Fast Advancement and Hardening Acceleration of Low-Condensation Alkaline PF Resins by Esters and Copolymerized Urea

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ABSTRACT: Low-condensation phenol-formaldehyde (PF) resins coreacted under alkaline conditions with up to 42% molar urea on phenol during resin preparation yielded PUF resins capable of faster hardening times than equivalent pure PF resins prepared under identical conditions and presented better performance than the latter. The water resistance of the PUF resins prepared seemed comparable to pure PF resins when used as adhesives for wood particleboard. Part of the urea was found by ^{13}C-NMR to be copolymerized to yield the alkaline PUF resin; whereas, especially at the higher levels of urea addition, unreacted urea was still present in the resin. Increase of the initial formaldehyde to phenol molar ratio decreased considerably the proportion of unreacted urea and increased the proportion of PUF resin. A coreaction scheme of phenolic and aminoplastic methylol groups with reactive phenol and urea sites based on previous model compounds work has been proposed, copolymerized urea functioning as a pre-branching molecule in the forming, hardened resin network. The PUF resins prepared were capable of further noticeable curing acceleration by addition of ester accelerators; namely, glycerol triacetate (triacetin), to reach gel times as fast as those characteristic of catalyzed aminoplastic resins, but at wet strength values characteristic of exterior PF resins. Synergy between the relative amounts of copolymerized urea and ester accelerator was very noticeable at the lower levels of the two parameters, but this effect decreased in intensity toward the higher percentages of urea and triacetin. ^{13}C-NMR assignements of the relevant peaks of the PUF resins are reported and compared with what has been reported in the literature for mixed, coreacted model compounds and pure PF and urea-formaldehyde (UF) resins. The relative performance of the different PUF resins prepared was checked under different conditions by thermomechanical analysis (TMA) and by preparation of wood particleboard, and the capability of the accelerated PUF resins to achieve press times as fast as those of aminoplastic (UF and others) resins was confirmed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 359–378, 1999

Key words: phenol-formaldehyde; phenol-urea-formaldehyde; wood adhesives; accelerators; wood particleboard; press time; curing time; resins

INTRODUCTION

Alkaline phenol-formaldehyde (PF) resins have been used successfully for many decades as exte-

rior wood adhesives for bonded wood products[1] 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 up to today has been their much slower press time as compared to melamine resins. This has allowed their substitution by the faster but less weather durable and more expen-

sive MUF resins to the detriment of PF resins. At parity of conditions, the fastest traditional PF resin can perhaps reach 12 s/mm board thickness versus approximately 7 s/mm board thickness for a MUF resin. As a consequence, the influence of many additives on their hardening acceleration under alkaline conditions has been studied in recent years.[2–8] Thus, PF hardening acceleration by catalytic surface activation by lignocellulosic materials has been reported,[9] as well as a variety of mechanisms based on PF hardening acceleration induced by carboxylic acid esters,[2–8] anhydrides,[10] amides,[5,6,11] and others, some of which are very effective but not yet implemented in the wood panels industry.

A swift increase of the average degree of polymerization of the resin by urea coreaction under alkaline conditions during PF resins manufacture[11,12] (expressed by the concept of molecular doubling[12]) in some cases has already been used to somewhat accelerate the resin. This approach must not be confused with either the preparation of acid-copolymerized PUF resins used as acid-hardening resins,[13–20] hence behaving as an aminoplastic resin, nor with the case of very advanced, very high-viscosity and high molecular mass PF resins dissolved in great proportions of urea added in the cold at the end of the reaction to reduce the over-all viscosity of the system[21] coupled with inorganic carbonates as accelerators.

In the molecular doubling of PF resins by urea coreaction under alkaline conditions, we must take care that the pH of the resin is not as high as in standard PFs, otherwise the equilibrium reaction

$$PF—CH_2OH + NH_2CONH_2 \leftrightarrow$$

$$PF—CH_2—NHCONH_2$$

shifts considerably to the left with unwanted results.[22] These types of resins, in which up to 5% urea by weight is used, are already produced and sold commercially worldwide by several companies, although this is not widely known. The acceleration by urea-induced (or other, more expensive molecules) molecular doubling can be explained on the basis of the relative reactivities of phenolic nuclei and urea for the methylol group of PF resins. Urea is incapable of condensing to UF resins in a fairly alkaline environment but its reaction with formaldehyde to form methylol ureas is actually at its fastest under alkaline conditions.[1] The same is valid with any source or type

of formaldehyde, included the methylol group of a PF resin (it is not valid for the methylol group of a UF resin as the inverse reaction, depolymerization, is favourite at rather alkaline pH).

However, the faster curing any resin becomes, the less cross linked and the less tight is its final network achieved at parity of application conditions,[23–25] and as a consequence, the lower is the strength of the panel.[25] Thus, to just achieve faster gel times is relatively easy, but to have also strong panels, hence a strong hardened resin network, while maintaining press times as fast as indicated by the gel times achievable may not be so easy.

This paper, then, addresses several aspects of the hardening acceleration of PF resins: (1) to bring to the highest limit the proportion of urea copolymerized during the alkaline molecular doubling of the average degree of polymerization of the resin during PF resins manufacture; this is to advance rapidly low-condensation PF resins to much higher average molecular mass in a much shorter time, to prepare with this approach a resin that is faster hardening and to prepare a PF resin of equal exterior performance but of lower cost by both increasing the proportion of urea in it as well as by markedly shortening the resin preparation time; and (2) to accelerate further the PF resin by adding to the above the use of an accelerating additive in the glue mix, the additive being a carboxylic acid ester; and (3) to see if synergic effects between the two approaches exist to accelerate initially low-condensation alkaline PF resol resins to a much faster rate of hardening.

