Improving the Performance of Urea-Formaldehyde Wood Adhesive System Using Dendritic Poly(amidoamine)s and their Corresponding Half Generations

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ABSTRACT: Full as well as half generations of dendritic poly(amido amine)s (PAMAMs) were introduced onto urea-formaldehyde (UF) wood adhesive system as modifiers to increase its stability and enhance the performance of the bonded wood joints with it. The effect of the modifiers on the physical properties and mechanical performance was discussed on the light of gel times, curing exotherms using differential scanning calorimetry (DSC), infra-red (IR), and shear strength measurements. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1348–1355, 2009

Key words: urea formaldehyde resin; modification; dendritic poly(amidoamine); wood adhesive

INTRODUCTION

Urea-formaldehyde (UF) resins belong to a class of thermosets referred as amino resins, which can be obtained as a result of urea condensation with formaldehyde under a wide range of conditions. Increasing annual production of UF resins is reported, reaching above 5 million metric tons in Europe alone in the last few years.[1,2] One of the major uses of these thermosetting resins is their application as adhesives in wood and furniture industry, their comparatively better performance over the other wood adhesive systems is ascribed to a package of advantages such as low cost, good water solubility and accordingly ease of application, high reactivity in addition to the relatively high strength on curing.[3] However, considerable drawbacks are limiting their extension; the presence of the highly cancerogenic free formaldehyde, low moisture, and water resistance, especially under conditions of high temperatures and humidities.[4,5] Numerous modification approaches were suggested for the treatment of these drawbacks.[2,5–8]
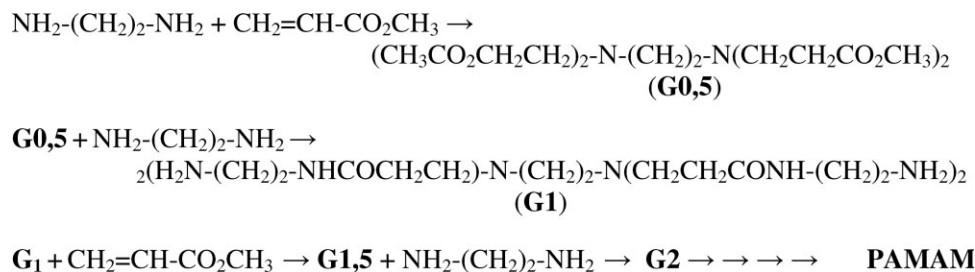
Dendritic and hyperbranched polymers with terminal functional groups represent a new class of polymeric compounds that attracted attention of many research groups. This class of macromolecules was reported in the literature to be effective tougheners for thermosetting resins such as epoxies,[9]

bismaleimide,[10] and vinylester.[11] Based on these interesting and promising data, Maminski et al.[12] introduced in a subsequent study a new modifying agent based on a hyperbranched polyether for improving the hardness and strength of UF resins, regrettably, their study did not extend to the application of the produced modified resin for wood bonding.

Meanwhile, a very attractive contribution by Karchesy and coworkers[13] reported the possibility of using a linear poly(ethyleneimine) as an adhesive component for wood which motivated us in a previous study[14] to incorporate different full generations of dendritic poly(amidoamine) to modify the network structure of UF resin during cure, due to the great similarity in its chemical functionality to the linear poly(ethyleneimine) with the difference in its core-shell architecture. The modified UF resin adhesive with poly(amidoamine) displayed better adhesion strength and enhanced reactivity as revealed by the gel time which indicates the involvement of the dendrimers with their enormous —NH$_2$ functionality at the peripheries in boosting the network structure against stress and the same is expected to happen with the ester-terminated poly(amidoamine)s where they can participate in the aminal formation with their internal secondary amine groups under basic conditions and later as well, with their newly formed hydroxyl groups in the crosslinking reactions under acidic condition through splitting off water as will be shown later in eqs. (1)–(3).

