

Enhancing the Properties of Urea Formaldehyde Wood Adhesive System Using Different Generations of Core-Shell Modifiers Based on Hydroxyl-Terminated Dendritic Poly(amidoamine)s

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ABSTRACT: Different generations of hydroxy-terminated dendritic poly(amidoamine) (Gn—OH) with ethylenediamine as a core were prepared by successive alternative addition of methylacrylate and the core up to the third generation while employing ethanolamine only in the last step of every full generation. The different generations prepared were used as modifiers for urea-formaldehyde (UF) resins. The enhanced durability and

stabilizing effect of the (Gn—OH)s along with the reduced levels of free formaldehyde and improved mechanical performance of wood joints glued with the modified resins are discussed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 370–375, 2010

Key words: urea formaldehyde; modification; dendrimers; wood adhesive

INTRODUCTION

The major advantage of the usage of urea-formaldehyde (UF) resins for wood bonding is the low price in addition to the formation of strong adhesion bonds under wide conditions. These advantages are limited by the poor durability and stability of the system, which account for the strength loss of the bonded joints with UF resins. It is necessary to improve these drawbacks for broadening the applications of this adhesive system compared with the other more expensive ones. Further, the formaldehyde emission from this adhesive system limits their use in interior, nonstructural applications.¹

UF resin must be modified to improve the network structure² and increase the overall system flexibility.³ Verification of these improvements by additives results in system stabilization.

Modification of UF resin should aim at improving the resin network resistance to moisture; ineffective modification leads to a failure of UF-bonded joints as a result of hydrolytic degradation (which is attributed to weak bonds holding the wood joints with UF resin), together with stress scission.

Additionally, the low reactivity of the secondary amides prevents the effective functionality of urea from rising much above 2 and hence leads to weak load-bearing ability.

This means that the formed network is very sensitive to losses in crosslink density because of hydrolysis or chain scission. Moreover, extreme interchain bonding causes lack of flexibility; hence, the system will no longer be able to take reversible action to stresses arising from cure shrinkage and moisture uptake.^{4–6} This highlights the need to optimize the existing structure of UF resin, especially when Irle and Bolton⁷ noted that the irreversible swelling in particleboard is lower with phenol formaldehyde (PF) resins than with UF resins as a result of the greater ability of PF to relax under the swelling stresses.

Recent approaches were suggested for the modification of UF resin to overcome these drawbacks. The adopted modifications were carried out using a latex system based on butadiene-styrene copolymer,⁴ acrylic latex,⁸ less active aldehyde such as glutaraldehyde on the expense of a part of formaldehyde,⁹ and fluorinated polyether additive,¹⁰ whose improvement was explained by a mechanism that somewhat related to the reduction of the interfacial tension of the resins, which improved the substrate wetting leading to better adhesion.

Maminski et al.¹¹ blended a commercially available UF resin with a hyperbranched polyether (HBP) obtained from glycerol. The mechanical properties of the cured polymeric blends, hardness and

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compression shear strength, were improved by 16%, and 17%, respectively, with respect to control, and this was achieved using 2–3% of the modifier. However, above 4 wt %, the plasticizing effect overwhelms the hardening effect and subsequently lowers both hardness and compressive strength. Unfortunately, this pioneer study was not extended to the use of the modified resin for application as wood glue.

Very recently, we reported¹² the modification of urea formaldehyde resin using different full generations of hyperbranched poly(amidoamine)s (PAMAM) as well as the corresponding ester-terminated half-generations. It was found that the durability as well as the mechanical performance of the wood structures based on this adhesive system were enhanced significantly, along with a marked decrease in the level of free formaldehyde. Continuing with this approach, we followed the procedure of Crooks and coworkers¹³ to synthesize hydroxyl-terminated full-generations of poly(amidoamine)s (Gn–OH) up to the third generation by substituting ethanolamine for ethylenediamine in the last steps of PAMAMs synthesis, so the properties of the UF resins as wood adhesive systems will be intensively studied after modification in the current work.

EXPERIMENTAL

Materials

Urea was obtained from El-Delta Company for fertilizers and chemical industries, Talkha-Egypt. Formaldehyde (37% solution) was supplied from El-Mansoura Co. for resins and chemical industries, Mansoura, Egypt. Methylacrylate, ethanolamine, and ethylenediamine were purchased from Aldrich, Milwaukee, WI, USA. Anhydrous aluminium chloride was a product of Merck-Schuchart Chemical Company, Darmstadt, Germany. Ammonium chloride was provided from Veblabor Chemie, Apolda, Germany. All other chemicals were of laboratory grade and used without further purification.

