

Fluorinated Polyether Additives To Improve the Performance of Urea–Formaldehyde Adhesives for Wood Panels

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ABSTRACT: Small amounts of fluorinated polyethers, and in particular a nonionic fluorinated polyether, can upgrade considerably the cold-water swelling and internal bond strength of wood particleboard bonded with urea–formaldehyde (UF) resins. The effect is maximized at an additive concentration of about 0.1 wt % with respect to the adhesive resin solid content. The effect of the fluorinated polyether appears to be greater with older UF resins, which have a more pro-

nounced colloidal state. The mechanism appears to be somewhat related to the reduction of the interfacial tension of the resins, with improved substrate wetting leading to better adhesion. The addition of a fluorinated polyether well in advance of resin use further enhances the improvement. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1683–1688, 2007

Key words: additives; adhesives; polyethers

INTRODUCTION

Urea–formaldehyde (UF) resins are polycondensates and constitute the most important and most used class of thermosetting wood adhesives. They are used in great quantities, million of tons yearly, for the production of wood particleboard, plywood, and other wood-panel types. The most important factors determining the properties of UF resins are (1) the relative molar proportions of urea and formaldehyde, (2) the reaction temperature, and (3) the various pH values at which condensation takes place. These factors influence the rate of the increase in the molecular weight of the resin. Therefore, the characteristics of the final resin differ considerably when one of these parameters is changed.

The advantages of UF adhesives include (1) initial water solubility (rendering them eminently suitable for bulk and relatively inexpensive production), (2) hardness, (3) nonflammability, (4) good thermal properties, (5) absence of color in cured polymers, and (6) easy adaptability to a variety of curing conditions.^{1,2} The greatest disadvantage of UF adhesive resins is bond deterioration caused by water and moisture. This is due to hydrolysis of their amino-

methylene bond and to the interference that water induces in the adhesion of hardened UF to wood substrates.^{3–5} Therefore, pure UF adhesives are used only for interior applications.

Many additives have been used⁶ to improve one or another aspect of UF-resin performance, with various levels of success. Some characteristics that are of importance in UF-bonded particleboards are the swelling in water of the panel (dimensional stability) and the panel tensile strength perpendicular to the board plane, which is known better as the internal bond (IB) strength. The latter is related directly to the UF-adhesive formulation and the mechanical performance of the hardened adhesive. The former is associated with the adhesive formulation and mechanical performance but is a result of the loss of structural integrity due to a deficiency of water resistance of the resin. Thus, any improvement obtained with small proportions of additives opens up new possibilities of improving this aspect of UF-resin performance.

Fluorinated poly(oxetane) surfactants are water-dispersible materials used to improve flow, leveling, and surface appearance in aqueous coatings. Theory does not immediately identify them as strong candidates to improve the performance of UF adhesives for wood when added to the resins in very small proportions. This article deals with the finding that fluorinated polymer surfactants, available commercially, improve the performance of UF resins as applied to wood panels.

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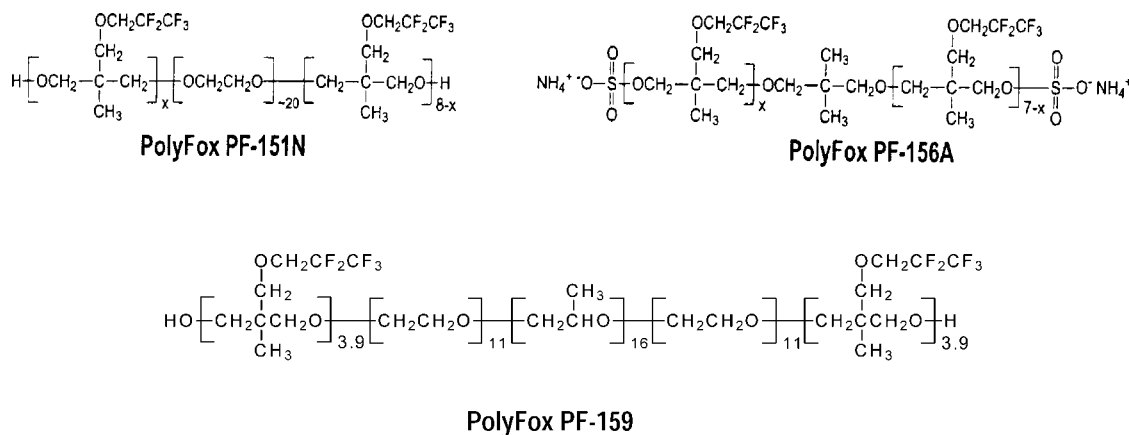


