

Urea–Formaldehyde–Propionaldehyde Physical Gelation Resins for Improved Swelling in Water

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ABSTRACT: Urea–formaldehyde (UF) resins' water tolerance and swelling thickness of interior-grade wood panels bonded with UF resins were improved markedly by introducing small amounts of UFPropional (UFP) polycondensates into the UF resin. ^{13}C NMR of urea–propanal (UP) resins showed that urea and propanal do react up to the formation of dimers. The water repellancy imparted by insertion in the resin of the alkyl chain of propanal limits the proportion of propanal that can be used. Gel permeation chromatography showed that this appears to be so because UP resins and UFP resins exist as an equilibrium between two separate intermingling phases, namely one in solution and the second in a state of physical gelation. This latter is

different from the state of physical gelation observed on ageing or advancement of formaldehyde-only based polycondensation resins. This physical gelation is brought on by the insertion in the resin of the water repellent chain of the propanal reacted with urea and constitutes a new state of physical gelation of polycondensates other than what was already reported in the literature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5131–5136, 2006

Key words: physical gelation; colloids; resins; swelling; water resistance; urea-formaldehyde; propanal; wood adhesives

INTRODUCTION

Water resistance and in particular swelling thickness of urea–formaldehyde (UF) bonded wood particleboard is always a subject of investigation to improve the performance of the UF adhesive in moist/wet conditions. Several systems have been researched and published over the years to indicate several routes of possible improvement. One route is the well-established addition of melamine to UF resins and their coreaction. Other routes have also been tried, among these even coreaction of UF resins with small amounts of isocyanates.^{1–6}

Among many other systems, of particular interest is the system based on the addition of aliphatic long chain di- and tri-amines,^{7,8} which was originally proposed to introduce better flexibility, hence better stress distribution in a hardened plywood glue-line. This was followed by the coreaction of a short chain aliphatic dialdehyde, succinaldehyde, to form UF–succinaldehyde resins capable of yielding plywood of improved water resistance.⁹ Succinaldehyde is a dialdehyde, involving after reaction with urea a $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ chain being inserted between ureas. This improves water repellancy, but also decreases its density of crosslinking. Both systems were excellent for plywood, where the construction of the panel protects more the glue-line from water dete-

rioration. It would be interesting to ascertain whether insertion of an aliphatic $(-\text{CH}_2-)_n$ chain as a pendant chain (rather than inserted) to the UF resin network would improve water resistance of the resin and swelling thickness of a board. For this purpose, what is needed is an aliphatic compound carrying a single aldehyde or amine/amide group. The length of the aliphatic chain cannot be too long, as very low solubility of the compound would severely limit or even completely inhibit its reaction with a water-based system such as UF. Thus, a C_4 chain such as in butyraldehyde will already inhibit coreaction in water with a UF. Of the aliphatic compounds tried, the longest chains while the compound was still relatively soluble to have sufficient coreaction were propionaldehyde ($\text{CH}_3\text{CH}_2\text{CHO}$) and propionamide ($\text{CH}_3\text{CH}_2\text{CONH}_2$).

This article deals with the preparation of urea–propionaldehyde resin precursors and their reaction with UF resins to yield UFPropionaldehyde (UFP) resins, as well as with the coreaction of propionamide with UF resins to yield UFPropionamide (UFPam) resins. The adhesives were tested on particleboard, where the more open panel construction (when compared with plywood) would show best any improvements the coreaction was able to introduce.

EXPERIMENTAL

Resins preparation and testing

The UF resin used was of commercial grade (BASF 350). The urea–propanal (UP) resin series were pre-

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TABLE I
Materials Balance for the Preparation of UP Resins

	UP1	UP2	UP3	UP4	UP5	UP6	UP7	UP8
Urea	60	60	60	60	60	60	60	60
Water	60	30	30	60	120	60	30	40
Propanal (97%)	35	35	60	120	120	60	35	20
Reaction time (min)	10	30	30	30	30	30	60	25
Propanal/urea molar ratio	0.58	0.58	1.0	2.0	2.0	1.0	0.58	0.33
Shelf life (h)	336	48	48	1	1	48	5	168