Synthesis of hydroxyl-terminated hyperbranched poly(amidoamine)s¹³

The hydroxyl-terminated hyperbranched poly(amidoamine)s were prepared in a sequential addition of methylacrylate and ethanolamine. Very briefly, ethylenediamine was used as a nucleophilic core and the Michael addition reaction was conducted in a methanolic solution for 12 h at 60°C by addition of a large methylacrylate excess and leads to a half-generation ($G = 0.5$), which is ester-terminated, whereas ethanolamine was used only in the last amination step to yield the hydroxyl-terminated PAMAMs. Repeating this sequence in an alternative fashion

leads to self-replication in a divergent manner to yield full generations that are amine-terminated. Strong vacuum was used beyond each step to remove excess reagent to avoid nonsymmetrically branched (defective) generations. The corresponding hyperbranched polymer-based hardeners were prepared by the neutralization of the amine-terminated full-generations of poly(amidoamine)s, according to the literature.¹⁴

Preparation of urea formaldehyde resins

UF resins were synthesized according to a traditional two-step procedure at $F/U = 1.5$. Formaldehyde (37%) was placed in the reactor, and the solution was adjusted to pH 7.5 with sodium hydroxide (20% wt/v). Subsequently, urea was added and the mixture was heated under reflux for 45 min. Then, the pH was changed to 5 with Lewis acid (1 : 1 molar ratio of anhydrous $AlCl_3$: ethanol) and the polycondensation reaction was continued for an additional 15 min. Finally, the pH was readjusted to 8.0 after cooling. The same method was followed for the preparation of modified UF resin, but it involved prior neutralization of formaldehyde using different generations of the hydroxyl-terminated poly(amidoamine)s up to the third one, then the appropriate amount of urea that gives F/U ratio of 1.5 was fed, and the process was completed as above.

Characterizations

The solid content was determined in three replicates by taking the difference of the weight before and after drying of 1 g of a UF resin into a disposable aluminum dish in an air oven at 120°C for 3 h. The viscosity of the UF resin adhesives was measured at 25°C with a cone plate viscometer (DV-III1, Brookfield, Middleboro, MA) with a No. 2 spindle at 60 rpm. The density of the resin was determined by weighing a 50-mL aliquot of UF resin in a mass cylinder at 25°C.¹⁵ The free formaldehyde content of the prepared resins was determined by the sodium sulfite method.¹⁶ The gel time was measured in three replicates for each resin using a stop-watch after the addition of various amounts of the curing agent (0.5, 1, and 3%) at 100°C. IR spectra of KBr discs saturated with the liquid resins were recorded on a JASCO FT/IR-6100 with 4 cm^{-1} resolution, Japan. DSC scans were performed on a LabsysTM TG-DSC16 at a heating rate of 5°C/min under argon atmosphere.

Application of the prepared resin as wood adhesive

Samples of plywood were prepared with the following dimensions: 2 × 0.5 × 10 cm^3 . The surface was

TABLE I
Properties of Modified UF Resins with Full-Generated Hydroxyl-Terminated Poly(amidoamine)s

Properties	Unmodified UF Resin	Modified UF Resins with Different Generations Of Poly(Amidoamine)s		
		G1—OH	G2—OH	G3—OH
Solid content, %	47.6	48.0	45	47.6
F.F., %	2.1	0.72	0.45	0.5
Density, g/cm ³	1.195	1.193	1.178	1.183
Viscosity, P	0.71	1.00	0.6	0.4
Gel time (s)	55	25	32	28

cleaned, and smoothed, and the hardener was added, based on the solid content of the resin, and mixed well just before application. The resin was spread over an area of (2 × 2 cm²) of the wood species, and the sample was pressed using a hydraulic press of two plates, both heated to 150°C under a pressure of 50 kg/cm² for 5 min.

Evaluation of joint strength

The necessary force to separate the two wood blocks was determined using a tensile testing machine Type 92-5001 MFG. MARK61-0825, AVK Budapest, Hungary, operated at a minimum velocity to evaluate the strength of the adhesive joint; the shear strength of a bonded joint was calculated as the load at shear divided by the contact area.