Figure 1 Structures of the polyfluorinated PolyFox polymers.

EXPERIMENTAL

Fluorinated polymer surfactants

Three fluorinated polymer surfactants were used—PolyFox PF-151N (nonionic fluorinated polyether), PolyFox PF-156A [anionic fluorinated polyether di(ammonium disulfate) salt], and PolyFox PF-159 (nonionic fluorinated polyether)—all supplied by Omnova Solutions, Inc. (Akron, OH). Their structures are shown in Figure 1. These materials were water-dispersible in all proportions. The surface tensions at saturation were 28, 24, and 28 mN/m for PF-151N, PF-156A, and PF-159, respectively. They were clear, low-to-medium-viscosity liquids (50 cps for PF-156A, 700 cps for PF-151N, and 1480 cps for PF-159) with 30, 50, and 100 wt % nonvolatiles, respectively, the solvent being a 50/50 water/butyl carbitol mixture, and the pHs were 4.5, 8.5–9.8, and 6–7, respectively.

UF resins

Commercial UF resins from two different reliable European companies were used for the experiments (BASF UF 350, Ludwigshafen, Germany). They were analyzed with ^{13}C -NMR.

Liquid-phase ^{13}C -NMR analysis

The liquid ^{13}C -NMR spectrum of the two UF resins was obtained on a Brüker MSL 300 FT-NMR spectrometer (Brüker, France). The chemical shifts were calculated with respect to $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{SO}_3\text{Na}$ dissolved in D_2O for NMR shift control.⁷ The spectra were taken at 62.90 MHz with approximately 1000 transients. The spectra were run with a relaxation delay of 5 s, and the chemical shifts were accurate to 1 ppm. The assignments of the different peak shifts observed (Table I) were both obtained from the relevant literature and calculated.^{7–17}

Preparation and testing of the glue mixes and wood particleboard

The glue mixes of the panels were prepared by the addition of 0, 0.05, 0.11, or 0.25 wt % fluorinated polymer to the relevant UF resin (as indicated in the tables).

Duplicate one-layer laboratory particleboards ($350 \times 310 \times 14 \text{ mm}^3$) were then produced from industrial wood chips (70 wt % beech and 30 wt % spruce) by the addition of a 10% total UF-resin solid concentration to dry wood particles pressed at a

TABLE I
Comparative Results of Particleboard Bonded with Adhesive Resin UF1 to Which Different Fluorinated Polymers Were Added

	Liquid PolyFox on the dry UF resin (wt %)	PolyFox grade	Average panel density (kg/m^3)	Cold-water swelling (%)		Average IB strength (MPa)
				2 h	24 h	
UF1 control	0.0	—	698	3.7	24.2	0.77
UF1	0.11	PF-151N	708	3.2	23.5	0.82
UF1	0.11	PF-156A	696	5.1	27.1	0.82
UF1	0.11	PF-159	703	4.1	26.2	0.88
Standard requirements						>0.35

TABLE II
Comparative Results of Particleboard Bonded with Adhesive Resin UF2 to Which Different Proportions of a Fluorinated Polyether Were Added