Thus, we decided to go further and use the ester-terminated precursors (G0.5, 1.5, and 2.5) of the previously used poly(amidoamine) as modifiers for UF

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$$NH_2\text{-}(CH_2)_2\text{-}NH_2 + CH_2\text{=}CH\text{-}CO_2CH_3 \rightarrow$$
$$(CH_3CO_2CH_2CH_2)_2\text{-}N\text{-}(CH_2)_2\text{-}N(CH_2CH_2CO_2CH_3)_2$$
$$\textbf{(G0,5)}$$

$$\textbf{G0,5} + NH_2\text{-}(CH_2)_2\text{-}NH_2 \rightarrow$$
$$_2(H_2N\text{-}(CH_2)_2\text{-}NHCOCH_2CH_2)\text{-}N\text{-}(CH_2)_2\text{-}N(CH_2CH_2CONH\text{-}(CH_2)_2\text{-}NH_2)_2$$
$$\textbf{(G1)}$$

$$\textbf{G}_1 + CH_2\text{=}CH\text{-}CO_2CH_3 \rightarrow \textbf{G1,5} + NH_2\text{-}(CH_2)_2\text{-}NH_2 \rightarrow \textbf{G2} \rightarrow \rightarrow \rightarrow \rightarrow \quad \textbf{PAMAM}$$

Scheme 1 Synthesis of dendritic PAMAM.

resin adhesive to investigate, based on this comparative study, whether the above-listed enhancements are attributed to the terminal amine functionality or just because of the ability of any dendritic/hyper-branched structure, irrespective of its polarity, to impose greater flexibility which qualifies the system to respond reversibly to stresses arising from cure shrinkage and wood swell-shrinkage cycles caused by moisture uptake and loss.

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, Egypt. Methylacrylate and ethylenediamine were purchased from Aldrich. Anhydrous aluminium chloride was a product of Merck-Schuchart chemical company, Germany. Ammonium chloride was provided from Veblabor Chemie, Apolda. All other chemicals were of laboratory grade and used without further purification.

Synthesis of ester-terminated dendritic poly(amido amine)s[15]

The poly(amido amine)s dendrimers were prepared in a sequential addition of methylacrylate (MA) and ethylenediamine (EDA) according to Scheme 1.

Briefly, ethylenediamine (18.03 g, 0.3 mol) was used as a nucleophilic core and the Michael addition reaction was conducted in methanolic solution for 12 h at 80°C by addition of a large methylacrylate excess so it leads to a half generation ($G = 0.5$) which is ester terminated, then the excess of methylacrylate has to be removed under vacuum, otherwise it will function as an initiator core to produce new 0.5 generations and subsequent lower generations entities during the following step which depends on the addition of EDA in a molar proportion of approximately 7 : 1 with respect to the pre-formed $G = 0.5$ intermediate to yield the $G = 1$ after running the reaction at the same conditions. Repeating this sequence in an alternative fashion leads to self-replication in a divergent manner to give half

generations with ester terminals or full generations which are amine terminated in a yield ranges from 76–80%. Strong vacuum was employed beyond each step to remove excess reagent to avoid nonsymmetrically branched (defective) generations.

General method for preparation of urea formaldehyde resins

UF resins were synthesized according to a traditional two-step procedure at $F/U = 1.5$. Thus, 100 mL formaldehyde solution (37%) was placed in the reactor, and then the solution was adjusted to pH 7.5 with sodium hydroxide (20 wt %). Subsequently, urea (49.3 g) 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 additional 15 min. Finally, the pH was readjusted to 8.0 after cooling.

Preparation of modified UF resins

The preparation of modified UF resins was quite similar to the general preparation method at the same ratio ($F/U = 1.5$). Typically, a tiny amount of each of the dendrimers (1.2–3 g) was added in the beginning to neutralize the acidity of the formaldehyde solution (37%), and the pH was adjusted with the amine-terminated modifier to pH 8 in the first stage while Lewis acid was used in the second stage. In case of half-generated modifiers, the reaction was carried out in one shot as the pH could not be adjusted beyond 7.2 with this modifier then urea was dissolved and the mixture was heated under reflux. The pH declined spontaneously to 5 within 45 min then the polycondensation reaction was continued for additional 15 min. Finally, the pH was readjusted to 8.0 with sodium hydroxide and the resin was stored under room temperature.