EXPERIMENTAL

PF Resins Preparation

PF resins with and without urea were prepared at F : P molar ratios of 1.2, 1.4, 1.5, 1.7, 2.0, 2.2, 2.5, and 2.8. The preparation procedure used is exemplified as follows for the resin composed of P : F molar ratio 1 : 1.7 and containing 24% molar proportion of urea on phenol coreacted in the resin (thus of F : [P + U] molar ratio = 1.37): 1.0 mole of phenol is mixed with 0.35 moles NaOH as a 30% water solution and 1.2 moles of formaldehyde (as a 37% formalin solution) in a reactor equipped of mechanical stirring, heating facilities and reflux condenser. After stirring for 10 min at 30°C, 0.24 moles of urea are added, and the temperature is slowly increased to reflux (94°C) over

Table I   Properties, IB Results and TMA Results of Low-Condensation Pure PF Resins as a Function of F : P Molar Ratio

F/P Molar Ratio	1.2	1.4	1.7	2.0	2.5	2.8
Viscosity (20°C) (mPa/s)	450	475	456	576	605	430
Gel time (min)	127	69	42	23	18	14
pH	12.1	12.1	11.4	11.5	12.0	11.8
Solid content (%)	52.3	50.5	48.6	46.1	44.2	41.8
IB dry (MPa)	0.48	0.54	0.62	0.87	0.97	0.97
IB 2 h boil (MPa)	0.18	0.25	0.36	0.43	0.42	0.31
Board density (g/cm^3)	0.698	0.703	0.689	0.704	0.699	0.648
TMA minimum deflection (μm)	19.0	18.4	17.8	13.9	12.9	12.4

a period of 30 min and under continuous mechanical stirring and kept at reflux for further 30 min. 0.5 moles of formaldehyde (as a 37% formalin solution) are then 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. Resin characteristics are then pH = 11, resin solids content = 50% ± 1%.

Thermomechanical Analysis (TMA)

The resins above were tested dynamically by TMA on a Mettler apparatus. Triplicate samples of beech wood alone, and of two beech wood plys each 0.6-mm thick bonded with each system, for a total, samples dimensions of $21 \times 6 \times 1.2$ mm were tested in nonisothermal mode between 40 and 220°C at a heating rate of 10°C/min with a Mettler 40 TMA apparatus in three points 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 calculation of Young's modulus E for each case tested. Because the deflections Δf obtained were proven to be constant and reproducible,[26,27] and these are inversely related to the values of the modulus, it is often the values of the deflection (in μm) that have been reported in the tables.

^{13}C-NMR Spectrum

The liquid ^{13}C-NMR spectrum of the PF resin used were obtained on a Brüker MSL 300 FT-NMR spectrometer. Chemical shifts were calculated relative to $(CH_3)_3Si(CH_2)_3SO_3Na$ dissolved in D_2O for NMR shifts control.[28] The spectra were done at 62.90 MHz for a number of transients of approximately 1000. All the spectra were run with a relaxation delay of 5 s, and chemical shifts were accurate to 1 ppm.

Wood Particleboard Preparation

Duplicate one-layer laboratory particleboard of $350 \times 310 \times 14$ mm dimensions were then produces by adding 9% PF resin solids content on dry wood particles pressed at a maximum pressure of 28 kg/cm^2 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/cm^3 unless otherwise indicated in the results tables. The panels, after light surface sanding, were tested for dry internal bond (IB) strength, for IB strength after 2 h boiling and 16 h drying at 105°C tested dried, and for IB V100 tested wet.[29] 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.

RESULTS AND DISCUSSION

Recent results have shown a clear correlation between the results of nonisothermal TMA curing in bending of aminoplastic and phenolic resin-bonded wood joints and the IB strength of wood particleboard prepared using the same resin systems when the boards are prepared under well-defined and reproducible conditions.[30,31] The results shown in Table I for a series of low-condensation and low molecular mass PF resins confirm this finding. Thus, in Table I it is shown that the IB strength of wood particleboard bonded with low-condensation PF resins in which the initial

(a)

(b)

Table II   Gel Times and TMA Results of Low-Condensation PF Resins of Different F/P Molar Ratios and at Different Molar Percentages of Coreacted Urea

Urea (% on Phenol)	0	6	12	18	24
F/P Molar Ratio	Gel Time (minutes)				
1.5	64.9	53.4	46.1	37.2	29.5
1.7	46	35.5	30.2	23.4	21.5
2.5	25.4	23.3	19.5	18.1	18.0
	TMA Deflection (μm)				
1.5		17.4	15.7	15.1	14.1
1.7	19.2	17.6	16.9	16.6	15.5
2.0	15.8	15.5	15.4	15.2	15.3
2.5	15.3	14.1	13.5	13.0	11.5

P : F molar ratio has been changed between 1 : 1.2 and 1 : 2.8 follows this trend for dry IB strengths, and the same is valid for IB strengths after 2 h boiling in the molar ratio range 1 : 1.2–1 : 2.5 (the noncorrelation appearing at the 1 : 2.8 molar ratio being attributable to well-defined and known factors of decreased reactivity of still free sites on already heavily substituted phenolic nuclei[1]). Equally apparent from Table I is the correlation between gel time and both board IB strength and minimum TMA deflection (and, hence, modulus) under the same set of conditions.[30,31] All these results confirm the well-known fact that an increase in molar ratio in a PF resin accelerates its curing, increases the IB strength of panels bonded with it, and decreases the TMA deflection (hence, increases the value of the bonded wood joint modulus)[1,30,31] (Fig. 1a). This occurs because an increase in P : F molar ratio corresponds to an increase in crosslinking of the final hardened resin network; hence, the bad effect of a faster gel time (leading to looser and, hence, weaker networks) is counterbalanced by a greater amount of crosslinking induced by the higher molar ratio of the resin. This is often not the case when faster resin curing must be obtained under conditions in which greater crosslinking cannot be obtained.