RESULTS AND DISCUSSION

Recent modifications of urea-formaldehyde resin are aimed at increasing water resistance, processing improvement, avoiding self-cure during storage and transportation,¹⁷ or lower formaldehyde emission.¹⁸

A wide spectrum of compounds was applied as modifying agents: aliphatic amines,¹⁹ dialdehydes,²⁰ and latexes.^{4,8} Maminski et al.¹¹ implied that hyperbranched polyether can be used as a modifier for urea-formaldehyde resins to improve hardness and strength, but the work did not extend to the application of the modified resin as wood adhesive. This motivated us in a previous study to use hyperbranched poly(amidoamine)s as modifiers for UF resin wood adhesive system,¹² where we found that the physical properties of the resin were improved by the incorporation of these modifiers along with the durability and performance. We used the poly(amidoamine) in its hydroxyl-terminated form up to the third generation to improve the UF resin properties.

First of all, the solid content (S.C.) was about 47% on average and was not affected much by the

insertion of the modifiers. In addition, the density was statistically unchanged (Table I).

It is obvious from Table I that the gelation time decreases significantly with the incorporation of the Gn—OH, which can be attributed to the increased reactivity of the resin after modification, since these materials are characterized by high functionality at the periphery, which contributes to the higher reactivity. This should lead to an integrated network structure of the resin with accordingly higher crosslink density and better adhesion strength, especially upon going to higher generations as experienced before, when the amine-terminated PAMAMs were used as modifiers.¹² However, it seems that the hydroxyl-terminated PAMAMs are not so effective in this issue (Table II). However, substituting ammonium chloride with dendritic hardeners served to increase the adhesion strength and improve the crosslinking efficiency even for the unmodified resin.

Further, the durability of the resin was prolonged on the one hand because of the enhanced solubility due to the presence of large number of hydroxyl groups belonging to the modifier at the terminals, and on the other hand because of the buffering effect of the nitrogen centers. Additionally, the lack of chain entanglement in the hyperbranched structures is a characterizing feature of dendritic structures; hence they act as elements that improve flexibility of the network system so the developed stresses arising from cure shrinkage and moisture uptake and loss will be easily relaxed (the stress will be more easily transferred) and the stability of the wood products based on this adhesive system may be enhanced. This can be further confirmed by following the adhesion strength of the bonded wood joints after 24-h immersion in cold water, where the loss in the mechanical strength was not as significant compared with the comparable samples without treatment, in particular when ammonium chloride was used as a nondendritic hardener (Table III). Another reason may be the higher resistance of the newly formed network structure to hydrolytic degradation after being strengthened by these modifiers.

Best of all is the observed dramatic decrease in the level of free formaldehyde (Table I). These types of

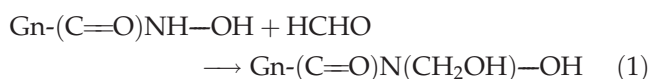
TABLE II
Shear Strength of Wood Joints Glued with Modified as Well as Unmodified UF Resins Using Different Types of Hardeners

Hardener	Shear Strength (kg/cm ²)			
	Unmodified	G1—OH	G2—OH	G3—OH
NH ₄ Cl	49	24.3	40	41.3
H1	78	44	>50.4	>57.3
H2	85	68.8	60	>64
H3	89	>71	>60	54.7

TABLE III
Shear Strength of Wood Joints Glued with Modified as Well as Unmodified UF Resins Using Different Types of Hardeners After Immersion in Cold Water for 24 h

Hardener	Shear Strength (kg/cm ²)			
	Unmodified	G1—OH	G2—OH	G3—OH
NH ₄ Cl	2	24	28	28.6
H1	23	28.8	30.7	36.6
H2	35	32	40	>53.3
H3	31	>34.3	30.7	40

modifiers can act as formaldehyde traps [mechanism is shown in eq. (1)], where the internal amide groups of the poly(amidoamine) can react with free formaldehyde under basic conditions (storage conditions) to form new methylol groups:



This was further proved by FTIR (Fig. 1), which shows the spectra of G3—OH (a) and the corresponding one after reaction with formaldehyde solution (b). It is clear that the weak N—H peak at 3100 cm⁻¹ diminished to a large extent whereas two peaks at 1644 and 1594 were assigned to C=O, which represent the carbonyl environment of G3—OH before and after trapping formaldehyde, respectively. Additionally, the bands between 3000 and 3600 cm⁻¹ were strongly perturbed, indicating a remarkable change in the chemical environment after the conversion of N—H to N—CH₂OH. It is worthy to mention that formaldehyde liberation from the system will be controlled effectively as a result of the enhanced network resistance to hydrolytic degradation of the weak bonds.

