

Poly(amidoamine) Dendritic Structures, Bearing Different End Groups, as Adhesion Promoters for Urea–Formaldehyde Wood Adhesive System

Hisham A. Essawy, Heba A. Mohamed

Department of Polymers and Pigments, National Research Center, Dokki 12311, Egypt

Received 3 November 2009; accepted 8 May 2010

DOI 10.1002/app.32767

Published online 27 July 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A series of core-shell poly(amidoamine) (PAMAM) dendritic compounds bearing different end groups such as —OH , NH_2 , and $\text{NH}_3^+\text{—Cl}$ up to the third generation were prepared via successive Michael addition of a nucleophilic core (ethylenediamine) to methylacrylate followed by amination steps using ethylenediamine for the amine-terminated while ethanolamine for the hydroxyl-terminated compounds, also the protonated ammonium salt terminated form was obtained by cationization of the amine-terminated form using hydrochloric acid solution. The Surface activity and aggregation behavior of the corresponding aqueous solutions of the prepared generations with their different end groups were studied and confirmed by surface tension measurements using ring method technique. The prepared dendrimers showed high surface activity and the measurements revealed their abil-

ity to self aggregate in water at very low concentrations, critical aggregation concentrations (CACs). The CACs were found to decrease with increasing the generation number, which implies that molecular weight and structure play important roles in controlling the surface activity and CAC. The dendritic compounds proved to be effective as adhesion promoters for urea formaldehyde (UF) resins when applied as wood adhesive systems, which was ascribed in partial to the improved wetting over the substrate, a role that is fundamentally related to the huge number of function groups present at the interface. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 760–767, 2011

Key words: adhesion; adhesives; crosslinking; self-assembly

INTRODUCTION

Dendritic polymers have become one of the fastest growing areas of polymer science because of their unique performance, such as three dimensional architecture, low intrinsic viscosity, good solubility, good miscibility, and high reactivity because of the presence of many terminal functional groups.^{1–3} The study of dendritic poly(amidoamine) (PAMAM) is among the fastest developing varieties in the last two decades.^{4,5} Dendritic PAMAM have many potential applications including nanoscale catalysts,^{6,7} reaction vessels,⁸ and drug carriers.⁹ It was observed that aqueous solutions of half generations of dendrimers exhibited substantial surface active properties compared to full generation dendrimers, which was accounted for by the facile hydrolysis of the ester-terminals of the half generations to carboxylic acid groups.⁴ Amines in general are extensively used as additives in many chemical processes. As an example, acrylate latex containing amine groups has

been taken as a polymeric crosslinking agent of the lattices with epoxy groups to enhance the properties of antiwater, antisolvent and the mechanical strength of the formed films.^{10–12} As dendritic materials are characterized by compact structure with densely packed peripheral functional groups so they can participate in intermolecular association leading to the formation of aggregates.¹³ The formation of large aggregates from the individual dendritic molecules proceeds mainly via hydrogen bonds. Different structures based on PAMAM have been used in combination with hydrophobic coils in the construction of assembled materials in solution, in the bulk state, and at the air–water interface.^{14–16} When the dendrimer concentration exceeds a certain threshold referred to as the critical aggregation concentration (CAC) they associate together via intermolecular forces and as a result large aggregates can be formed. Generally, CAC can be determined by various techniques, such as static light scattering (SLS), fluorescence or dye solubilization technique, and surface tension measurements.¹⁷ The CAC values measured by different techniques were found to decrease gradually with increasing generation number.¹⁸ This work investigates on the evaluation of using finite amounts of dendritic compounds, based on polyamidoamine (PAMAM), bearing different

Correspondence to: H. A. Essawy (hishamessawy@yahoo.com).

end groups at the terminals, such as $-\text{NH}_2$ and $-\text{OH}$ (as nonionic surfactants) in addition to the quaternary ammonium salt formed after cationization of the amino-terminated ones with hydrochloric acid solution (as cationic surfactants) as a function of the generation number whereas the surface activity of anionic surfactants with $-\text{COOH}$ terminals, derived from facile hydrolysis of the ester-terminated precursors in aqueous media, could be indirectly proved by the enhanced adhesion imparted by urea formaldehyde adhesive system applied to wood substrates, after modification with finite amounts of these additives, due to the increased wetting on the substrate.

EXPERIMENTAL

Materials

Methylacrylate and ethylenediamine were purchased from Aldrich. Methanol and ethanolamine were products of Merck-Schuchart chemical company, Germany. All other chemicals were of laboratory grade and used without further purification.