pared and the proportions and reaction times are given in Table I. All the reactions were carried out in a glass reactor equipped with a reflux condenser and under continuous mechanical stirring. The reaction was carried out at 90°C, pH = 5, and after the reaction time indicated in Table I, the pH was adjusted to 8 by the addition of 33% NaOH water solution and the resin was cooled and stored. The resin UPF1 was prepared by mixing in a glass reactor equipped with condenser 60 g urea, 60 g water, and 35 g propanal. The pH was adjusted to 5 by the addition of formic acid. The temperature of the mixture was increased to 90°C and the mixture was allowed to react for 10 min under continuous mechanical stirring. Formurea (116 g) (composed of 54% formaldehyde, 23% urea, and 23% water) was then added and the reaction continued at pH = 5 and at 90°C for 15 min. Urea (10 g) premixed with 10–15 g water was added at the end of the reaction, and the mixture was cooled and stored. For use in the glue-mixes, the UFP1 resin was added to the UF resin in the glue-mix a few minutes before application to the board and mixed well.

Gel permeation chromatography

Samples of each of the UP1-UP8 resins and of the UFP resin described earlier were analyzed by gel permeation chromatography (GPC). A Waters 515 HPLC pump and GPC system was used and the resins analyzed through a Styragel HR1 column (for determination of M_w between 100 and 5000) at an elution rate of 1 mL/min, after polyethylene glycol (PEG) calibration of the column. The PEG samples used for calibration had M_w of 200, 300, 400, 600, 1000, 2000, 3400, 8000, 10,000. Each resin sample after having been dissolved in dimethylformamide was tested without having been filtered to detect any possible molecular associations. A Waters 410 refractometer was used as the detector.

^{13}C NMR

The liquid ^{13}C NMR spectra of all the seven commercial polyurethane resins used were obtained on a Brüker DSX 400 FT-NMR spectrometer. Chemical

shifts were calculated relative to tetramethylsilane at ambient temperature for NMR shifts control. The spectra were obtained at 62.90 MHz for approximately 1000 transients. All the spectra were run with a relaxation delay of 5 s and chemical shifts were accurate to 1 ppm.

Board testing

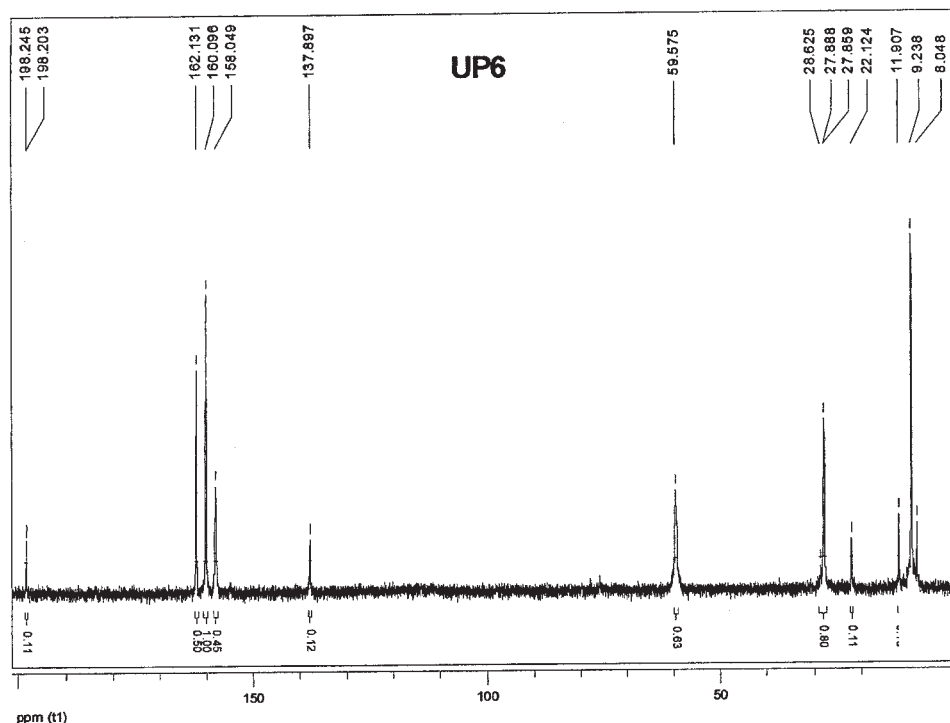
Duplicate one layer laboratory particleboard of 350 × 310 × 16 mm dimensions were prepared by adding 10% total resin solids content on dry wood particles pressed at a maximum pressure of 28 kg/cm² followed by a descending pressing cycle, at a press temperature of 195°C and for a total pressing time of 5 min.