Characterizations

The solid content was determined in three replicates by taking the difference of the weight before and after drying of 1 g of UF resin into a disposable

TABLE I
Properties of Modified UF Resins with Full-Generated Poly(amido amine)s

Properties	Unmodified UF resin	Modified UF resin with different generations of poly(amido amine)s		
		G1	G2	G3
Solid content (%)	47.6	48.3	49	51
F.F. (%)	2.1	1.2	0.95	0.7
Density (g/cm^3)	1.195	1.192	1.193	1.191
Viscosity (P)	0.71	0.96	0.95	1.3
Gel time (sec)	55	45	40	31

aluminum dish in 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-II1, Brookfield, Middleboro, MA) with no. 2 spindle at 60 rpm. The density of the resin was determined by weighing 50 mL of UF resin in a mass cylinder at 25°C. 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 ground cured resins were recorded on a JASCO FT/IR-6100 with 4 cm^{-1} resolution, Japan after extraction with distilled water for the full-generated modifiers or THF for the half-generated modifiers. DSC scans were performed on a Labsys^{TM} TG-DSC16 at a heating rate of 5°C/min under argon atmosphere.

Application of the prepared resin as wood adhesives

Samples of plywood were prepared with the following dimensions 2 cm × 0.5 cm × 10 cm. The surface was cleaned, smoothed then the hardener was added, based on the solid content of the resin and mixed well just prior to application. Approximately 1.5 g of the resin was spread over an area of (2 cm × 2 cm) from the wood species and the sample was pressed using a hydraulic press of two plates, both heated to 150°C under pressure of 50 kg/cm^2 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

In a study carried out by Maminski et al.,[12] the significant improvement of the mechanical properties, hardness (16%), and compressive shear strength (17%), of cured urea-formaldehyde resin in the presence of a hyperbranched polyether, was encouraging for us to study similar modification systems of UF resin based on either hydrophilic or moderately hydrophobic dendritic structures especially that this interesting study did not extend to focus on the use of this system as wood adhesive. The enhancement in the mechanical properties was ascribed on the one hand to the action of hyperbranched polymer like a multifunctional crosslinker providing higher crosslink density and on the other hand to the formation of hydrogen bonds between the hydroxyl groups of hyperbranched polyether and carbonyl groups of urea which resulted in higher stiffness and strength. Surprisingly, when higher fractions of the modifier in the blend exceeded a critical limit, it acted like a plasticizer introducing some flexibility into the network and lowering its compressive strength. The authors did not refer in their study to which extent was the participation of the hyperbranched modifier in the formed network and what is the impact of the degree of branching and hence the content of the hydroxyl groups on the mechanical properties of the cured resin. We considered these aspects are critical points that needed to be more investigated. Thus, we concentrated on the use of full generations of poly (amidoamine) (G1, 2, and 3) bearing active —NH$_2$ terminals that may involve in the curing reaction and network formation, as well as their less active corresponding half-generated species that are terminated with (—(C=O)—OCH$_3$) groups (G0.5, 1.5, and 2.5), and study their effects on the physical and mechanical characteristics of UF resins to be used as wood adhesive systems (Tables I and II).

Interestingly, far better prolongation of the shelf life was observed for the prepared resin, exceeding 15 months at the time of addressing this paper in