Synthesis of dendritic poly(amido amine)s

The dendritic poly(amidoamine)s were prepared in a sequential addition of methylacrylate and ethylenediamine.⁴ Very briefly, ethylenediamine was used as a nucleophilic core and the Michael addition reaction was conducted in methanolic solution for 12 h at 60°C by addition of a large methylacrylate excess so leads to half generations ($G = n + 0.5$) which are ester terminated. Repeating this sequence in an alternative fashion leads to self-replication in a divergent manner to yield full generations which are amine terminated. Strong vacuum was employed beyond each step to remove excess reagent to avoid nonsymmetrically branched (defective) generations. The corresponding ammonium salts forms were prepared by neutralization of the amine-terminated full generations of poly(amidoamine)s according to the literature.¹⁹

Synthesis of hydroxyl-terminated dendritic poly(amido amine)s

The hydroxyl-terminated dendritic poly(amidoamine)s were prepared in a sequential addition of methylacrylate and ethanolamine.²⁰ In a similar manner, ethylenediamine was used as a nucleophilic core and the Michael addition reaction was conducted in methanolic solution for 12 h at 60°C by addition of a large methylacrylate excess so leads to half generation ($G = n + 0.5$). In this case, ethanolamine was employed afterwards beyond each half

generation step instead of ethylenediamine to yield the hydroxyl-terminated dendrimers.

Samples preparation for surface tension measurements and critical aggregation concentrations

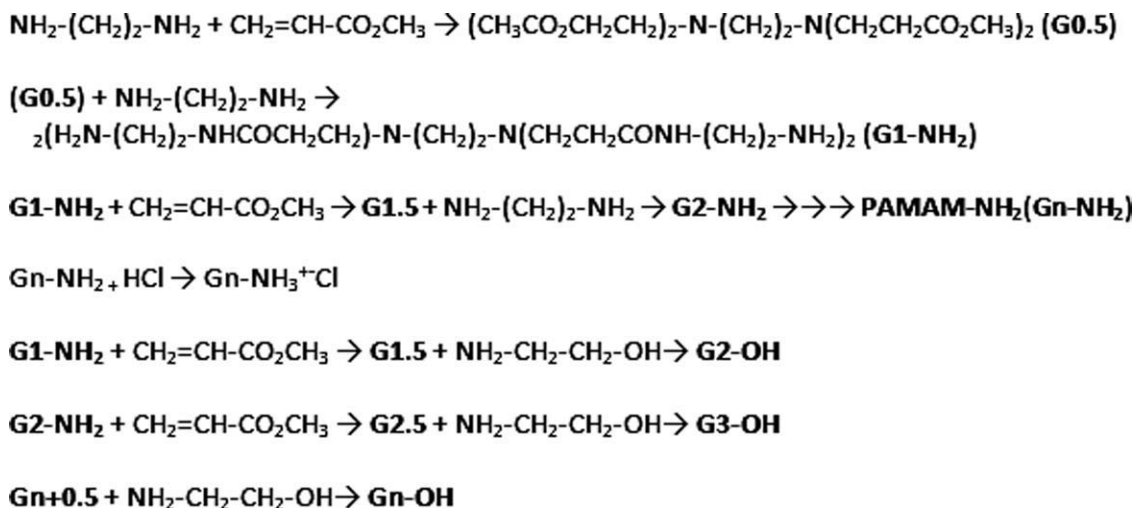
Each of the prepared generations up to the third one with different end groups ($-\text{OH}$, $-\text{NH}_2$, $-\text{NH}_3^+\text{Cl}^-$) was dissolved in distilled water at room temperature giving a stock solution that was diluted multiply to cover concentrations range from 1×10^{-7} to 1×10^{-1} mol/L. The critical aggregation concentration (CAC) of the prepared aqueous samples was determined at 20°C using Krüss tensiometer K6, which consists of a ring connected to a balance beam immersed into a liquid then the interfacial tension is expressed by: $\sigma = k/4\pi r$, where k is the force necessary to withdraw the ring against interfacial tension and r corresponds to the average value of the outer and inner-ring diameter (ASTM D 1331-89). The values were corrected according to the surface tension of the distilled water (72.6 mN/m). CAC was determined as the beginning of the plateau in a plot representing the relation between surface tension and concentration.

