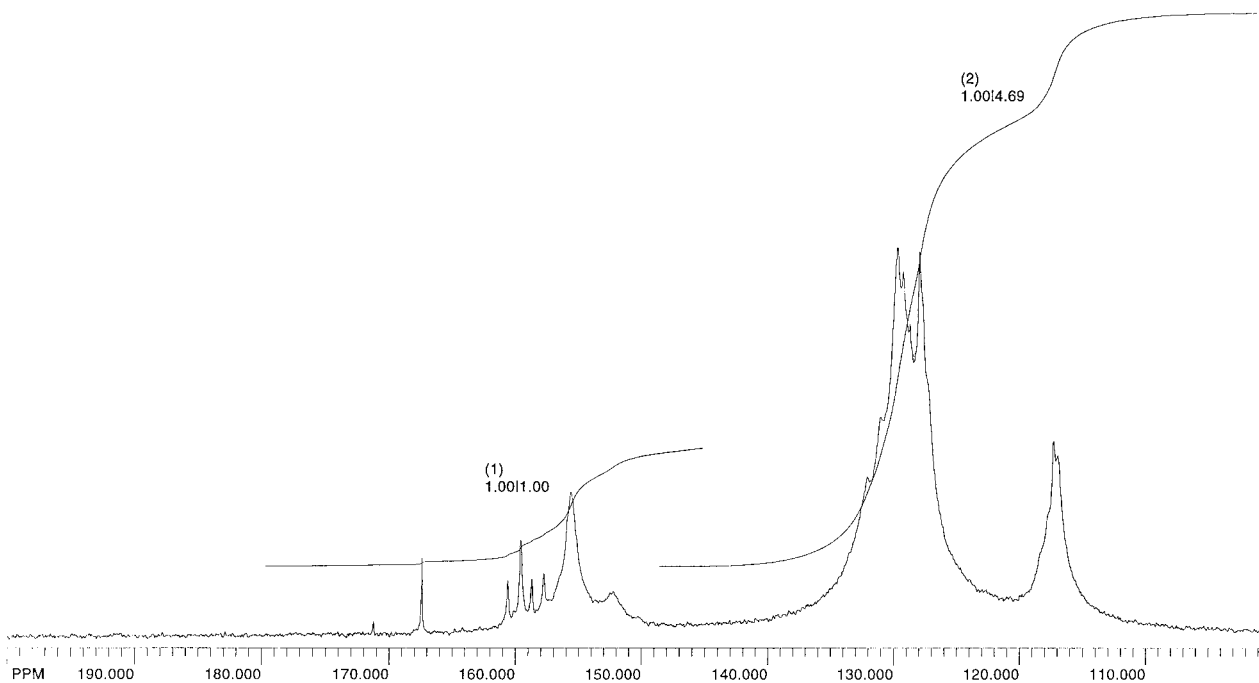


Figure 4 The detail of the 110–170 ppm region of the ^{13}C -NMR spectrum of a liquid PF resin with 5% sodium carbonate.