The aimed average density for all the panels comprised between 700 and 720 kg/m³. The panels, after light surface sanding, were tested for wet swelling after 2 and 124 h immersion in cold water, for dry internal bond (IB) strength, and for IB strength after variable time of boiling tested dry after 16 h redrying.

RESULTS AND DISCUSSION

The preparation of a number of different UP resins (Table I) led at first to some unexpected results. None of these resins, on addition of a hardener, hardened in gel time tests at 100°C, even in the presence of a hardener. This would indicate that urea and propionaldehyde have not reacted. However, all resins had a very limited shelf life, from the 2 weeks of UP1 to the 30 min of UP7 and UP8, indicating a very advanced, well polymerized resin.

These data did not fit with each other. Thus, if the reactivity of the resin was so low not to gel at 100°C, not even with a hardener, it would not be possible to have such a short shelf life at ambient temperature as obtained, shelf life and gel time of the resin being in relation. Conversely, the short shelf life observed should correspond to a resin of very high reactivity presenting very fast gel times. As the facts did not fit, it became evident that one of the phenomena observed in one of the two experiments was different from gel time or shelf life. ^{13}C NMR examination of all the


 Figure 1 ^{13}C NMR of UP resin UP6.

resins yielded clear proof that urea and propionaldehyde had reacted, but not extensively. Thus, in Figure 1, the NMR spectrum of UP6 clearly shows that both first reaction products such as $\text{H}_2\text{NCONH}-\text{CH}(-\text{OH})\text{CH}_2\text{CH}_3$ and condensation products of low level of condensation such as $\text{H}_2\text{NCONH}-\text{CH}(-\text{CH}_2\text{CH}_3)-\text{HNCONH}_2$ had formed. The low reaction rate of propanal with urea led only to dimers is not illogical indicating that the hardening rate of such a resin should be very low, hence the gel time would be very long, as indeed observed experimentally. The data from the gel time test were then corrected. The reason of the short shelf life was then identified as due to the water repellency of the CHCH_2CH_3 chain of propanal once this is introduced in the resin. This caused precipitation of the greater part of the UP resin as soon as a certain number of propanal molecules were inserted in the chain; from the NMR in Figure 1 and Table II, it seems that separation of phase occurs as early as two propanal bridges between ureas have formed. Once precipitated due to the water intolerance of the side chain, these oligomers do not react anymore, being out of the water phase in which condensation reactions of this type proceed.

As a result of these findings, the resins are victims of the same positive effect, water repellancy that the propanal alkyl chain is used to introduce. It is evident then that only a mixed UFP resin, a resin in which the proportion of propanal is strictly limited, could be

 TABLE II
 ^{13}C NMR Shifts Assignment for UP and UPF1 Resins

Groups	ppm
UP resins ^a	
H_2NCONH_2	162
$\text{H}_2\text{NCONH}-\text{CH}(-\text{OH})\text{CH}_2\text{CH}_3$	160
$\text{H}_2\text{NCONH}-\text{CH}(-\text{CH}_2\text{CH}_3)-\text{HNCONH}_2$	158
$\text{H}_2\text{NCONH}-\text{CH}(-\text{OH})\text{CH}_2\text{CH}_3$	59.6
$\text{H}_2\text{NCONH}-\text{CH}(-\text{CH}_2\text{CH}_3)-\text{HNCONH}_2$	59.6
$\text{R}-\text{HNCONH}-\text{CH}(-\text{OH})\text{CH}_2\text{CH}_3$	27.8
$(\text{HO}-)_2\text{CH}-\text{CH}_2\text{CH}_3$	22.1
$\text{R}-\text{HNCONH}-\text{CH}(-\text{OH})\text{CH}_2\text{CH}_3$	9.2
$(\text{HO}-)_2\text{CH}-\text{CH}_2\text{CH}_3$	8.6
UPF1 resin ^b	
$\text{CH}_3\text{CH}_2\text{COO}^-$ and/or	
CH_3COO^-	180.5
HCOO^-	170.3
H_2NCONH_2	162.1
$\text{H}_2\text{NCONH}-\text{R}'$	160.4
$\text{R}'-\text{HNCONH}-\text{R}'$	158.9
$\text{H}_2\text{NCONH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{HNCONH}_2$	67.9
$\text{H}_2\text{NCONH}-\text{CH}_2\text{OH}$	63.6
$\text{H}_2\text{NCONH}-\text{CH}(-\text{OH})\text{CH}_2\text{CH}_3$	59.6
$\text{H}_2\text{NCONH}-\text{CH}(-\text{CH}_2\text{CH}_3)-\text{HNCONH}_2$	59.6
$-\text{NH}-(-\text{CH}-\text{R}'')-\text{CH}_2-\text{NH}-$	52.4
$-\text{NH}-\text{CH}_2-\text{NH}-$	45.9
$\text{CH}_3\text{CH}_2\text{COO}^-$ and/or	
$\text{R}-\text{HNCONH}-\text{CH}(-\text{OH})\text{CH}_2\text{CH}_3$	28.5
$(\text{HO}-)_2\text{CH}-\text{CH}_2\text{CH}_3$	23.1
$\text{CH}_3\text{CH}_2\text{COO}^-$	9.6