Techniques

IR spectra of KBr discs saturated with the dendrimers were recorded on a JASCO FT/IR-6100 with 4 cm^{-1} resolution, Japan. Finnigan Mat SSQ 7000 mass spectrometer was used for molecular mass determinations. Additionally, Agilent 1100 series, gel permeation chromatography (GPC), Germany, equipped with refractive index detector was used for performing some molecular weight measurements for the hydroxyl-terminated dendrimers using THF as an eluent and calibrated PL gel 5 μm , (100, 10⁴, 10⁵ Å) on series columns against polystyrene standard. Wood samples (2 × 0.5 × 10 cm) for adhesion measurements were cleaned, smoothed then the hardener was added to the resin, based on the solid content of the resin, and mixed well just before application. The resin was spread over 2 × 2 cm^2 of the wood species and the joint was pressed using a hydraulic press of two plates, both heated to 150°C for 5 min under pressure of 50 kg/cm^2 . The shear strength for each joint was evaluated using a tensile testing machine Type 92-5001 MFG. MARK61-0825, AVK Budapest, Hungary, operated at a minimum velocity.²¹⁻²⁴

RESULTS AND DISCUSSION

The frequent use of amines, especially in their polymeric forms, as additives during processing of polymeric materials, adhesion promoters, hardeners for some thermoset polymers or activators during many



Scheme 1 Synthesis of dendritic PAMAMs bearing different end groups.

chemical processes (e.g. emulsion polymerization) lie behind this study as the research focus on dendritic amines such as PAMAM, has tremendously grown during the last few years, because of their interesting properties that can impart new properties or help to improve others.

The synthesis of dendritic PAMAM generally begins with a nucleophilic core such as amines thus the growth of these materials proceeds in a divergent manner to give repeating units that form different interior layers, radially attached to the initiator core and exterior terminal functionality attached to the outermost interior generation.

Our synthesis steps started with ethylenediamine (EDA) as an initiator core and the repeating units of the interior layers were constructed in a sequential fashion by exhaustive Michael addition of methacrylate to the amine functionality to give subunits or half generations with ester moieties (**Gn+0.5**).^{21,22} Amidation of the resulting esters in a subsequent step with ethylenediamine gives another subunits. Completion of this sequence leads to a full generation with amine terminals (**Gn-NH₂**). Repeating this sequence was followed up to the third generation so we obtained dendritic structures of **G1-NH₂**, **G2-NH₂**, and **G3-NH₂**. The quaternization of these amino terminals with hydrochloric acid solution results in the same basic structures but with cationic end groups hence we obtained from this step the corresponding quaternary salts **G1-NH₃⁺-Cl**, **G2-NH₃⁺-Cl**, and **G3-NH₃⁺-Cl**.²³ Similarly to the amine-terminated dendritic structures, we obtained the analogs hydroxyl-terminated (**G1-OH**, **G2-OH**, and **G3-OH**) following the same synthetic route with the difference that ethanolamine was used in the last amidation steps only instead of ethylenediamine.²⁴ Scheme 1 details the steps employed for the synthesis of the different PAMAMs dendrimers.

The characteristic peaks of amine-terminated PAMAM (**G1-NH₂**) can be recognized from the spectra shown in Figure 1: NH₂ stretching appears at 3460 cm⁻¹ while the C-H stretching appears at 2981 cm⁻¹. The peak at 1674 cm⁻¹ is ascribed to the amides carbonyls in addition to C-N stretching at 1470 cm⁻¹. On the other hand, the spectra of **G1-OH** shows a peak at 3394 cm⁻¹ which was ascribed to OH while those at 1657 and 1081 cm⁻¹ can be accounted for by amide (C=O)NH and C-O stretching, respectively.

The theoretical molecular weights of the different dendritic structures that should have been obtained considering divergent growth without any nonsymmetric branching, that lead to defective dendrimers, can be shown in Table I. Mass spectroscopy was used for molecular weight determination but was limited by the potential of this analytical method to measure parent ion peaks of only up to approximately 1000 so the measurements would not be extended beyond the first generation for each type. The collected molecular mass data (not shown) for

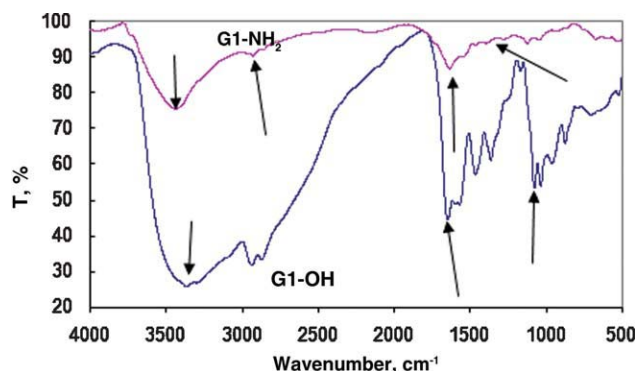


Figure 1 FTIR spectra of (a) **G1-NH₂**, (b) **G1-OH**. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

TABLE I
Theoretical Molecular Weights of the Obtained Dendritic Structures

	G1	G2	G3
G-OH	520	1436	3268
G-NH ₂	516	1428	3252
G-NH ₃ ⁺ -Cl	662	1720	4282

G0.5 illustrated a parent ion peak at 405, which is in complete accordance with the theoretical value whereas the parent ion peak for G1-NH₂ was obtained at 457, which reveals immature defective growth.