	Liquid PolyFox on the dry UF resin (wt %)	PolyFox grade	Average panel density (kg/m ³)	Cold-water swelling (%)		Average IB strength (MPa)
				2 h	24 h	
1. UF2 control	0.0	—	701	6.3	16.1	0.45
2. UF2	0.05	PF-151N	702	4.3	14.3	0.50
3. UF2	0.11	PF-151N	691	4.5	13.6	0.48
4. UF2	0.11	PF-151N	706	3.7	15.7	0.57
5. UF2	0.25	PF-151N	709	4.6	15.4	0.65
Standard requirements						>0.35

maximum pressure of 28 kg/cm² (2 min from the platen contact to a high pressure, including maintenance of the high pressure) followed by a descending pressure cycle of 1 min at 12–14 kg/cm² and 2 min at 5–7 kg/cm², at 190–195°C, for a total pressing time of 5 min. The moisture content of the resinated chips was 12%. All the panels had densities between 0.685 and 0.710 g/cm³. The panels, after light surface sanding, were tested for dry IB strength.

RESULTS AND DISCUSSION

Because these experiments were designed to examine whether a certain type of additive would improve the performance of adhesives for particleboard, only one-layer boards were prepared. This is the only reason that the average percentage of water swelling reported is higher than that for commercial three-layer boards. For three-layer boards, the average swelling results would be about half of those reported in Tables I and II. The laboratory particleboard results in Table I show that all three of the fluorinated polymer additives increased the average IB strength of the UF-bonded panels. However, with respect to cold-water swelling, only one of the fluorinated polyethers appeared to improve the percentage of swelling in cold water of the panel in comparison with the results observed for the control. At first, these results might not have been statistically significant; therefore, a second series of particleboards were made in which the fluorinated polyether yielding the best result in Table I was tested at three different levels of addition.

As fluorinated polyether surfactants of this type need some time in water to hydrate and dissolve completely (discussed later), that is, 16–24 h in water to become fully solvated, one of the cases was tested with the surfactant added either just at the moment of composing the glue mix (hence just before the

pressing of the board) or 24 h after the addition of the additive to the UF resin (Table I).

The results in Table I indicate several main trends. First, the resins to which the additive was added all gave better IB strength results and better swelling percentages after both 2 and 24 h of cold-water immersion. The majority of these results were significant statistically.

More interesting, however, was the case in which the fluorinated polyether was dissolved in the resin 24 h before the glue mix was composed, as recommended by the fluorinated polyether manufacturer (Omnova Solutions). At parity of addition, this case gives a much improved percentage of cold-water swelling after 2 h of immersion and much better IB strength. The difference in the 24-h cold-water swelling percentage between the cases in which the additive was predissolved in the resin (case 4, Table II) and not predissolved in the resin (case 3, Table II) appeared to be nonsignificant because of the variation of some of the results. The fluorinated polyethers are added through the dilution of pure materials or from concentrated solutions above the critical micelle concentration. To function effectively as surfactants, the aggregates or micelles of the fluorinated polyethers must be solvated. There is a finite period of time required for solvation. Typically, micelle breakdown kinetics are slow in comparison with those of analogous hydrocarbon surfactants.^{18,19}

Equally interesting is the finding that an increase in the fluorinated polyether addition greater than 0.11 wt % with respect to the resin solids does not yield any further cold-water swelling improvement; in fact, an increase in the swelling is noted. This is the result of an effect observed frequently with surfactants in general. At higher concentrations, aggregation and micellization (as discussed earlier) occur and render the molecules ineffective for their designated task. Furthermore, an excess of the surfactant can find its way to an undesirable interface, leading to deleterious effects such as dewetting or loss of

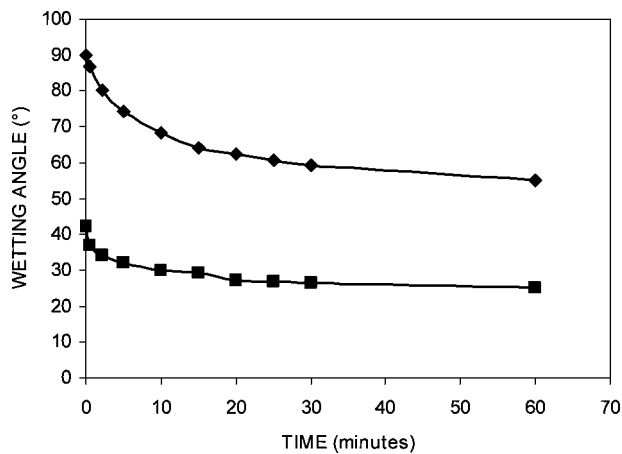


Figure 2 Variation of the water wetting angle as a function of time of wood particleboard bonded with a UF resin. The upper curve shows the control, and the lower curve shows the addition of PolyFox.