TABLE II
Properties of Modified UF Resins with Half-Generated Poly(amido amine)s

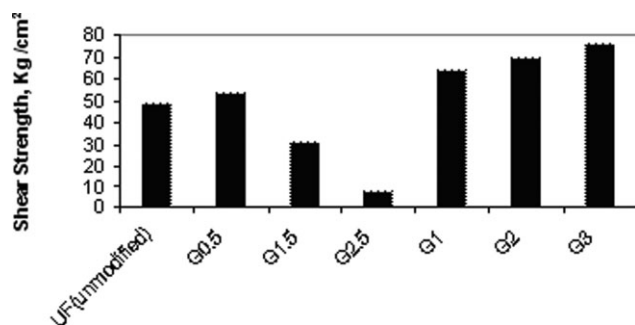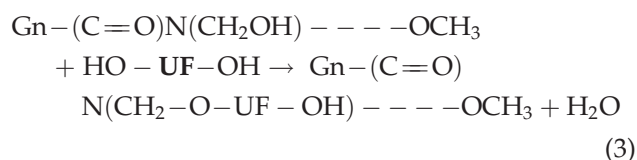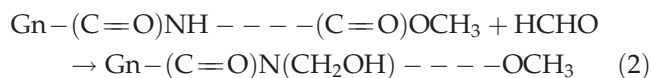| Properties	Unmodified UF resin	Modified UF resin with different generations of poly(amido amine)s		
		G0.5	G1.5	G2.5
Solid content (%)	47.6	47.1	47.6	46.8
F.F. (%)	2.1	2	1.9	1.7
Density (g/cm^3)	1.195	1.193	1.192	1.189
Viscosity (P)	0.71	2.4	2.2	1.95
Gel time (sec)	55	63	65	105

Figure 1 Adhesion strength of bonded wood species with modified UF resins in the presence of 3% NH_4Cl as a curing agent.

both cases. This contradicts to a little extent with the decline of the gel times of the modified resin with the full-generated dendritic modifiers, which translates into increase in resin reactivity compared with the unmodified resin especially in the case of G3 on the contrary to the gel times of the modified resins where half-generations of the dendrimers were employed, in particular, in the case of G2.5 as the gel time was approximately doubled when compared with the unmodified resin which reflects the much less reactivity of the modified resin with the ester terminated dendrimers (Gn + 0.5) which holds mainly for the prolonged shelf life. The variation in the solid content as well as the density of the prepared resins was statistically insignificant.

The higher reactivity of the modified resins with —NH_2 terminated modifiers versus those of ester-terminated ones was more apparent from the elevated levels of the carcinogenic free formaldehyde in case of modification with species of half-generations (very close to those of the unmodified resin) with respect to the corresponding levels of the modified resins with full-generated dendritic structures.

It can be noticed that along with the deactivation of the UF resin by the modification with half generations of dendrimers relative to those of full-generations, they exhibited higher viscosities (mostly doubled up to G2 but to a lesser extent for G3), the same was applicable on comparing the viscosity of unmodified UF resin ($\sim$ one third of the modified resins with half-generations). A reasonable explanation for this rise in viscosity (thickening) may be the formation of aggregates caused by hydrophobic intermolecular interactions[17] upon the existence in a surrounding medium of hydrophilic nature so it is imperative that the alkyl parts of the peripheral ester groups with their nonpolar character are the mean cause of these intermolecular hydrophobic interactions which more often supports the assumption that ester-terminated modifiers did not contribute so much to the formed network structure via chemical interactions but through imposing some flexibility

into the formed network.[12] However, the possibility might still exist for further condensation reactions with the UF resin through the internal amide groups before and after methylolation. This can be illustrated according to eqs. (1)–(3):

$$Gn-NH_2 + HCHO \rightarrow Gn-NH-CH_2OH \quad (1)$$

$$Gn-(C{=}O)NH-{-}{-}{-}(C{=}O)OCH_3 + HCHO$$
$$\rightarrow Gn-(C{=}O)N(CH_2OH)-{-}{-}{-}OCH_3 \quad (2)$$

$$Gn-(C{=}O)N(CH_2OH)-{-}{-}{-}OCH_3$$
$$+ HO-\mathbf{UF}-OH \rightarrow Gn-(C{=}O)$$
$$N(CH_2-O-UF-OH)-{-}{-}{-}OCH_3 + H_2O$$
$$(3)$$

Two sets of the prepared adhesives based on the polarity of the dendritic modifiers were employed for bonding wood species in presence of NH_4Cl as a curing agent (3 wt %) under the curing conditions listed in the experimental part, along with unmodified resin as a control.