It is known that the synthesis of this type of materials exhibits nonideal growth, which can be caused in many ways by incomplete Michael addition, intramolecular cyclization and fragmentation due to retro-Michael addition hence under nonoptimized conditions, such as incomplete alkylation and amidation, subsequent growth leads to nonsymmetric branched (defective) dendrimers, which makes analysis by nuclear magnetic resonance (NMR) not very much diagnostic especially when the synthesis steps are too long and carried out in consecutive fashion.

However, molecular weight measurements using gel permeation chromatography (GPC) could only be carried out up to G1-NH₂ due to solubility limitation in THF of the higher generations. The GPC profile of G1-NH₂ shown in Figure 2 shows a weight average molecular weight of 665 g/mol, which is even higher than the obtained value determined by mass spectrometry for the sample, which may indicate that a possible nonsymmetric bridging rather than branching started to be pronouncing. All in all, the synthesis of these dendritic compounds is described in details with an intensive characterization of their structures in the work done by Tomalia et al.⁴

The surface activity of the prepared generations with different end groups and their ability to assem-

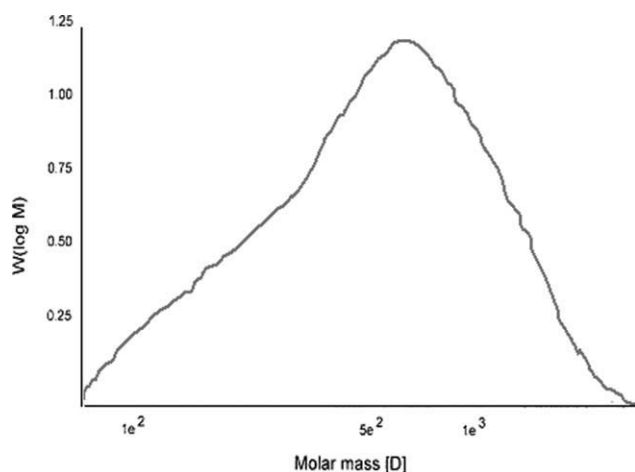


Figure 2 GPC profile of G1-NH₂.

TABLE II
Surface Tensions and CACs of Aqueous Solutions Containing Dendritic Polymers with Different End Groups

End group	Generation NO	Surface tension (mN/m)	CAC (Mol/L)
-OH	G1-OH	49.6	7×10^{-3}
	G2-OH	49.1	1×10^{-3}
	G3-OH	48.3	4×10^{-4}
-NH ₂	G1-NH ₂	49.1	4×10^{-3}
	G2-NH ₂	48.5	7×10^{-4}
	G3-NH ₂	47.1	1×10^{-4}
-NH ₃ ⁺ -Cl	G1-NH ₃ ⁺ -Cl	47.4	1×10^{-3}
	G2-NH ₃ ⁺ -Cl	45.6	4×10^{-4}
	G3-NH ₃ ⁺ -Cl	44	7×10^{-5}

ble in water and form large aggregates via secondary forces at very low concentrations (critical aggregation concentration (CAC)) can be investigated using surface tension measurements. Different series of aqueous solutions for each of the obtained dendrimers up to the third generation, comprising concentration range 1×10^{-7} to 1×10^{-1} mol/L, in addition to distilled water as a blank, were prepared for surface tension measurements at 20°C and the results are listed collectively in Table II. CAC was determined as the concentration at which an asymptotic value for surface tension can be reached.²⁵

The results obtained for the solutions of the hydroxyl-terminated dendrimers are displayed in Figure 3. In general, the surface tension of distilled water can be lowered with increasing the concentration of the dendrimer up to asymptotic value. It can be drawn from the figure that the CAC of G1-OH was acquired at around 7×10^{-3} mol/L while the coupled surface tension was 49.6 mN/m. A minor shift to a lower surface tension value was observed for G2-OH (49.1 mN/m) whereas CAC was not very