adhesion between interfaces. In general, a curve of the performance versus the surfactant concentration tends to be a concave-downward, hyperbolic curve, with the apex of the curve coinciding with the critical micelle concentration or interface saturation.

The addition of a small proportion of a fluorinated polyether appears to improve considerably UF-resin

performance in applications such as particleboard adhesives. The question to be asked is why this is true. It is for this reason that measurements of the water contact angle on the surface of UF-bonded boards were performed. The results are shown in Figure 2.

The upper curve in Figure 2 is the control, that is, the one for the UF-bonded boards in which 0.1% extra water was added to the UF resin. The lower curve is for the UF-bonded boards in which 0.1% PolyFox PF-151N fluorinated polyether was added to the UF resin. At first, the result appears unexpected: the curve with the additive has a lower wetting angle. This is unusual if one thinks that the board swelling results support the idea that the additive should increase, rather than decrease, the wetting angle and improve the swelling percentage of the panel in cold water. However, the higher IB strength values in Table II, when coupled with better wetting (hence a lower wetting angle) of the board surface induced by the fluorinated polyether in Figure 1, indicate that a different mechanism appears to be operative.

The fluorinated polyether allows the resin to more effectively wet the substrate, and this is a necessary component for proper adhesion between two surfaces to occur. Better adhesion translates to a higher IB