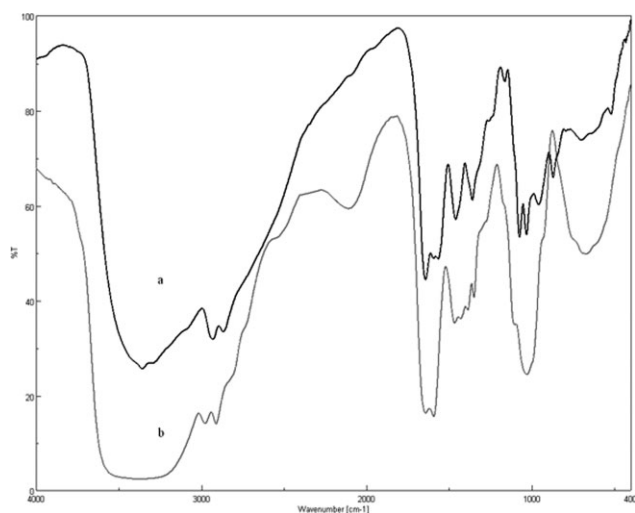


Figure 1 FTIR spectra of G3—OH (a) and the corresponding spectra after reaction with formaldehyde (b).

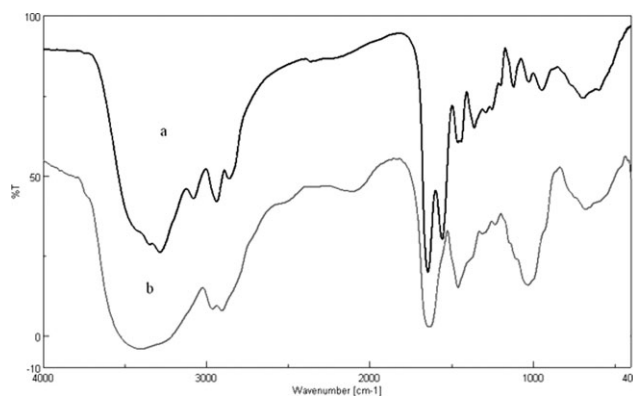


Figure 2 FTIR spectra of G2—NH₂ (a) and the corresponding spectra after reaction with formaldehyde (b).

Moreover, keeping in mind that the generations did not grow in a symmetric fashion because of the probable incomplete removal of excess reagents beyond each step, which is usual during synthesis of dendritic structures, the remaining species that are terminated with amino groups can also function as scavengers of formaldehyde through a Schiff's base reaction as shown in eq. (2):



This can be easily evidenced from the IR spectra of the pure poly(amidoamine) [Fig. 2(a)] and the corresponding spectra after reaction with formaldehyde, where it can be detected that in addition to the expected perturbation in the 3000 to 3600 cm⁻¹ region, one of the carbonyl bands, namely that one at 1644 cm⁻¹, became broad and shifted to 1636 cm⁻¹ after conversion to C=N— [Fig. 2(b)]. The same is noticeable for UF resins modified with amine-terminated modifiers by the appearance of a shoulder at 1540 cm⁻¹, as indicated in Figure 3(b). It is virtually absent in the spectra belonging to the

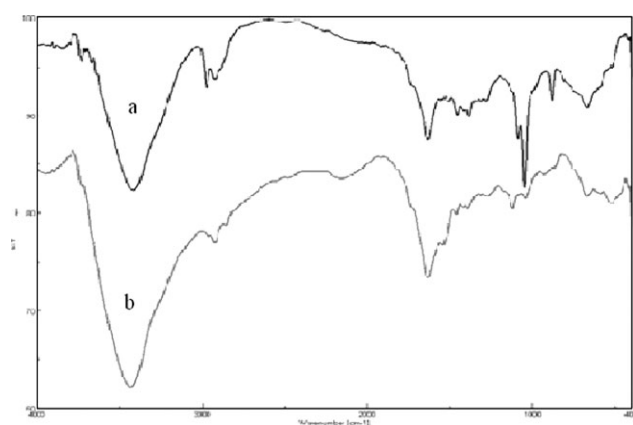


Figure 3 FTIR spectra of cured resins before (a) and after modification with G2—NH₂ (b) in the presence of 3% NH₄Cl as a curing agent.¹²