Figure 1 reveals the better bonding strength for the systems based on full-generated modifiers relative to their modified analogues with half-generations, as it attained close values to the bonded joints with unmodified resin (G0.5), while decreased noticeably on going up to higher half generations (G1.5, G2.5). This further proves the involvement of the —NH_2 terminals in the network formation in the former case [eq. (1)] while in the latter the plasticization imparted by the much less active ester-terminated modifier was predominant together with the participation of either the internal amide groups or their corresponding new formed hydroxyls in the crosslinking ways eqs. (2) and (3).

The influence of 24 h immersion in cold water of the bonded wood joints with these adhesives on the bond strength is presented in Figure 2. As expected, the joints bonded with unmodified resin were seriously affected with a catastrophic failure while those
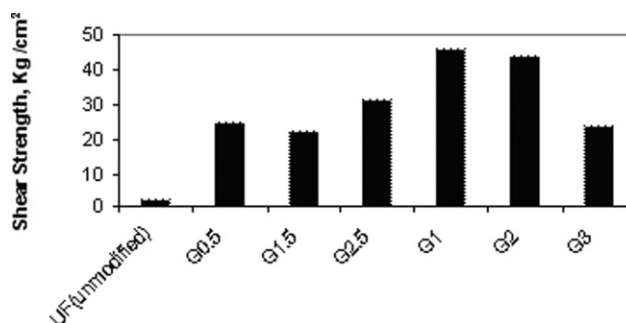

Figure 2 Adhesion strength of the bonded wood species presented in Figure 1 after 24 h immersion in cold water.
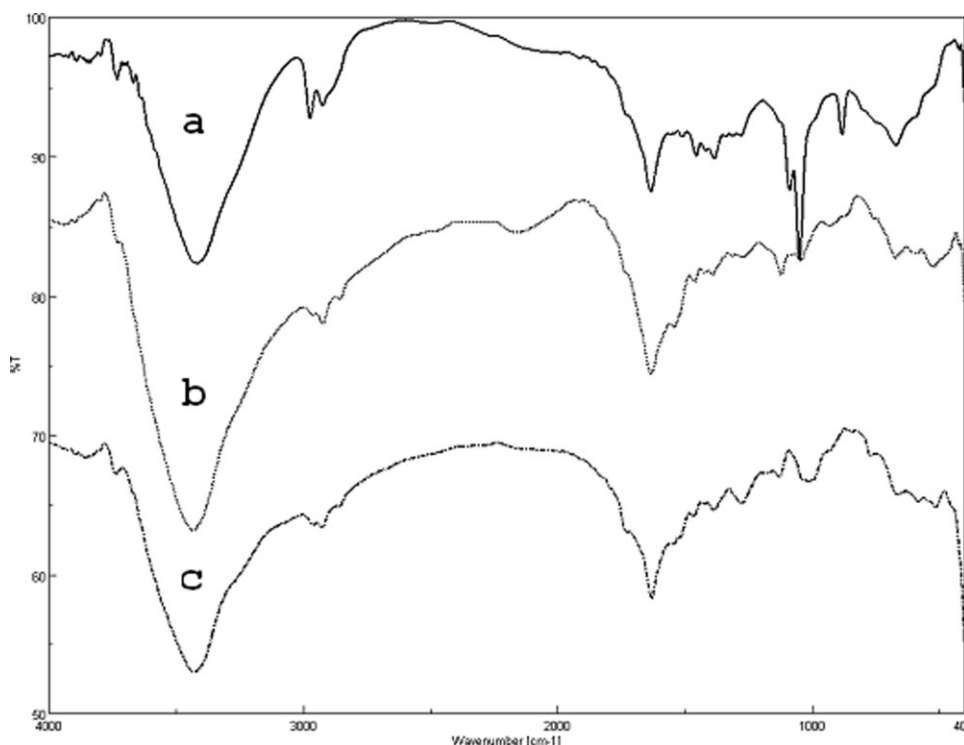
Figure 3 FTIR spectra of cured resins before (a) and after modification with G2 (b) as well as G1.5 (c) modifiers in the presence of 3% NH_4Cl as a curing agent.