Figure 1b shows the case of a PF resin of fixed molar ratio used to bond a wood joint tested by TMA at different heating rates: the faster the heating rate is, the lower is the value of the maxi modulus (and the higher is the value of the deflection).[23–25]

Table II and Figure 2a show the curves of the variation of modulus as a function of the temperature for increasing amounts of urea added to the PF resin during the resin preparation and possibly copolymerized in the PF resin. The results indicate that increasing the amount of urea leads to faster gel times, this because of the increase in molecular size of the polymer.[11,12] More important is that the TMA minimal deflection at complete curing of the joint becomes smaller, and hence, that the maximum value of the modulus of the joint increases with increasing amounts of urea copolymerized in the resin leading to a stronger and more crosslinked network (Fig. 2a). The synergic effect of urea and P : F molar ratio on both gel time and strength of the final network (as related to decreasing values of the TMA deflection) is shown in Table II and Figure 2b, indicating that the two effects can be combined. This latter result would be expected, because increasing the P : F molar ratio also means an increase in

Figure 1   (a) Variation of Young's modulus during resin curing of beechwood joints bonded with low-condensation pure phenol-formaldehyde (PF) resins as a function of temperature and of F/P molar ratio (PFs 1.2, 1.4, 1.7, 2.0, 2.5, 2.8) in nonisothermal thermomechanical analysis (10°C/min). (b) Variation of Young's modulus during resin curing of beechwood joints bonded with low-condensation pure phenol-formaldehyde (PF) resins as a function of time in nonisothermal thermomechanical analysis under different heating rate conditions: 5, 7.5, 10, 20, 40, 50, 60, and 70°C/min.

(a)

(b)

the total [P + U] : F molar ratio. It is also evident from Table II, but moreso from Figure 2b, that the rate and extent of the improvement observed by combining the two effects at first diminishes and then improves rapidly the higher the molar ratio and the amount of urea become. The two effects then contribute synergically to gel time acceleration and to the increased network strength. However, this occurs very noticeably at the lower amounts of the two parameters, with increases in the value of the two parameters rapidly leading to a zone of ever-diminishing improvement up to a molar ratio of 1 : 2.0. Because the improvements in gel time and in network strength seem to tend to an asymptotic value up to molar ratio 1 : 2 (Table II, Fig. 2b), this means that the cause of the effects induced by urea and molar ratio is very possibly the same; namely, increased final crosslinking. This is important, because it means that possible copolymerization with urea of the PF resin leads at lower PUF molar ratio to the same strength of the final network obtained by pure PF resins of much higher molar ratio: such a result has considerable applied importance, because in this manner, we can limit formaldehyde concentration in both the liquid and hardened final PUF resin. It is also evident, however, that the combination of the urea and molar ratio effects is only able to give a limited improvement of gel times and curing rates of the PF resins, while still mantaining its strength characteristics. This is already a considerable improvement in the case of very advanced pure PF resins the faster gel time of which, under similar conditions, is never faster than 20–24 min, but is nonetheless insufficient to venture to pressing times and curing times comparable to those achievable with aminoplastic resins (on the order of 2–3 min when catalyzed[1]).

Similar trends are observed in Figure 3a for the same pure PF resin and in Figure 3b for the same PF resin in which a fixed amount of urea has been copolymerized with, but where increasing amounts of triacetin accelerator have been used. It is clear then, that addition of urea during PF resin preparation and addition of triacetin to a PF resin in the glue mix before curing present similar effects: (1) to accelerate resin cure; and (2) to counterbalance by an increased amount of crosslinking the decrease of strength this may cause. This is valid, notwithstanding that the mechanisms by which urea and triacetin are capable of achieving improved crosslinking are well known to be different.[6,11,12]

This similarity in behavior of urea and triacetin prompts a few questions. First, to what extent are increasing amounts of urea copolymerized with phenol in the PF resin? Second, what causes the increase in strength and crosslinking observed in the case of the two additives, even if they are used in such a different manner? Third, is there a synergic effect on final strength of urea and triacetin when used in combination in the PF resin? To answer the first of the above questions, a series of PF resins presenting the same P : F molar ratio (P : F = 1 : 1.7) prepared in presence of increasing amounts of urea (thus, at progressively lower [P + U] : F molar ratio) were examined by ^{13}C-NMR spectra. A few of these relevant spectra are presented in Figures 4 to 9.