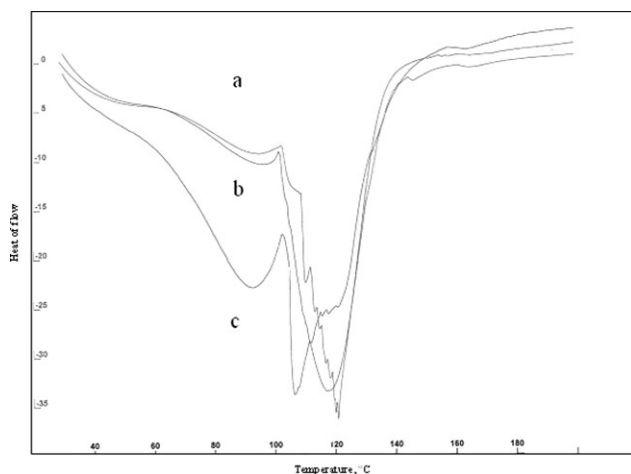


Figure 4 DSC curing thermograms of UF resin before (a) and after modification with G1.5-(C=O)OCH₃ (b) and G1-OH PAMAMs (c) in absence of any hardener.

resin before reaction with the dendritic modifier [Fig. 3(a)].

This is in complete accordance with our previous work,¹² in which it was proved that dendritic poly(amidoamine) with amine terminals could function very effectively as modifiers for UF resins during the cure process and network formation. The improvement of the mechanical performance of the joints, based on this adhesive system, after modification was ascribed to their chemical nature as a multifunctional cohardener forming inhomogeneity centers (hard knots) within the polymer network on curing.¹¹ In addition, the lack of entanglement for the dendritic modifiers favors their action of imposing greater flexibility to UF resins, which is hard and brittle in origin due to the high crosslinking density; hence the modification qualifies the resin to respond reversibly to stresses arising from either cure shrinkage or wood swell-shrinkage cycles caused by moisture uptake and loss. The same applies to the corresponding hydroxyl-terminated poly(amidoamine)s. The impact of this modification translates in the meantime to boosting of the original linkages that were susceptible to hydrolytic degradation before the inclusion of the hard knots and eventually prevents the exclusion of formaldehyde from the network structure.

It was reported in research done by Glazkov⁴ that wood capillary size is in the order 20 to 40 to 100 to 200 nm, depending on the kind of wood, interfibrillar pores (7 to 10 nm), and oligomer molecules (7 to 40 nm), where it was found that the introduction of a latex into UF resin binder decreased the surface tension, wetting angle, and viscosity, which favored better wetting and more uniform coverage of the external surface of the wood with the binder. Further, it reformed penetration of the binder into

capillary porous structure of wood particles, since the latex particles are coarse (100 to 1000 nm), ensuring more uniform thickness of the adhesive layer.

All these improvements may be gathered by the introduction of the dendritic modifiers into UF resin. The diameter of the dendrimers up to G4.5 is in the order of 7.8 nm.²¹ This may be considered to cause more penetration of the resin into the capillary pores of the wood since their inclusion in the network structure, starting from the second generation, decreases the viscosity (Table I). As well, their improving action on the solubility ensures better wetting, which gives good return with respect to the formation of uniform coverage on the external surface of the wood; hence, shear strength was enhanced significantly.

Figures 4 through 6 compare the curing thermograms of different UF resins before and after modification, using different hardeners. Figure 4 shows that a major part of the network formation belongs to the modified resin with either ester- or hydroxyl-terminated-PAMAMs [Fig. 4(b,c)] started to cure at lower temperatures compared with the unmodified UF resin (F/U = 1.5) [Fig. 4(a)], showing that the reactivity was heightened by the incorporation of the modifiers. However, in general, the total cure time was about the same and the change of the exotherm shape, especially after modification with Gn-OH, may indicate the proceeding of the cross-linking via different mechanisms during the curing process, that is, any remaining amino terminals