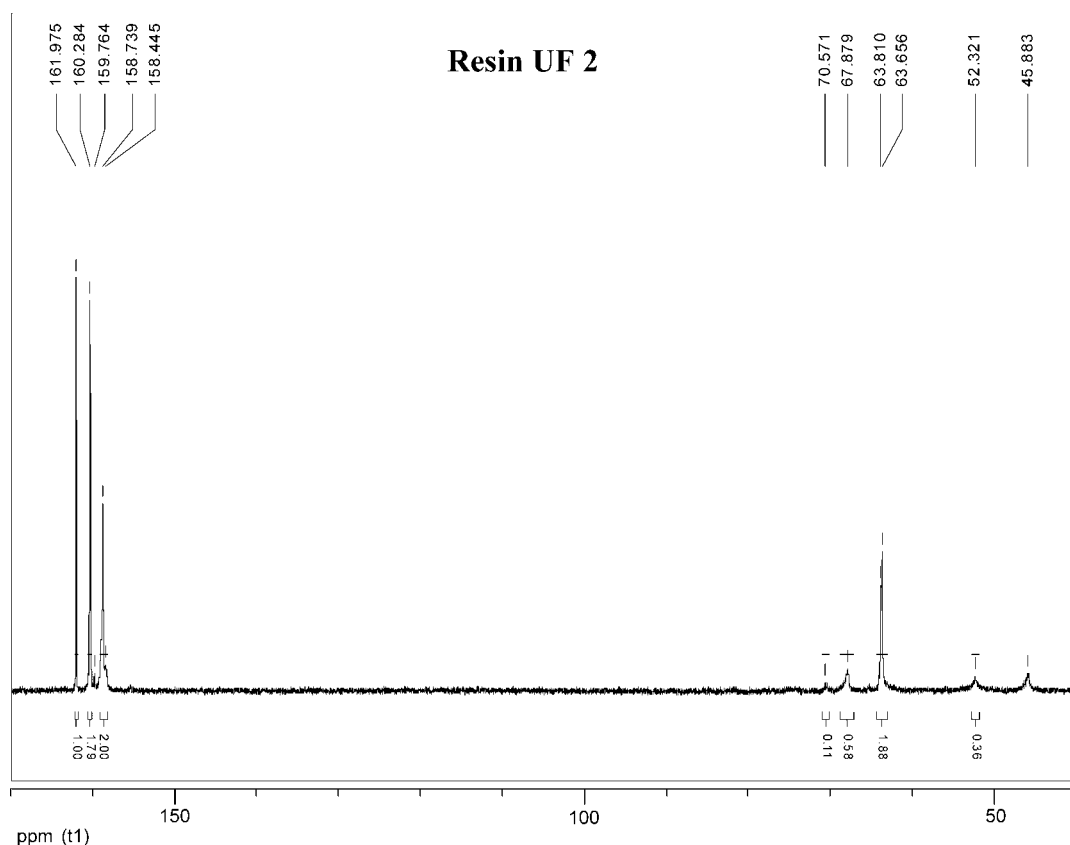


Figure 3 ^{13}C -NMR spectrum of resin UF2.

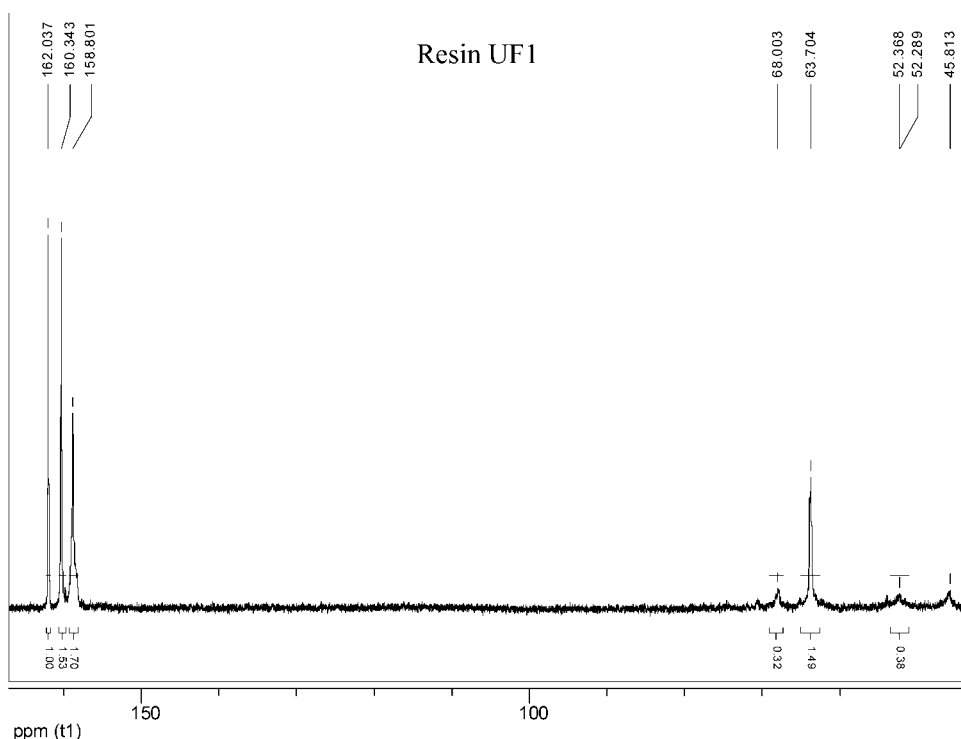


Figure 4 ^{13}C -NMR spectrum of resin UF1.

strength of the board (Tables I and II). As aminoplastic resins such as UF resins are partly in colloidal suspensions,^{20–22} any additive that decreases the surface tension will help to break the colloid and hence promote film formation and improve adhesion and surface coverage by the resin. The increased resin wetting and performance of the wood-composite board with the fluorinated polyether additive are results of the unique properties of a short-perfluoroalkyl-chain, ethoxylated surfactant. Typically, fluoro-surfactants are much more effective and efficient amphiphiles than analogous hydrocarbons. This includes, of course, the interfacial activity, which is critical to the current discussion. Long-perfluoroalkyl-chain surfactants would not have much compatibility with a UF resin (or many other interfaces, for that matter) and would, therefore, not be expected to be effective in increasing the performance of a UF resin to which they were added. The fluorinated polyethers used here have moderate surface tensions at saturation (20–30 mN/m)^{23,24} in comparison with long-perfluoroalkyl-chain surfactants (18–22 mN/m)²⁵ and would, therefore, be expected to be more compatible with the interfaces to be adhered. Increased compatibility between the two interfaces (the UF resin and wood) should result in a lowered interfacial tension between the two materials and better wetting.