^a $\text{R} = -\text{H}$ or $-\text{CH}(-\text{OH})\text{CH}_2\text{CH}_3$.

^b $\text{R}' = -\text{CH}_2-$ or $-\text{CH}(-\text{CH}_2\text{CH}_3)-$ and $\text{R}'' = -\text{H}$ or $-\text{CH}(-\text{CH}_2\text{CH}_3)-$.

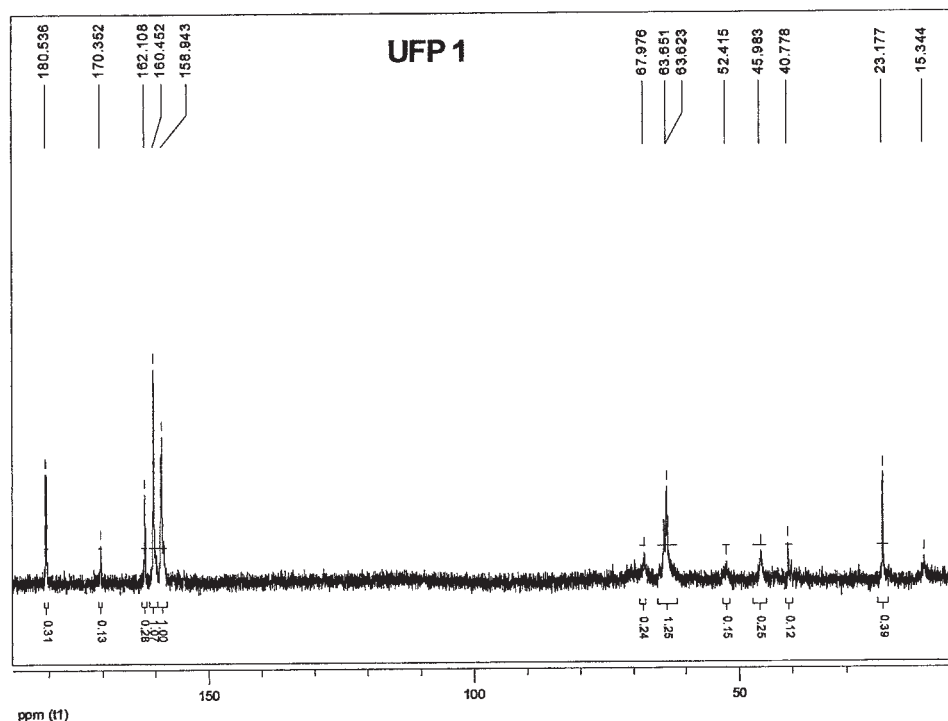


Figure 2 ^{13}C NMR of UFP resin UFP1.

prepared to exploit the water repellancy of the alkyl chain.

Resin UFP1 was the mixed resin of relative molar ratio U : F : P = 1 : 1.3 : 0.4, which was developed to use the properties of propanal. This resin also presented the same problems as the UP resins but to a much lesser extent, mainly it had much longer shelf life, at least 4 weeks before phase separation started. The UFP1 resin so prepared was used to mix with a commercial UF resin to a very limited proportion to maintain the properties of the UF resin but upgrade the swelling thickness of the panel, especially in cold water. Figure 2 shows the ^{13}C NMR of resin UFP1, and its shift assignments are summarized in Table I. It is interesting to note that the peaks indicating the presence of propanal are very small indicating that even at this low extent of reaction the resin is in a state between solution and phase separation, with a good part

of the propanal reacted part already over the edge. As in all cases, both for the UP and the UFP resin, the phase out of solution is not a solid precipitate but a colloid. All aminoplastic resins in cases of physical gel and pregel are in colloidal state.¹⁰⁻¹⁵ It is interesting that in the case of these resins, the physical gel state occurs when the resin is not even near to any chemical gelling/hardening.