based on the full-generated modifiers showed good resistance to deterioration in bond strength in the order G1 > G2 > G3 which was also the case for the equivalent systems based on the half-generated modifiers but unpredictably more sounding for the one with G2.5 modifier as it exhibited four times bond strength as high as before the immersion and preponderated the other formulated systems with G0.5 and G1.5. In a similar way, Pizzi and co-workers[18] carried out a very interesting study to accelerate the hardening of low condensation alkaline phenol-formaldehyde resins by some esters and outlined that the bond strength of the wood particle-board was almost doubled after 2 h immersion in boiling water. This was explained out by a certain flexibility of these additives to upgrade the performance of the resin and of the board bonded with it. This situation may in fact be realized in both cases to the overall flexibility acquired which promoted the formed networks not only to stand firm against crack and fracture but also to cyclic stress imposed by repeated wet-dry cycles.

A more confirmative FTIR spectra of cured resins using 3 wt % ammonium chloride in absence as well as in the presence of amine and ester-terminated modifiers, respectively, is displayed in Figure 3(a–c). Appearance of a new peak at 1350 cm^{-1}, ascribed to —CH$_3$ groups of the ester-terminated modifier could be observed in the spectra [Fig. 3(c)]. Also, for both cases the emerged broadening of the carbonyl peaks

at 1670 cm^{-1} indicate the existence of carbonyls with different chemical environments which can be considered a strong argument that proves the chemical linking of the modifiers during network formation and subsequent curing [Fig. 3(b,c)]. Moreover, the strong collapse of the C—O peak that normally appears at 1000 cm^{-1} [Fig. 3(a)] after modification, may reveal the strong hydrogen bonding initiated by the inserted amine terminals or internal amides. Once more, the elevated broadness of the peak pertaining to —NH$_2$ after modification together with the perturbation at the range 2850–2950 cm^{-1} (which is a result of the incorporation of —CH$_2$—CH$_2$ originating from the ethylenediamine moiety) verifies the assumption of their inclusion as reactive modifiers during the network formation and cure process.

Figure 4 shows the DSC thermogram of the cure process of unmodified UF resin ($F/U = 1.5$) in the presence of 3% NH_4Cl which consists of three exothermic peaks whose first one, extends in the range 60–106°C followed by other two main peaks, the first extends from 106–114°C, while the other one starts at 114°C and halts at 133°C.

In the presence of the amine–terminated modifier, the curing process differed significantly and became more complicated, the main exotherms were moved upward [Fig. 5(a–c)] but became sharper and taller which supports the absolute higher reactivity with respect to the unmodified resin. However, replacing the ester-terminated modifier instead of the amine
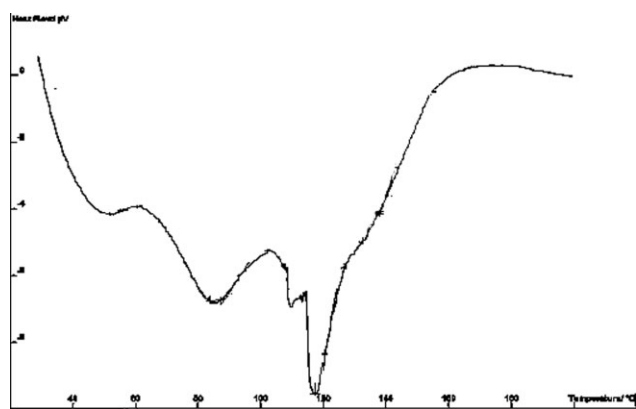
Figure 4 DSC curing thermogram of unmodified UF resins in the presence of 3% NH$_4$Cl as a curing agent.

analogue affected the resin activity as it lasted for longer times during the cure process [Fig. 6(a–c)] with the curing peaked at even higher temperatures but became broader to a much higher extents which reflects the lower reactivity.

It is thought that these differences do not stem from the difference of reactivity between the amine and ester-terminated modifiers but mostly the decline in the level of free formaldehyde in the first case (Table I) inhibits the catalytic role of NH$_4$Cl which acts effectively in the presence of sufficient amounts of free formaldehyde and decomposes into hexamethylenetetramine in addition to HCl, the liberated acid enhances the curing process.