Figures 4–8 show the ^{13}C-NMR spectra of the resins at 12% and higher molar addition of urea in the PF resin. The assignement of the shifts for the relevant species observed for the different resins are indicated in Table III. A few features of interest can be observed: urea and phenol species bound to each other by methylene bridges can easily be observed mainly (but not only) in the region of the carbonyl group of urea. Thus, to the signal of the C=O of unreacted urea at 162.7–163.3 ppm are always associated the signals of the C=O groups of monosubstituted, disubstituted, and even trisubstituted ureas. Precise assignements of the species observed have been reported for the reaction under acid conditions[15–20] and under alkaline conditions[11] of hydroxybenzyl alcohols model compounds with urea, and thus, the peaks observed for the coreaction products of urea with phenol in the formation of the PUF resin under alkaline conditions can be assigned

Figure 2   (a) Variation of Young's modulus during resin curing of beechwood joints bonded with low-condensation phenol-formaldehyde resins (F : P = 1.7, named PF 1.7) as a function of temperature and of molar percentage coreacted urea in nonisothermal thermomechanical analysis (10°C/min). (b) Variation of the maximum value of the Young's modulus during resin curing of beechwood joints bonded with low-condensation phenol-formaldehyde (PF) resins as a function of molar percentage coreacted urea and of F/P molar ratio in nonisothermal thermomechanical analysis (10°C/min).

(a)

(b)

Figure 4 ^{13}C-NMR spectrum of liquid phase phenol-formaldehyde (PF) resin of F/P molar ratio 1.7 and 12% coreacted molar urea.

with certainty. The signals that can be noticed belong to both 2-hydroxybenzyl urea (161.2–161.4 ppm) and 4-hydroxybenzyl urea (160.3–160.5 ppm), although sometimes only one of these is present, and, in general, to two or three peaks characteristic of N,N′ bis(4-hydroxybenzyl) urea (159.4–159.7 ppm), of N,N′ bis(2-hydroxybenzyl) urea (160.5–160.6 ppm), of N,N bis(4 hydroxybenzyl) urea (160.0–160.3 ppm), and tris(4-hydroxybenzyl) urea (159.3 ppm). In some cases, the pres-

ence of one, rather than the other, of these species is confirmed by the signals in other regions of the spectra. As the spectra at 12, 18, and 24% urea addition were done quantitatively a few trends could be noticed: the percentage of total phenol bound through methylene or methylene ether bridges to urea or to UF oligomers increases from 54% in the case of the PF at 12% urea substitution, to 61 and and 63% for the resins in which urea substitution is of 18 and 24%, respectively.

Figure 3 (a) Variation of Young's modulus during resin curing of beechwood joints bonded with low-condensation pure phenol-formaldehyde (PF) resin of F/P molar ratio = 1.7, as a function of temperature and of triacetin percentage, in nonisothermal thermomechanical analysis (10°C/min). (b) Variation of Young's modulus during resin curing of beechwood joints bonded with low-condensation pure phenol-formaldehyde (PF) resin of F/P molar ratio = 1.7 and 24% coreacted molar urea, as a function of temperature and of triacetin percentage, in nonisothermal thermomechanical analysis (10°C/min).

Figure 5 ^{13}C-NMR spectrum of liquid phase phenol-formaldehyde (PF) resin of F/P molar ratio 1.7 and 18% coreacted molar urea.

To the same degree, the percentage of total urea that remains unreacted is 40, 40, and 47% for the same three resins. As the amount of urea addition moves to 30, 36, and 42%, the amount of unreacted urea increases; whereas it seems that for the substituted urea species, a stable maximum is attained, and the relative proportions of hydroxybenzyl urea becomes progressively higher than the proportion of bis(hydroxybenzyl) ureas. All this seems logical if we consider that, because in the resins tested the P : F molar ratio is 1 : 1.7, by increasing the percentage of urea added, the [P + U] : F molar ratio decreases from 1 : 1.52 to, respectively, 1 : 1.44, 1 : 1.37, 1 : 1.1.31, 1 : 1.25, and 1 : 1.20 for the 12, 18, 24, 30, 36, and 42% level of urea substitution. Thus, it seems that the greater proportion of urea that coreacts usefully with the phenol in the PUF resin is attained at about 18% molar urea addition, although the proportion of copolymerized urea is still almost as high in the 12 and 24% urea addition resins.

These results are confirmed by the dry and, moreso, by the 2 hours boil IB results reported in Table IV, which provide a macroscopic correspondence with what was observed in NMR analysis. Because the resins of the spectra were all at a P : F molar ratio ratio of 1 : 1.7, considering the results above, it was interesting to examine by NMR a resin of higher molar ratio and a higher amount of urea to check whether, by increasing the molar ratio, we could increase the proportion of urea coreacted in the PUF resin. The ^{13}C-NMR spectrum in Figure 9 is that of a UF resin of P : F molar ratio of 1 : 2.5, in which 30% urea has been added in the reaction. From the spectrum, it is evident that the proportion of unreacted urea is much lower than what is observed for the resins in Figures 5–8; that no hydroxybenzyl urea is present but only one type of bis(hydroxybenzyl)-urea, indicating that a much greater proportion of urea is, in fact, copolymerized in the resin with no "pendant" urea molecules attached to the PF skel-

Figure 6 ^{13}C-NMR spectrum of liquid phase phenol-formaldehyde (PF) resin of F/P molar ratio 1.7 and 24% coreacted molar urea.

eton; that no free ortho- or para sites capable of reaction are present in the resin (absence of peaks in the 115–120 ppm region); that a higher proportion of methylol groups are present on phenolic nuclei (64.6 ppm), that the urea is copolymerized in the resin mainly as highly branched UF oligomers [55.3 ppm (this being unusual under alkaline conditions where the urea condensation reaction is very much disfavored), and 73 ppm]; but also that free formaldehyde is very much present in the resin (methylene glycol signal at 82.8 ppm); whereas, in the resins in Figures 4 to 8, no free formaldehyde was present.