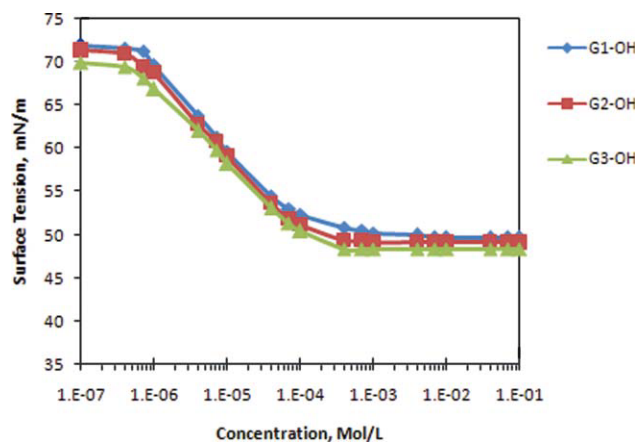


Figure 3 Surface tension of aqueous solutions containing G_n-OH dendrimers as a function of concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

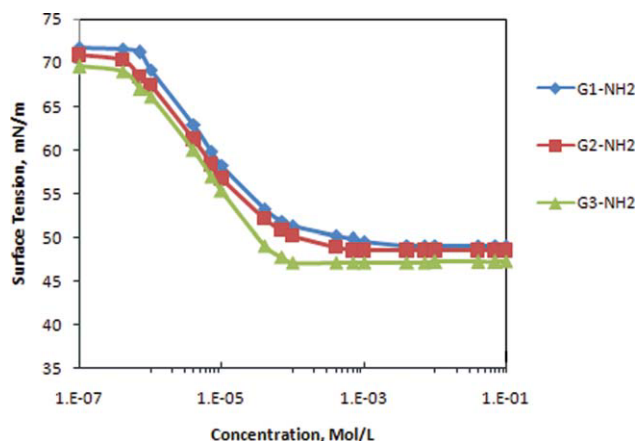


Figure 4 Surface tension of aqueous solutions containing $G_n\text{-NH}_2$ dendrimers as a function of concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

much changed, 1×10^{-3} mol/L. More decrease in surface tension was attained upon going up to generation 3 (48.3 mN/m) at a CAC of 4×10^{-4} mol/L. This is unquestionably attributed to the associated increase in the end groups content upon going up to higher generations thus the existence of the polar -OH terminal groups at the air-water interface is responsible for the surface activity.

Monotonic behavior was found for aqueous solutions of the amine-terminated dendritic structures and the general trend for the relation between the surface tension and concentration is typical as for the hydroxyl-terminated structures (Fig. 4) with more pronounced effect for the amino groups on the CAC than for the hydroxyl groups. There was a considerable backward shift in the CAC starting from G3 (1×10^{-4} mol/L at a surface tension 47.1 mN/m in comparison with 4×10^{-3} mol/L at 49.1 mN/m and 7×10^{-4} mol/L at 48.5 mN/m for G1 and G2, respectively).

The same relation was set for dendritic structures based on the protonated amine-terminated dendrimers as shown in Figure 5. Once more, the surface tension decreases with increasing the concentration of the aqueous solution of dendritic salts and also with increasing the generation number. G1- $\text{NH}_3^{+}\text{-Cl}$ acquired CAC at 1×10^{-3} mol/L, a concentration at which the surface tension of the water decreased to 47.4 mN/m. As expected, going up to G2 of this type with protonated ends gave rise to a CAC of 4×10^{-4} mol/L at a surface tension of 45.6 mN/m. Further decrease in the CAC can be noticed for G3- $\text{NH}_3^{+}\text{-Cl}$ which reached 7×10^{-5} mol/L with a corresponding surface tension of 44 mN/m. The decrease in the CAC is always related to the tremendous increase in the functional terminal groups which cover large area at the air-water interface.

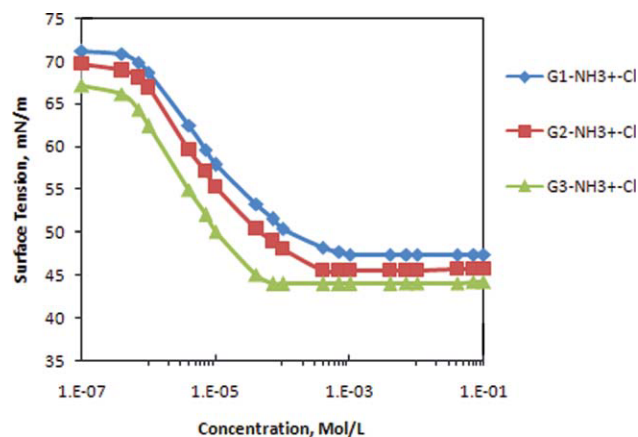


Figure 5 Surface tension of aqueous solutions containing quaternary salts of the amine-terminated dendrimers as a function of concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In conclusion, the surface activity for a dendritic structure is sensitive to its chemical structure, functional groups at the chains ends and their relevant aqueous concentrations. So as to emphasize which function group at the periphery of the dendritic structure skeleton can be more surface active, a comparative representations of surface activity of the third generation of each series are overlaid in Figure 6 which shows that the surface activity of the different dendrimers at their third generation for a given concentration can be arranged in the following order: $G3\text{-NH}_3^{+}\text{-Cl} > G3\text{-NH}_2 > G3\text{-OH}$ whereas the related CACs can be ordered in a reverse sequence to surface activity which means that the occupied area per a terminal group at the air-water interface is increasing in the same direction where CAC decreases.