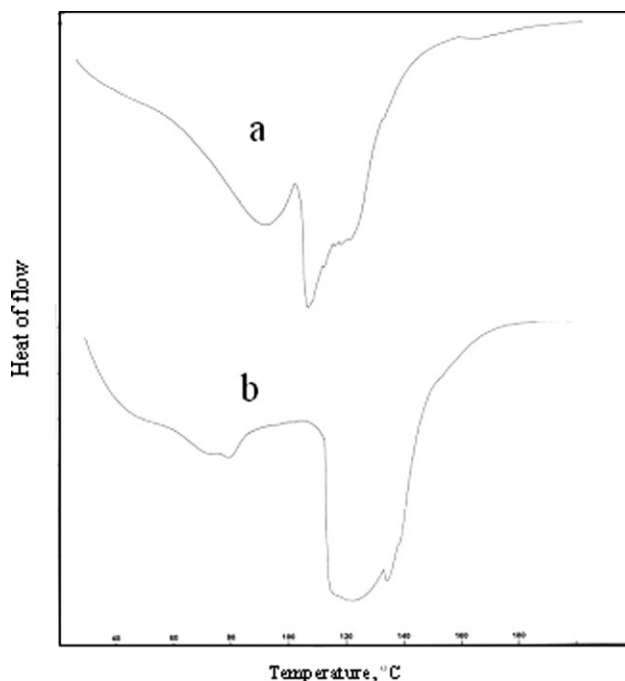


Figure 5 DSC curing thermograms of modified UF resin with G1-OH in the absence (a) and presence of 3% NH₄Cl (b), respectively.

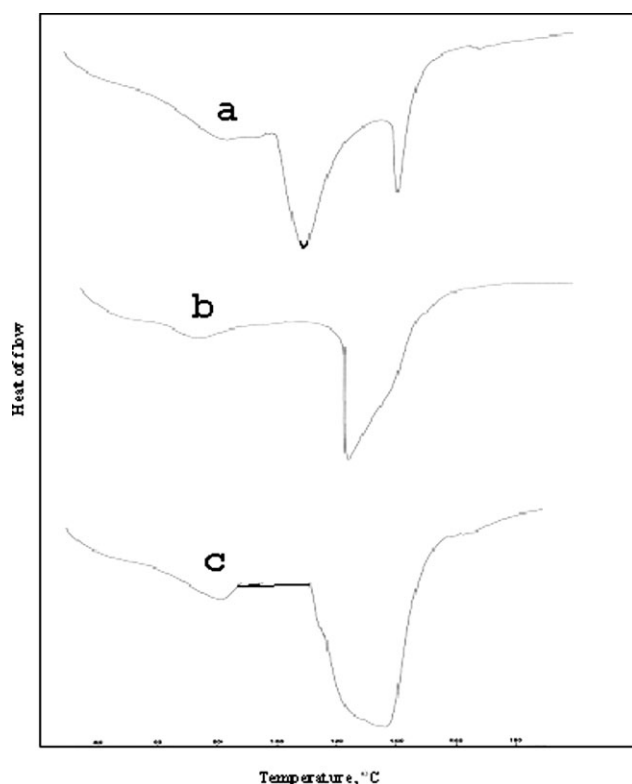


Figure 6 DSC curing thermograms of modified UF resin with G1—OH in presence of 3% H1 (a), H2 (b), and H3 (c), respectively.

together with the newly formed hydroxyl terminals can be involved together in the curing process with UF resin functionality.

Further, comparing the exotherms of the modified UF resin with G1—OH in the absence and presence of 3% NH_4Cl [Fig. 5(a,b)] reveals, surprisingly, that the process takes more time in the presence of the hardener. This may be explained from one side by the elevated resin reactivity after modification with a modifier bearing a high content of reactive end groups, whereas in using a hardener like NH_4Cl , which is active only in the presence of a reasonable amount of free formaldehyde, and since a good network formation in the presence of a multifunction modifier leads to collapse in the level of free formaldehyde (Table I), it appears that the presence of NH_4Cl in the absence of a sufficient amount of free formaldehyde can delay the curing process. This gives rise again to the pronounced reactivity of the resins after modification with the dendritic compounds.

It is very interesting to note that the modified UF resin cured in the presence of 3% of the dendritic hardeners, H1, H2, and H3, respectively, exhibited much higher reactivity with H1 [Fig. 6(a)] compared with the resin cure in the presence of H2 and H3, which displayed broad exothermic peaks [Fig. 6(b,c)] with the maximum attained at longer times. This may point out that a relation between the use of

these higher-generated species of dendrimers in the cationic form as hardeners and the speed of the curing process might exist. The emergence of a new minor peak at higher temperatures during cure with H1 may reveal that a portion of the resin cured only thermally without H1.

CONCLUSIONS

Hydroxy-terminated dendritic poly(amidoamine)s can be used as an effective modifier for urea-formaldehyde resin adhesives in resin stability and enhanced mechanical strength of wood structures, based on this adhesive system in addition to the retardance of self-curing during storage due to the enhanced solubility and the ability of these modifiers to act as buffering systems, keeping the pH unchanged during the course of storage. In addition, they can function as traps for free formaldehyde and reduce its level extensively.

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