From this, it is evident that increasing the amount of formaldehyde will allow us to shift the optimum macroscopic performance in resins of greater proportions of urea addition than that which is indicated in Table IV; hence, higher than 18–24% urea addition. It is interesting to note that, for all resins, some of the urea is in a branched or potentially branched configuration by itself as indicated by the presence of the peaks (rather small) 72.6–73 ppm. In regards to the

second question above; to achieve merely a faster gel time is relatively easy; from Figure 1b above, it is evident that to have also strong panels while maintaining press times as fast as indicated by the gel times achievable may not be as easily achieved.

To avoid such a problem, we can use a molecule that contributes to prebranching of the resin, thus acting as a more rapid (more rapid than phenolic nuclei, that is) networking center. More reactive prebranching molecules can then be added to the PF resin, as is done with urea. We could consider using another type of molecule on top of urea. If urea increases the crosslinking density of the PF resin, addition of another prebranching molecule on top of urea will not improve the situation. If, instead, the mechanism of urea strengthening of the PF resin is another one, further addition of another, more effective, prebranching molecule will further improve the strength results. The TMA results in Table V, when using melamine on top of urea, indicate that the results are not improved, and, hence, confirm that the function of urea added in the PF

Figure 7 ^{13}C-NMR spectrum of liquid phase phenol-formaldehyde (PF) resin of F/P molar ratio 1.7 and 36% coreacted molar urea.

resin is that of a branching agent more effective and quicker reacting than phenol and that the improvement in strength of the network as shown by TMA is given by increased crosslinking density induced by the presence of urea.

If we consider that the reaction of monomethylation of the phenol under alkaline conditions has been reported[32,33] as having a rate constant of 5.25×10^{-6} l/(mol s) for each ortho site and of 6.2×10^{-6} l/(mol s) for each para site; whereas, that of monomethylation of urea at pH 7. is of the order of 1×10^{-4} l/(mol s) for each site[34] and of the order of 3×10^{-4} l/(mol s) at alkaline pH,[1] it is possible to deduce what occurs (see Scheme below): at alkaline pH when urea and phenol are

both present in presence of formaldehyde, both phenol and urea react to form methylolated ureas and methylolated phenols, with the urea reacting faster and, hence, in greater proportion. A greater amount of methylol ureas than methylol phenols will have formed. The inverse reaction of decomposition of the methylol urea will somewhat limit the proportion of methylolated urea over methylolated phenol. To this effect, a calculation of the degree of advancement of the reaction of methylolation of urea under alkaline conditions can be carried out by the use of the following formula (see reference 50):

$$p/[2(1-p)] = \exp[(-\Delta G^{\theta})/(2RT)] \qquad (1)$$

Figure 8 ^{13}C-NMR spectrum of liquid phase phenol-formaldehyde (PF) resin of F/P molar ratio 1.7 and 42% coreacted molar urea.

Figure 9 ^{13}C-NMR spectrum of liquid phase phenol-formaldehyde (PF) resin of F/P molar ratio 2.5 and 30% coreacted molar urea.

Fig. 8

Fig. 9

Table III ^{13}C-NMR Shifts and Group Assignments for the Different PUF Resins

F/P Molar Ratio	Literature Shift[39–49] (ppm)	Urea, Molar % Shifts					
		12% 1.7 (ppm)	18% 1.7 (ppm)	24% 1.7 (ppm)	30% 2.5 (ppm)	36% 1.7 (ppm)	42% 1.7 (ppm)
C=O							
Unreacted urea	163.0[15–20]	162.7	162.9	162.9	162.5	163.1	162.6
4-Hydroxybenzylurea	160.4[15–20]	160.3	—	—	—	—	160.3
N,N′-bis(4-hydroxybenzyl)urea	160.6[15–20]	—	160.5	—	—	—	—
N,N-bis(4-hydroxybenzyl)urea	160.0[15–20]	—	—	160.0	159.8	160.0	—
Tris(4-hydroxybenzyl)urea	159.3[15–20]	—	159.4	159.3	159.6	159.3	—
2-Hydroxybenzylurea	161.3[15–20]	161.4	161.6	161.2	—	161.2	161.2
N,N′-bis(2-hydroxybenzyl)urea	160.0[15–20]	—	—	160.0	—	160.0	—
(Ar)COH							
para-substitution							
N,N-bis(4-hydroxybenzyl)urea, C1	158.3[15–20]	158.5	—	—	—	—	—
tris(4-hydroxybenzyl)urea, C1	157.9[15–20]	157.7	—	—	157.0	157.3	—
ortho-substitution							
2-hydroxybenzyl urea, C1	156.2[15–20]	—	—	—	—	156.1	156.3
(Ar)*C*—C							
ortho, para reacted sites	127.6–133.9[41–48]			126–134			
2-hydroxybenzylurea, C2	128.5[15–20]					128.4	
(Ar)*C*—H							
meta unreacted sites	127.4–132.9[46–48]			126–134			
tris(4-hydroxybenzyl)urea, C3, C5	129.0[15–20]					129.0	
tris(4-hydroxybenzyl)urea, C9, C11	129.2[15–20]					129.2	
2-hydroxybenzylurea, C3	130.0[15–20]					130.2	
2-hydroxybenzylurea, C5	129.8[15–20]					129.5	
para unreacted sites	119.0–120.9[46–48]			119–121			
2-hydroxybenzylurea, C2	120.3[15–20]					118.9	
ortho unreacted sites	115.4–116.0[46–48]			115–118			
2-hydroxybenzylurea, C6	116.6[15–20]					117.0	
—CH$_2$—							
CH$_3$O—CH$_2$—O—CH$_2$—OH	93.4,[39] 95.0[41]	94.2	94.5	94.0	—	—	—
ortho-Ph—CH$_2$—O—CH$_2$OH	90.0[46,48]	90.0	—	—	90.0	—	—
para-Ph—CH$_2$—O—CH$_2$OH	89.3[47]	—	—	—	88.3	—	—