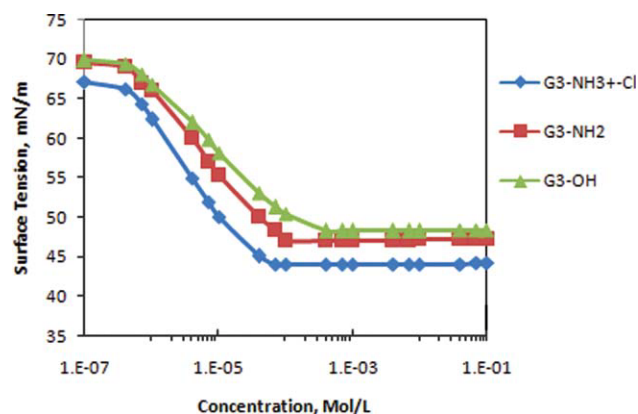


Figure 6 Surface tension measurements of aqueous solutions containing dendrimers with different end groups at their third generation as a function of concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Glazkov²⁶ found previously that latex as colloidal systems can be introduced into urea formaldehyde resin-based binders where the performance of the resins was upgraded markedly. Upgrading was explained by the introduction of latex particles that decreased the surface tension, wetting angle, and viscosity which favored better wetting and more uniform coverage of the external surface of the wood filler with the binder. Correspondingly, Pizzi and coworkers²⁷ used water-dispersible fluorinated poly(oxetane) surfactants to improve the flow, leveling, and surface appearance of urea formaldehyde resin in aqueous coating and it was found that their addition could improve the performance of UF resins as applied to wood panels which was accounted for by a mechanism that somewhat related to the reduction of the interfacial tension of the resins, with enhanced substrate wetting leading to better adhesion.

Recently, Essawy et al.^{21–24} suggested the use of various dendritic structures, based on poly(amidoamine)s bearing different end groups such as $-\text{NH}_2$,²¹ $-\text{COOCH}_3$,²² and OH groups,²⁴ as additives to modify the properties of urea formaldehyde resin used for the purpose as wood adhesives where it was found that many of the resins properties could be strongly improved.

With respect to the dendritic structures with $-\text{NH}_2$ and OH end groups, we found that a set of advantages were reached with very small amounts of these additives.^{21,24} Such improvements are decreased levels of free formaldehyde, which is known to be highly carcinogenic substance, in addition to a significant decrease in the gel time which translates into a substantial increase in the resin reactivity whereas the viscosity was found to increase after the resin modification with these types of additives. Each of the above-listed improvements was explained according to the chemical structures of the modifiers and the possible changes imparted to the resin after modification which ensured these impacts on the resin properties and performance. Basically, it can be realized that this may be obtained through increased rate of collision between the reacting species after being modified with additives possessing huge number of reactive groups at the terminals despite the associated increase in viscosity unless we consider that this increase was limited and did not reach to the extent that can hinder the collision while their participation in the reaction with huge number of reactive terminal end groups is responsible for the enhanced reactivity as translated from the gel times shortening.

Further, it was found that the use of these additives could amplify the adhesion strength noticeably. Undoubtedly, this is principally explained by the ability of active end groups to decrease the surface

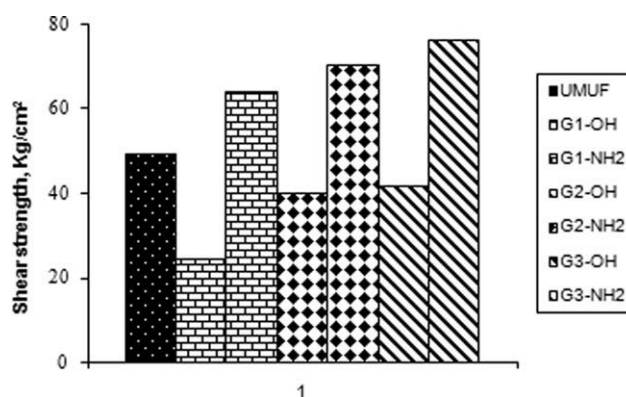


Figure 7 Adhesion strength of modified urea formaldehyde resin in comparison with the unmodified resin using NH_4Cl as a hardener.