A further point of interest is the influence of the resin used on the final board results. UF1 in Table I is made by a different manufacturer than the

UF2 resin in Table II. Additional work, not presented here, has shown that the improvement in the results obtained by the addition of a fluorinated polyether is more evident when UF2 is used rather than UF1. If one compares the results obtained with the two controls in Tables I and II, one can perceive that the unmodified UF2 resin is a better resin than the unmodified UF1 resin both for 2 h swelling and for IB results. The lower performing of the two resins shows greater improvements in the results through the inclusion of the fluorinated polyether additive. Thus, the addition of the fluorinated polyether tends to equalize the performance of the two resins. As a result, the use of this type of additive permits the use of simpler, less expensive resins without any decrease in the performance.

Nonetheless, comparing the two resins to see whether any major differences exist between them is of interest. Figures 3 and 4 show the ^{13}C -NMR spectra of the UF1 and UF2 resins. Upon a first impression, the two resins appear almost identical, but when the peak integral areas reported in Table III are compared, some differences become evident. First, both are excellent E1-type UF formulations. Second, according to Table III, UF2 is a more advanced polymerized resin than UF1, as can be seen by the higher integral values of $>\text{C}=\text{O}$ of unreacted urea with respect to $>\text{C}=\text{O}$ of polyreacted ureas and for methylene bridges ($-\text{NH}-\text{CH}_2-\text{NH}-$) and branched methylene

TABLE III
Shifts of the Main Peaks and Their Relative Integrated Areas for the UF1 and UF2 Resins

	Shift (ppm)	UF1 integral	UF2 integral
>C=O, monoreacted urea	162	1.00	1.00
>C=O, <i>N,N'</i> -bireacted urea	160	1.53	1.79
>C=O, trireacted urea	158–159	1.70	2.00
–NH–CH ₂ OCH ₂ –NH–	70–71	—	0.11
–N(CH ₂ OH) ₂	67–68	0.32	0.58
–CH ₂ OH	63–64	1.49	1.88
–(–CH ₂ –)N–CH ₂ –NH–, branched	52–53	0.38	0.36
–NH–CH ₂ –NH–, linear	45–46	—	—

bridges [–(–CH₂–)N–CH₂–NH–]. UF2 might be a slightly more reacted resin, an older resin, or one with proportions of formaldehyde that are higher than those for UF1. The latter does contribute to the effect; the proportion of formaldehyde is slightly higher because there is a higher proportion of reactive methylol groups (–CH₂OH) in UF2, as indicated by this group integral with respect to that of UF1. However, the main cause of the difference noted is that UF2 is an older resin, having been stocked for a few months before use. Thus, when used without an additive, it gives boards presenting lower strength results and poorer swelling; therefore, its substrate wetting and adhesion are worse. Furthermore, it is more colloidal because of its age and is consequently more in need of a material that can improve the film-forming capability by decreasing the interfacial tension and hence improve the adhesion.

CONCLUSIONS

Small amounts of fluorinated polyethers can upgrade considerably the cold-water swelling and IB strength of wood particleboard bonded with UF resins. The effect is maximized at a fluorinated polyether additive concentration of about 0.1 wt % with respect to the adhesive resin solid content. The older or more advanced the UF resin is, the more pronounced its colloidal state is, and the more evident the effect of fluorinated polyethers appears to be. The mechanism appears to be somewhat related to the decrease in the surface tension of the resin, with improved substrate wetting leading to better adhesion. The addition of the fluorinated polyether well in advance of resin use, to allow complete solvation of the additive, further improves the results.

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