$HOCH_2$—O—CH_2OH	87.3[47]	—	—	86.8	—	—
HO—CH_2OH (free HCHO)	82.9,[44] 83.1[41]	—	—	82.8	—	—
—N(—CH_2OH), and —N(—CH_2—)CH_2OH	72.7,[45] 71.6–72.8,[39,42] 73.5[40,44,49]	72.8	72.5	73.0	73.0	72.6
ortho-Ph—CH_2—O—CH_2—Ph and —NH—CH_2—O—CH_2—NH—	72,[15] 70.8,[47,48]	—	—	71.5	71.2	71.0
	71.1[40,44,49]	—	—	—	—	—
para-Ph—CH_2—O—CH_2—Ph and —NH—CH_2—O—CH_2—NH—	69.1,[15]	—	—	69.0	—	—
	69.0,[45] 69.4[39,41]	—	—	68.0	—	—
ortho-Ph—CH_2—O—CH_2OH and —NH—CH_2OH	66.6,[47,48]	—	—	66.5	—	—
para-Ph—CH_2OH and —NH—CH_2OH	66.6,[43] 66.5–66.8[40,44,49]	—	—	—	—	—
	64.7,[15] 65.5,[47,48]	64.7	64.4	64.6	64.5	64.5
	62.2,[45] 63.7–65.2,[39] 64.5–65.2,[42] 64.8[44]	62.1	62.0	62.3	62.0	62.0
diortho $HOCH_2$—Ph—CH_2OH	61.6–62.3[47,48]	—	—	—	—	—
ortho Ph—CH_2OH	61.1,[15] 61.4–61.5[47–48]	61.4	61.3	—	61.3	61.3
—N(CH_2—)CH_2N(CH_2—)—	59.4,[39,42] 59.8[45]	56.0	55.5	55.3	—	—
—N(CH_2—)CH_2NH—	54.5–54.8,[42] 55.5,[40,43,44,49] 54.5[45]	54.8	54.5	55.1	54.8	54.5
—$NHCH_2NH$—	49.0[39,40,43,45,49]	49.4	49.5	49.6	49.8	49.7
and para-Ph—CH_2N(CH_2—)CO— and Tris(4-hydroxybenzyl)urea	49.2[15]	—	—	—	—	—
and Tris(4-hydroxybenzyl)urea	49.1[20]	—	—	—	—	—
ortho-Ph—CH_2—N(CH_2—)CO—	46.4[15]	46.0	46.0	46.0	—	—
Tris(4-hydroxybenzyl)urea and N,N'-bis(4-hydroxybenzyl)urea	44.7[20]	—	—	44.5	—	—
	44.3[20]	—	—	—	43.7	43.7
para-Ph—CH_2—NHCO—	44.2[20]	—	—	43.2	—	—
p,p Ph—CH_2—Ph, and N,N'-bis(4-hydroxybenzyl)urea	39.7,[17,48] 40.6,[15] 41.0[46]	40.5	40.5	40.5	40.4	40.4
and N,N'-bis(4-hydroxybenzyl)urea	40.6[20]	—	—	—	—	—
and N,N'-bis(4-hydroxybenzyl)urea	40.6[20]	—	—	—	—	—
o,p Ph—CH_2—Ph	35.0,[47,48] 35.5–35.9,[46] 35.8[15]	35.5	35.5	35.5	35.0	—

Table IV IB Strength of Softwood Particleboard Bonded with a Low-Condensation PF Resin of F/P Molar Ratio of 1.7 When Increasing Molar Percentage of Coreacted Urea up to 42%

	IB Dry (MPa)	IB, 2 h Boil, Tested Dry (MPa)
PF control	0.88	0.20
+ 6% Urea	0.91	0.26
+ 12% Urea	1.07	0.30
+ 18% Urea	1.09	0.31
+ 24% Urea	1.12	0.28
+ 30% Urea	0.98	0.25
+ 36% Urea	0.94	0.24
+ 42% Urea	0.96	0.25

where p is the degree of conversion at the equilibrium of the methylolation and demethylolation reactions, ΔG^{θ} is the standard Gibbs energy variation, T is the temperature in degrees Kelvin, and R is a constant (1.987 cal/g mol K). When introducing the reported activation energies of the urea forward methylolation reaction (17.5 kcal/mol)[34] and of the methylol urea demethylolation reaction (17.1 kcal/mol),[34] we obtain a degree of

advancement $p = 0.60$; hence, at equilibrium under the conditions used, 60% of the urea is present as methylol ureas. This compares well with a degree of conversion of 65%, at the equilibrium, of the more reactive melamine extrapolated by reported kinetic values (see reference 51) to the same conditions used herein.

However, although methylolated phenols do proceed to the reaction of condensation to form dihydroxydiphenyl methanes (II), methylolated dihydroxydiphenyl methanes (I), and higher phenolic oligomers linked by methylene bridges, methylolated ureas cannot achieve this, because their equivalent condensation reaction does not occur under the alkaline environment (pH 11) used.[1,34] The phenolic nuclei of phenol and of the growing PF polymer, however, can react with the methylol groups carried on the urea, inducing copolymerisation (III, IV) to form bridges to single ureas or to chain of ureas linked by methylene ether bridges (the only condensation more favored for urea at alkaline pH). This explains the higher network strength obtained as urea is trisubstituted in the original copolymer and, thus, constitutes a center of branching as well as of molecular doubling already present in abundance before hardening.