tension effectively and their potential to increase the wetting of the resin on the substrate surface thus led to enhanced adhesion.^{22,24} Figure 7 briefly shows the amplification acquired in shear strength with respect to the unmodified urea formaldehyde resin (UMUF) when any generation of amine-terminated modifiers was used. Unexpectedly, the improvement in shear strength did not extend to the modified resin with the hydroxyl-terminated modifiers upon using NH_4Cl as a hardener (Fig. 7) which may be attributed to the higher functionality of the former and therefore better involvement in the network formation and strengthening. On the contrary, it started to be realistically improve when the dendrimers-based hardeners were applied as curing agents, the best result was afforded for a joint glued using a modified UF resin with G1-OH by employing 3 wt % of the hardener derived from the quaternization of G3-NH₂ with HCl ($>71 \text{ Kg/cm}^2$).²⁴

In a previous study, Essawy et al.²³ applied the dendritic polymers with amino terminals, after their conversion to hydrochloride salts forms ($\text{Gn-NH}_3\text{Cl}$, $n = 1-3$), as hardeners for unmodified UF resins instead of ammonium chloride with the significance to prove that they act efficiently and strongly improve the adhesion strength which confirms that the role of these additives is not only abbreviated to their end groups and real participation in the chemical build up of the resin network but also extended to their surface activity and drowning of the surface tension, which facilitates the spreading of the resin over the substrate accordingly better adhesion was ensured. This is fully shown in Figure 8 with an example showing how the dendritic hardeners affect the shear strength of wood joints glued with unmodified urea formaldehyde resin (UMUF) in comparison with the conventional curing system, NH_4Cl .

Interestingly, applying the dendritic hardeners for modified UF resins with the amino-terminated

dendrimers provoked the resins to encounter improved adhesion up to G2-NH₂. In contrast, the combination of G3-NH₂ modified UF resins with any of the dendritic hardeners induced a remarkable loss in the adhesion strength.²¹ This can be clarified by the over plasticization conferred by the combination which proves that the enhanced wetting and decreased surface tension are not the sole factors that influence the adhesion process. This result matches well with the finding of Maminski et al.²⁸ who used hyperbranched polyether as a modifying agent for UF resins and found that beyond a critical concentration there was a negative impact on the mechanical properties which was attributed to overplasticization.

To further investigate how the additives upgrade the performance of the resins we concentrate on their action to decrease the surface tension out of many explanations presented previously.^{21–24} The dendritic structures with $-\text{COOCH}_3$ terminals, which are known to be less active, were employed as modifiers in very finite amounts to avoid initial phase separation, as they are weakly soluble in water.²² The same advantages were observed (mostly the shelf life and free formaldehyde level and to a little extent the adhesion strength) which is explained by their rapid hydrolysis in high contents to $-\text{COOH}$ groups⁴ at the terminals. Irrespective of their participation in the network formation, these active groups exhibit high surface activity so can decrease the surface tension thus increase the wetting of the wood substrates with the resin. The instability of this intermediate (with $-\text{COOCH}_3$ terminals) and rapid conversion to $-\text{COOH}$ terminated dendrimers is the rationale why we could not evaluate their surface activity.

Scheme 2 shows a proposed mechanism for the way the dendrimers act to upgrade the properties of urea formaldehyde resin especially the stability, adhesion strength and resistance of the resulting bonds to moisture and consequently deterioration. It is well

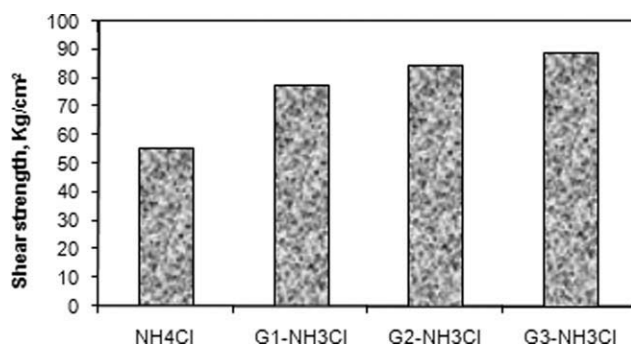
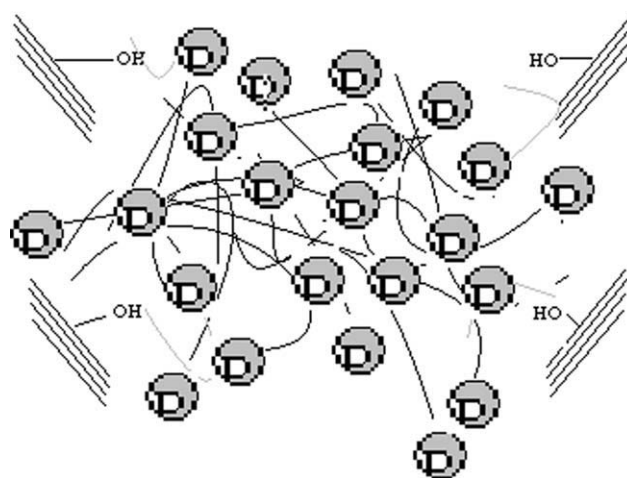


Figure 8 Adhesion strength of wood joint glued with unmodified urea formaldehyde using 3 wt % of different hardeners types.