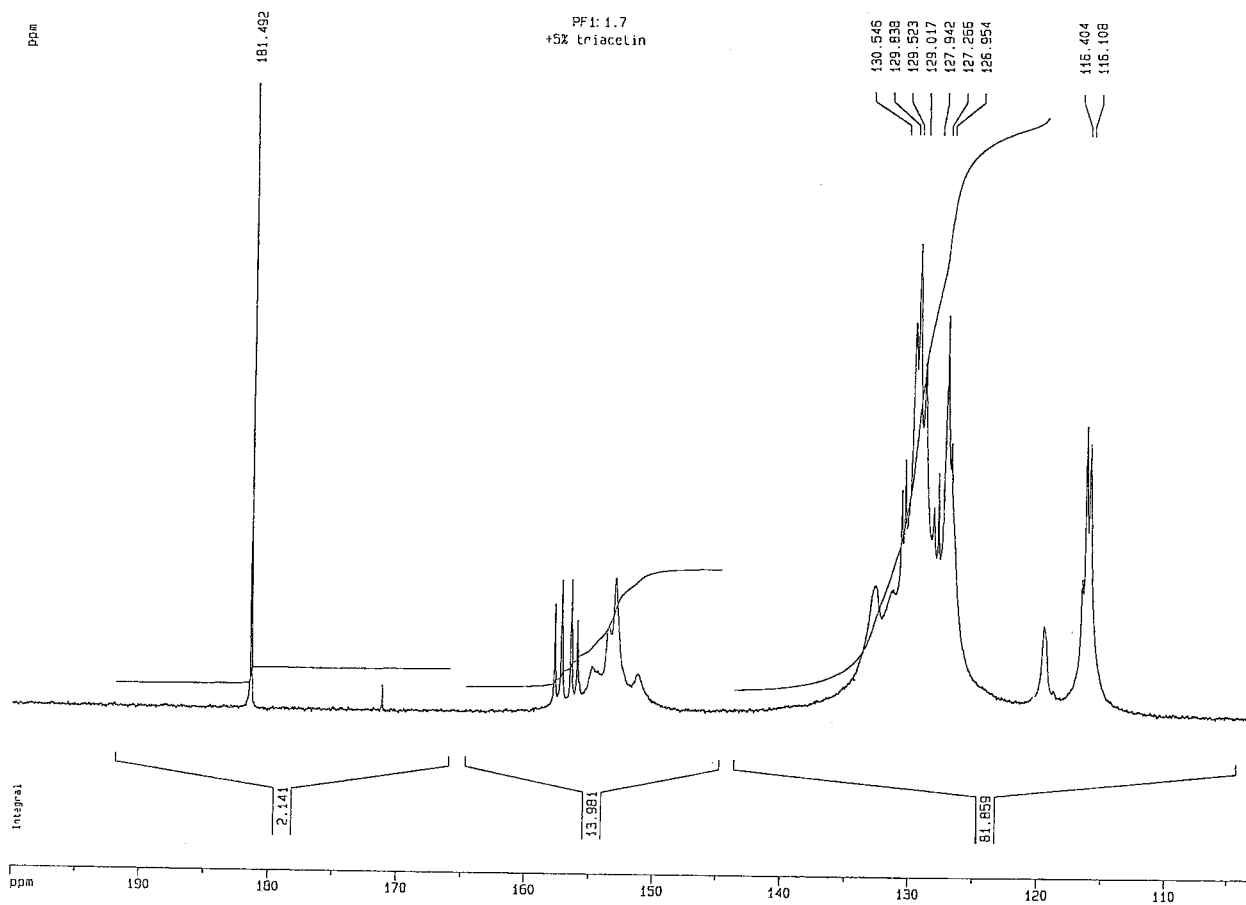
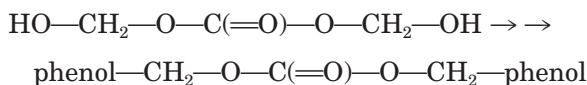
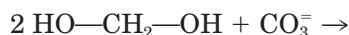
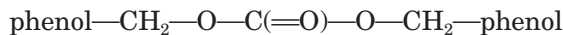
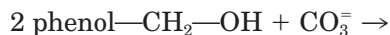


Figure 5 The detail of the 110–170 ppm region of the ^{13}C -NMR spectrum of a liquid PF resin coreacted with 5% glycerol triacetate (triacetin) during resin preparation.