Reactions I, II, III, IV, and V all occur; whereas, reaction VI cannot occur under alkaline conditions.[1,34] Presence of free HCHO in the reaction environment (for example, both initially or as a

Table V   TMA Deflection Results of a PF Resin of F/P Molar Ratio 1.7 Coreacted with 24% Molar Proportion of Urea in Presence of Melamine as a Further Prebranching Molecule

	TMA Deflection (μm)
PF + 24% Urea, control	14.7
PF + 24% Urea + 5% melamine	16.1
PF + 24% Urea + 10% triacetin, control	12.9
PF + 24% Urea + 5% melamine + 10% triacetin	19.8

second addition of HCHO in the reaction) will lead to further methylolation on —NH$_2$, —NH— and substituted phenolic sites, and the reactions schematically represented in the above scheme restart with methylolation followed by the formation of methylene bridges. Compounds of type II; namely, 2-hydroxybenzylurea and 4-hydroxybenzylurea, will pass on reaction with formaldehyde to the bis(hydroxybenzyl) ureas, as will compounds of type III and IV, all these compounds being observed in the ^{13}C-NMR spectra in Figures 4–9, as well as two higher mixed oligomers and mixed networks. As observed in the spectra F : P 1.7, cases in which 12, 18, and 24% molar urea is coreacted will lead to a slight predominance of bis(hydroxybenzyl)ureas because of the relatively higher proportion of formaldehyde used. Conversely, in the P : F 1 : 1.7 at 36 and 42% molar urea addition in which the proportion of formaldehyde is lower and urea higher, the hydroxybenzylureas predominate over the bis(hydroxybenzyl)-ureas, with this predominance becoming more marked with increasing amounts of urea or decreasing amounts of formaldehyde. In this context, the finding that in the P : F 1 : 2.5 resin with 30% molar addition of urea there is no trace of hydroxybenzylureas, but only bis(hydroxybenzyl)-ureas are observed, is to be expected. The same reactions above also contribute to the hardening of the resin, with both phenolic and urea-based methylol groups taking part in the hardening process. Thus, the parameter of importance affecting copolymerization of urea and phenol with formaldehyde under alkaline conditions is the molar ratio urea : phenol : formaldehyde.

Furthermore, the urea-induced molecular doubling reaction alone gives a faster gel time (Table

II) by itself. This can be explained by both the increase in molecular size of the polymer at equivalent viscosity attributable to a higher degree of branching,[35] with the consequent lower number of steps to lead to crosslinking. Urea accelerating the curing of the PF resin is then partly a structural modification effect and not a catalysis effect under alkaline conditions. However, this is not all. Under alkaline hardening of the PUF resin, the methylol groups on phenolic nuclei, which are those reacting to methylene bridges to form the finished hardened network, will again react faster with still unreacted sites present on the urea rather than on the free sites of phenol; in short, the mixed reaction of methylol phenol with a urea site rather than the reaction of the same phenolic methylol with a free phenolic site. This effect also contributes to the acceleration of the hardening reaction.

The whole becomes an exercise in balance of properties: the fast gel time which decreases eventually the tightness of cross-linking of the network obtained, and the rapid branching molecules effect that increases cross-linking without lengthening (most often shortening) the gel time. This requires good control of conditions. This is then an important concept, and a necessary requirement to achieve fast press times coupled with strong hardened resin networks, hence high value of the I.B. of the panel bonded with such fast pressing resins.

Addressing the third question above, the results of gel time and TMA deflection of PF resins prereacted with urea and mixed with triacetin shown in Table VI and the wood particleboard IB strength results shown in Table VII indicate that a synergy effect between urea and triacetin does, indeed, exist, but only up to a certain level. At too high an amount of urea, the triacetin has no effect anymore, and at too high an amount of triacetin, urea has no effect (on the contrary, a deleterious effect seems to occur). This confirms that part, but not all, of the effect of triacetin is based on a further cross-linking mechanism which has already been described,[2,3,6,12] and some part of the triacetin remains linked or copolymerized in the final network. That this is the case is shown by the amounts of triacetin that have remained in the solid network, as determined by gross gravimetry, shown in Table VIII. The results shown in Table 8 cannot pretend to indicate the exact amounts of triacetin that has coreacted with the network simply because a certain amount of it might just be still trapped in it, but they are

Table VI Gel Times and TMA Results of a Low-Condensation PF Resin of F/P Molar Ratio 1.7, at Different Molar Percentages of Coreacted Urea and at Different Percentages of Triacetin

Triacetin (%)	Gel Time (s)					
	0.0	2.5	5.0	10.0	15.0	20.0
0% Urea	44	30	20	7	2	——
6% Urea	36	31	26	9	4	——
12% Urea	32	26	19	10	4	——
18% Urea	27	22	17	7	2	——
24% Urea	20	14	9	5	2	——

Triacetin (%)	TMA Minimum Deflection (μm)					
	0.0	2.5	5.0	7.5	10.0	15.0
0% Urea	19.2	17.0	15.6	14.4	14.2	16.6
6% Urea	17.3	16.2	16.2	15.4	14.6	14.5
12% Urea	16.5	16.0	15.7	14.7	13.9	23.6
18% Urea	15.9	15.2	14.9	13.9	15.9	19.8
24% Urea	14.7	14.4	14.4	14.0	12.9	20.6

indicative nonetheless especially when taken in combination with more precise evidence presented previously[6] and above.