This draws the attention that the modified UF resin with amine-terminated modifier is too active to self cure efficiently even without any hardener at appropriate temperatures, while in the presence of the less active modifier (ester-terminated), it did not contribute so effectively into the network structure which translates into higher levels of free formaldehyde (Table II) that activates the cleavage of NH$_4$Cl, hence the liberated acid should cause more cure advancement, nevertheless, it lasted for longer times due to the less reactivity of the system [Fig. 6(a–c)]. These data agree well with the recorded gel times in both cases. In view of that, it is believed that the enhanced resin reactivity was mostly attributed to —NH$_2$ terminals of the modifier even in the presence of very tiny amounts of NH$_4$Cl which is actually the case due to the deactivation of a major part of NH$_4$Cl by the low levels of free formaldehyde. Additional evidence can be found in the second case, where ester-terminated modifier was employed, the presence of more activated species of NH$_4$Cl by
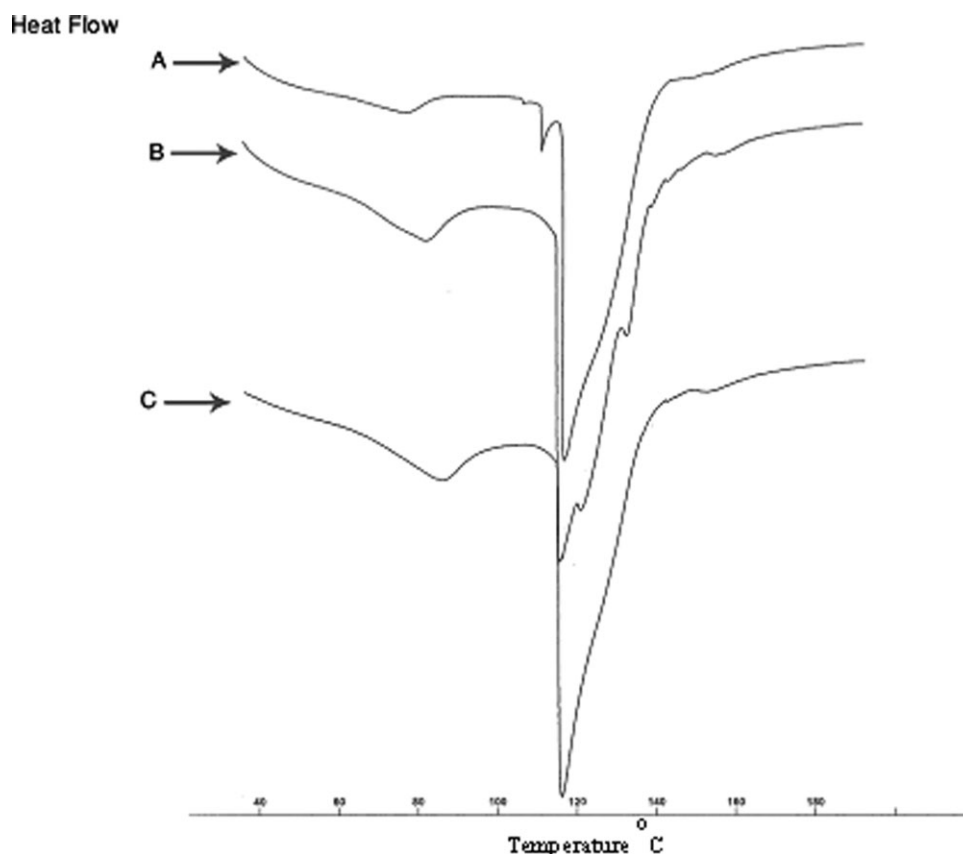