reaction. The ^{13}C -NMR spectra shown in Figures 3–5 give some indication of what occurred. Figures 3 and 4 compare relevant details of the spectra of PF+ guanidine carbonate and a PF+ sodium carbonate: the peaks at 167.5 ppm are due to CO_3^- (theoretical¹⁵ 168.5 ppm), and then a series of four sharp peaks are seen in the narrow range of 157–161 ppm. Some of these can be interpreted as being due to the $>\text{C}=\text{NH}$ of the guanidine and the presence of HCO_3^- . Because three of these peaks are also present in the case of the PF+ sodium carbonate (160.4 ppm; 159.4 and 159.3 ppm superimposed; 158.4 ppm), it can be deduced that three of the peaks (the three more downfield) are due to the carbonate and belong to species derived from the carbonate equilibria, such as NaHCO_3 , Na_2CO_3 , HCO_3^- , while the fourth peak more upfield (157.6 ppm) is instead due to the $>\text{C}=\text{NH}$ of substituted guanidine. This is however not the case for the PF resin to which triacetin was added during resin preparation where four peaks appear in the same region (Fig. 5). Because carbonates were shown to be present in the water used (as tested separately by NMR, data not shown), three of these peaks again belong to the carbonates (same shifts) but the fourth at 156.5 ppm likely belongs to the $-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{O}-\text{CH}_2-$ (theoretical¹⁵ shift = 156.5 ppm), thus at the reaction of one of the carbonic ion species either with the free formaldehyde (which in solution is present as $\text{HO}-\text{CH}_2-\text{OH}$, methylene glycol) or with two methylol groups of the phenolic resin. Because the quantitative spectrum indicates that the amount of such a compound is small, it can only be an intermediate phase of one of the acceleration mechanisms in action and not the final product. This means that one of the carbonic acid ions may function just as a catalyst of the reaction of crosslinking through one of the following reactions:



or



followed by subsequent rearrangement to methylene bridges. The same mechanisms can be envisaged in the case of guanidine carbonate, where the function of bridging can be taken both by the carbonate ion when it is present and from the guanidine itself. That these might be the mechanism involved is shown by the higher proportion of *o*, *p* methylene bridges than *p*, *p* methylene bridges observed by CP-MAS in hardened PF resins containing either triacetin or guanidine carbonate. No other evident major changes in any of the spectra can be observed, indicating that possibly the main role in accelerating the resin is played by the carbonates and that the main role of the guanidine and triacetin is that of facilitating, catalyzing, and improving the action of the carbonate, at least in PF resins. (Other mechanisms have been found to have important roles in resins using more reactive phenols, such as resorcinol.¹⁴)

CONCLUSIONS

Guanidine carbonate was shown to be an accelerator of PF resins that, while yielding slightly slower gel times than triacetin when added to a PF resin glue mix, is also capable of giving glue-mix pot lives on the order of several days, hence being long enough to be premixed with the resin long before use. Triacetin and guanidine carbonate used as simple glue-mix additives were both shown to increase the ultimate strength of the resin bond, whatever the length of the curing time used for the purpose. Triacetin was also shown to be usable during PF resin preparation rather than just being added to the glue mix, yielding better resins capable of giving higher bond values without great acceleration of the gelling of the resin itself. The mechanisms involved in the acceleration of PF resins introduced by both compounds appears to be based on facilitating reactions of crosslinking involving carbonic acid ions present in the resin solution.

REFERENCES

1. Pizzi, A. *Advanced Wood Adhesives Technology*; Dekker: New York, 1994.
2. Oldörp, K.; Marutzky, R. *Holz Roh Werkstoff* 1998, 55, 75.
3. Ohyama, M.; Tomita, B.; Hse, C.-Y. *Holzforchung* 1995, 49, 87.

4. Zhao, C.; Pizzi, A.; Garnier, S. *J Appl Polym Sci*, 1999, 74, 359.
5. Pizzi, A.; Stephanou, A.; Antunes, I.; De Beer, G. *J Appl Polym Sci* 1993, 50, 2201.
6. Pizzi, A.; Stephanou, A. *J Appl Polym Sci* 1993, 49, 2157.
7. Pizzi, A.; Stephanou, A. *Holzforschung* 1994, 48(2), 150.
8. Pizzi, A.; Stephanou, A. *J Appl Polym Sci* 1994, 51, 1351.
9. Roll, W. In *Proceedings of the International Contributions to Wood Adhesives Research Symposium*, Forest Products Society Annual Meeting, Merida, Mexico, July 1998.
10. Pizzi, A.; Probst, F.; Deglise, X. *J Adhes Sci Technol* 1997, 11(4), 573.
11. Pizzi, A. *J Appl Polym Sci* 1997, 63, 603.
12. Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH: Weinheim, 1987.
13. German Standard DIN 68763. *Spanplatte: Flach-Pressplatten für das Bauwesen*, 1982.
14. Pizzi, A.; Garcia, R.; Wang, S. *J Appl Polym Sci* 1997, 66, 255.
15. Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd ed.; Springer: Berlin, 1989.