The results in Table VII detailing the IB strength results of wood particleboard prepared at long press times, hence being of low dependence on the improvement of strength caused by faster gel times, clearly indicate that the faster gel times and improved TMA values can be translated into better applied results for the IB of wood particleboard, at least within a limited range of urea and triacetin addition. They also confirm that the main effect of the triacetin is to increase the final strength of the hardened adhesive resin independent of the acceleration induced, a fact

again confirming that a further crosslinking mechanism is also at play.[2,3,6]

To obtain proof that acceptable performance at much faster hot-press times can, indeed, by achieved, wood particleboard was made with one of the PUFs with triacetin; namely the PF + 24% urea + 10% triacetin. Now, the fastest commercial pure PF resins when used at 190°C to press particleboard give results that satisfy the relevant standards only down to press times as fast as 12–13 s/mm. Faster press times are on record, but these are obtained at higher temperature, or they use very particular systems in which carbonate accelerators are used, or a considerable part of the resin is not a PF.[21,36,37] The requirements of

Table VII IB Strength of Hardwood Particleboard Bonded With a Low-Condensation PF Resin of F/P Molar Ratio of 1.7 at Increasing Molar Percentage of Coreacted Urea and of Triacetin (at Long Press Times)

Triacetin (%)	IB Dry (MPa)			IB 2 h Boil (MPa)		
	0	2.5	7.5	0	2.5	7.5
0% Urea	0.58	0.84	1.05	0.14	0.40	0.60
6% Urea	0.60	0.85	1.08	0.17	0.41	0.43
12% Urea	0.64	0.87	1.09	0.18	0.40	0.44
18% Urea	0.68	0.92	1.08	0.20	0.43	0.45
24% Urea	0.71	1.04	1.12	0.23	0.45	0.48

Table VIII   Percentage Triacetin Reacted and Incorporated in Final Adhesive Network (by Reaction or by Coprecipitation)

Triacetin (%)	0.0	2.5	5.0	7.5	10	15
PF 1.7	0	12.4	37.1	48.6	59.8	68.6
PF 1.7 + 6% Urea	0	73.2	91.7	59.5	72.4	82.2
PF 1.7 + 12% Urea	0	64.5	71.3	68.1	67.3	88.5
PF 1.7 + 18% Urea	0	84.9	78.6	78.2	82.6	76.8
PF 1.7 + 24% Urea	0	50.8	67.6	71.3	68.4	88.7

the European Norm standard[38] and German DIN standard[29] require a dry IB strength of the board ≥ 0.35 MPa and a wet IB strength after 2 hours in boiling water ≥ 0.15 MPa. The results in Table IX indicate that much faster press times still yielding results satisfying the relevant standards are possible. Thus, press times of 8.5 s/mm are within the requirements of the standard, and only the wet result of the panels at 7.1 s/mm is just under the requirements of the standard at press temperatures as low as 190°C. The use of higher temperatures (200–220°C) as accepted in more modern particleboard lines today will definitely allow press times as fast as 7 s/mm, or faster, still yielding boards of performance acceptable to the relevant standards.

CONCLUSIONS

Low-condensation phenol-formaldehyde (PF) resins coreacted under alkaline conditions with up to 42% molar urea on phenol during resin preparation can yield PUF resins capable of faster hardening times than equivalent pure PF resins prepared under identical conditions and presenting

better performance than the latter. Part of the urea is copolymerized to yield the alkaline PUF resin; whereas, especially at the higher levels of urea addition, unreacted urea is still present in the resin. Increase of the initial formaldehyde to phenol molar ratio considerably decreases the proportion of unreacted urea and increases the proportion of PUF resin. The PUF resins curing can be accelerated further by adding an ester accelerator, glycerol triacetate (triacetin) being the ester used in this study, to reach gel times as fast as those characteristic of catalyzed aminoplastic resins, but at unimpaired strength values. Synergy between the relative amounts of copolymerized urea and ester accelerator is rather marked at the lower levels of the two parameters, but this synergy decreases at the higher percentages of urea and triacetin. It was also possible to assign a majority of the ^{13}C-NMR shifts of the relevant peaks of the PUF resins. The relative performance of the different PUF resins prepared was checked under different conditions by both TMA and by preparation of wood particleboard, and the capability of the accelerated PUF resins to achieve press times as fast as those of aminoplastic (UF and others) resins is confirmed.

Table IX   Effect of Shortening the Pressing Time on IB Strength of Hardwood Particleboard Bonded with a PF Resin of F/P Molar Ratio 1.7 Coreacted with 24% Urea and Added 10% Triacetin

Press Time (s)	Press Time (s/mm)	IB Dry (MPa)	Board Density (g/cm^3)	IB 2 h Boil (MPa)	Redried Tested Wet (V 100)	Board Density (g/cm^3)
300	21.4	0.85	0.753	0.23	0.16	0.752
240	17.1	0.93	0.758	0.28	0.17	0.751
180	12.9	0.95	0.729	0.29	0.17	0.729
150	10.7	0.95	0.732	0.30	0.17	0.725
120	8.5	0.81	0.751	0.22	0.15	0.751
100	7.1	0.52	0.735	0.15	0.13	0.735
90	6.4	0.49	0.741	0.11	0.10	0.741

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