Figure 5 DSC curing thermograms of modified UF resins with different generations of poly(amidoamine)s in the presence of 3% NH$_4$Cl as a curing agent, (A) G1, (B) G2, and (C) G3.
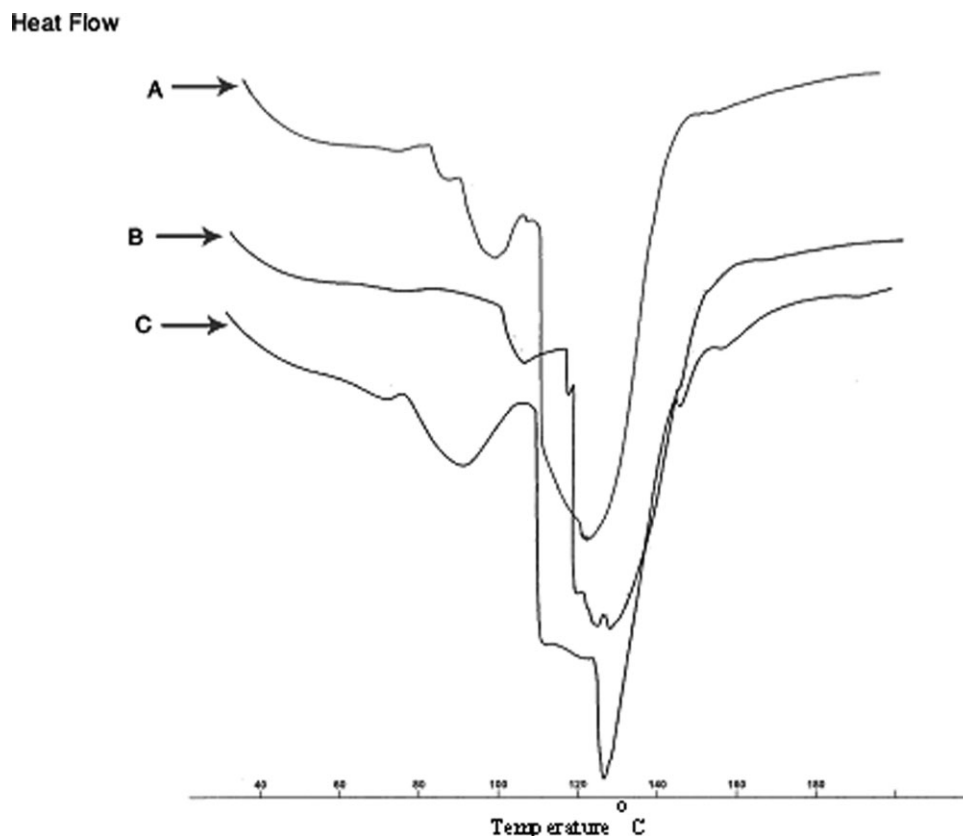
Heat Flow

Figure 6 DSC curing thermograms of modified UF resins with different half generations of poly(amidoamine)s in the presence of 3% NH_4Cl as a curing agent, (A) G0.5, (B) G1.5, and (C) G2.5.

the higher levels of free formaldehyde did not succeed to accelerate the cure process.

So it seems that going up to higher generations of the amine-terminated modifiers upgraded the reactivity as the maximum goes backward to lower temperature which is the reverse in the case of the ester-terminated modifiers on going up to higher half generations.

It should be stressed from the shape of the curing profile after modification that these new partners appear to introduce additional crosslinking reactions in the UF resin system, with the $-NH_2$ peripheral groups in the first case while in the second case with the interior $-(C=O)-NH$ groups.

Generally, it can be noticed that the consequential complication in the curing was not experienced in a similar DSC study of the cure process by Ebewele et al.[5] where urea-capped with different amines, were used as modifiers beside urea, the modifiers acted successfully in decreasing the internal stress developed during resin cure and improved the ability of the cured resin to withstand cyclic stress.

Commonly, the F/U ratio for most of the current wood adhesive UF resins for plywood is around 1.15 so the employed ratio in this work is still considered to be high hence more research is being

dedicated in our laboratory to lower this ratio to near 1.15.

CONCLUSIONS

The interesting molecular structure of dendrimers can be exploited as reactive modifiers for thermosetting resins like UF wood adhesive system to add more flexibility to the formed network, which helps to reduce the internal stress developed during the cure process and swell-shrinkage cycles after water uptake and loss in addition to their very promising role in prolonging the shelf-lives of the produced modified resins and improving the mechanical performance of the wood joints glued with these adhesive systems. However, more research is being done to obtain a F/U ratio of approximately 1.15, as for most of the current wood adhesive UF resins for plywood.

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