The existence of the phase separation can also be observed by GPC when this is done without prefiltering the resins. In Figures 3-5 are shown the GPC chromatograms of a concentrated solution of urea in water, as a control, and of UP2 and UP6. The high concentration of urea solution gives a signal peaking at around M_n 223-229. This was repeated several times with different amounts of water, but still in fairly concentrated solution. Sometimes, a much smaller peak at M_n 114-120 appears. As the M_n of urea is 60, it is evident that the high concentration forces the urea to be strongly associated by secondary forces.

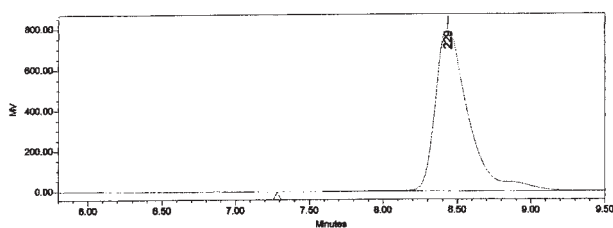


Figure 3 Control GPC of concentrated urea solution.

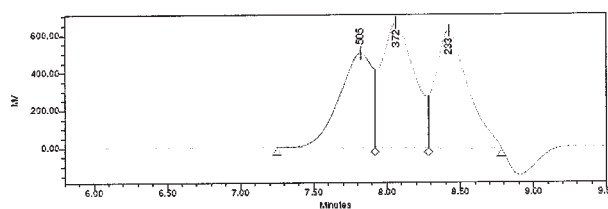


Figure 4 GPC of UP resin UP2.

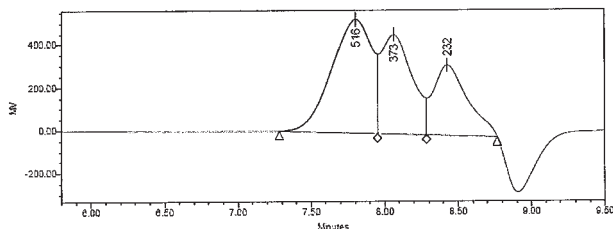
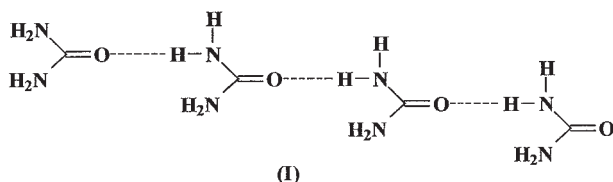
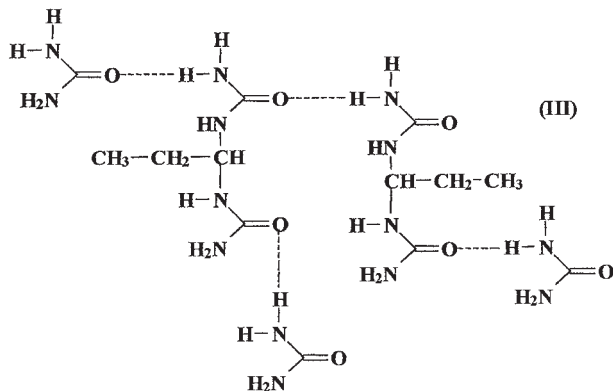


Figure 5 GPC of UP resin UP6. Note: GPC of UP4 is identical to this.

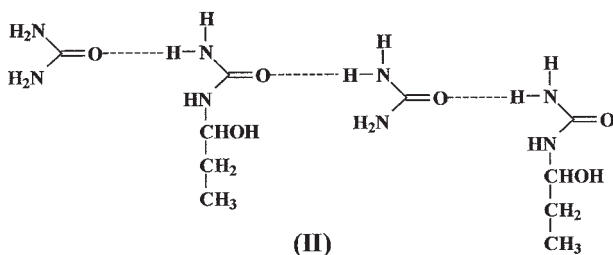
Thus, a M_n of 223 corresponds to an association of the type



For the cases of UP2 and UP6 in Figures 4 and 5, three signals can be observed: one peaking at M_n 223 (I), one at M_n 373–373 (II), and one at M_n 505–519 (III). The signals present different relative areas according to the resin tested (UP2 or UP6). Signal (I) is the urea alone, and signal (III) corresponds to a mix of secondary forces bound ureas, some of which have reacted with propionaldehyde and some of which have not; in the case of M_n 505, the general type of formula being



Signal (II) being an intermediary case of the type



These are only examples of the higher frequency structures, as the width of the signals indicates that all sorts of intermediate species between (I), (II), and (III) are present.

The signals peaking at (I), (II), and (III) are in line with the species found by NMR and shown in Figure 1 and Table II for the UP resins.

Comparing Figures 4 and 5, the relative area of the signals peaking at (I), (II), and (III) changes. Thus, both increasing the proportion of propanal (UP6) and lengthening the reaction time (UP4, not shown as identical to UP6 distribution, Fig. 5) shifts the relative relevance of the peaks more toward (II) and (III), as it would be expected. As the relative proportion of (III) increases, the shelf life decreases; in reality, the physical gelation state due to the separation of phase arrives earlier.

In the case of the UFP resin, the GPC chromatogram in Figure 6 indicates also three main signals, but one notices a considerable shift in the peak M_n of each and a considerable increase of the area for much higher molecular masses, as expected. Thus, the first signal peaks at M_n 273 indicating on the four coordinated ureas the presence of three $-\text{CH}_2-$ bridges ($=42 M_n$ more) introduced by the reaction with formaldehyde or a $-\text{CH}_2-$ bridge and a $-\text{CH}_2\text{OH}$ group. Both cases as well as other intermediates are likely to be present.

Such difference is maintained for peak (II) also. It appears also from peak (III) in Figure 6 that the scheme shown earlier for the UP resins is reproduced but with monomethylolated methylene-bisurea dimers and trimers throughout in place of urea itself, still with UP condensates present.

In Table III are reported the results of particleboard made with a commercial UF resin to which are added progressively higher (within limits) proportions of UFP1. The percentage swelling thickness results in cold water after 2 and 24 h immersion are considerably improved on the addition of a small proportion (5%) of UFP1. Higher proportion does not improve further this property, low values for which are much appreciated by board manufacturers. As regards immersion in boiling water, the panels are far from presenting any exterior properties, although an increase in the proportion of UFP1 is related to a decrease of

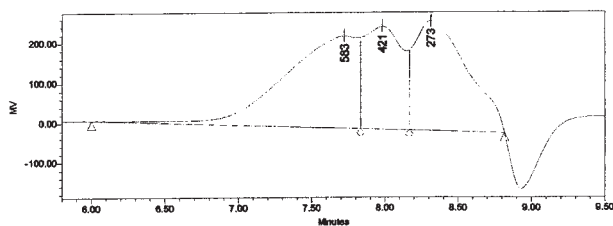


Figure 6 GPC of UFP resin UFP1.

TABLE III
Test Results of Wood Particleboard Bonded with a Commercial UF to Which Have Been Added Different Percentages (Solids on Solids) of UFP1 Resin

	Density (kg/m ³)	Swelling thickness (2 h in cold water; %)	Swelling thickness (24 h in cold water; %)	Swelling thickness (10 min in boiling water; %)	Dry IB strength (MPa)	IB strength after 6 min boiling (MPa)	IB strength after 10 min boiling (MPa)
UF 100%	720	25.1	29.3	73.0	0.95	0.07	0.0
UF 95% + UFP 5%	710	13.64	20.7	59.7	0.81	0.14	0.06
UF 90% + UFP 10%	721	18.99	20.6	47.9	0.92	0.16	0.05
UF 85% + UFP 15%	718	18.31	21.1	44.3	0.67	0.13	0.05
UF 80% + UFP 20%	717	14.65	22.4	44.3	0.78	0.17	0.04

the percentage swelling thickness but not to any improvement in IB strength. They are interior resin of much better interior properties and no more, the optimum additions of UFP for this purpose being at 5% addition within the interval and under the conditions tested. This is so because at higher proportions of UFP1, the problems outlined earlier of slower gel times and shorter shelf life due to a physical gel condition appear.

CONCLUSIONS

In conclusion, UF resins of improved water tolerance and swelling thickness of interior-grade wood panels bonded with UF resins were improved markedly by introducing small amounts of UFP polycondensates into the UF resin. The water repellancy imparted by insertion in the resin of the alkyl chain of propanal limits the proportion of propanal that can be used. This appears so because UP resins and UFP resins exist as an equilibrium between two separate intermingling phases, namely one in solution and the second in a state of physical gelation. This latter is different from the state of physical gelation observed on ageing or advancement of formaldehyde-only based resins. This physical gelation is brought on by the

insertion in the resin of the water repellent chain of the propanal reacted with urea.

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