Scheme 2 Mechanism of action of the dendrimers to upgrade the properties and performance of urea formaldehyde resin.

known that due to the resin reactivity it reacts spontaneously during storage and the condensation advances to the extent that decreases the solubility and accordingly the reactivity to a critical limit due to the limitation and consumption of $-\text{OH}$ groups at the surface, which appears in the figure as partial crosslinks in the bulk, right then the resins convert to a colloidal state which means low level of water tolerance. The adsorption of the dendritic aggregations, presented previously by chemical equations in scheme 1 and represented in scheme 2 by D in a circle, with their reactive end groups at the resinous chain ends enhances very much the solubility and keeps the reactivity of the resin unchanged for much longer periods. Furthermore, the participation of a dendritic end with huge number of end groups ($-\text{NH}_2$ and $-\text{OH}$) in the build up of interfacial bonds through further condensation with reactive OH groups from the cellulosic materials and in the mean time completion of the resinous internal network (which is actually the element that bear any mechanical stress) will help to rise the resistance of the formed joint to mechanical stress and hydrolytic degradation induced by moisture absorption.

CONCLUSIONS

1. Dendritic polymers with reactive groups at the chain ends can assemble via secondary forces and form large aggregates at very low concentrations.
2. The formation of aggregates is associated with a significant decrease in the surface tension of their aqueous solutions.
3. Their existence at the air–water interface is responsible for their surface activity.

4. Their incorporation in formulations containing urea formaldehyde resins intended for use as wood adhesive can strongly upgrade the resins properties which can be shortly explained by the enhanced wetting of the resin over the substrate surface in addition to their participation in the build up of the polymer network with their huge number of reactive end groups.

The authors are cordially thankful to Mrs Nadia Hussein for the preparation of the dendrimers. The authors are also indebted to the administration of the National Research Center for providing funding and facilities to carry out this work.

References

1. Frechet, J. M. J. *Science* 1994, 263, 1710.
2. Uhrich, K. E.; Hawker, C. J.; Fréchet, J. M. J.; Turner, S. R. *Macromolecules* 1992, 25, 4583.
3. Inone, K. *Prog Polym Sci* 2000, 25, 453.
4. Tomalia, D. A.; Baker, H.; Dewald, J. *Polym J* 1985, 17, 117.
5. Balogh, L.; Tomalia, D. A. *J Am Chem Soc* 1998, 120, 7355.
6. Zhao, M.; Sun, L.; Crooks, R. M. *J Am Chem Soc* 1998, 120, 4877.
7. Pittelkow, M.; Moth-Poulsen, K.; Boas, U.; Christensen, J. B. *Langmuir* 2003, 19, 7682.
8. Zhao, M.; Sun, L.; Crooks, R. M. *Adv Mater* 1999, 11, 217.
9. Beezer, A. E.; King, A. S. H.; Martin, I. K.; Mitchel, J. C.; Twyman, L. J.; Wain, C. F. *Tetrahedron* 2003, 59, 3873.
10. Nakamura, Y.; Okubo, M.; Matsumoto, T. *Kobunshi Ronbunshu* 1982, 38, 485.
11. Magnet, S.; Guillard, J.; Pichot, C. *Prog Org Chem* 1992, 20, 73.
12. Zhang-Qing, Y.; Bo-Geng, L.; Bao-Fang, L.; Zu-Ren, P. *Colloids Surf* 1999, 153, 31.
13. Van Hest, J. C. M.; Baars, M. W. P. L.; Elissen-Roman, C.; Van Genderen, M. H. P.; Meijer, E. W. *Macromolecules* 1995, 28, 6689.
14. Iyer, J.; Hammond, P. T. *Macromolecules* 1998, 31, 8757.
15. Frey, H.; Lorenz, K.; Stuhn, B.; Mulhaupt, R. *Macromolecules* 1997, 30, 6860.
16. Kim, C.; Kim, K. T.; Chang, Y.; Song, H.; Jeon, H. *J Am Chem Soc* 2001, 123, 5586.
17. Wang, B. B.; Zhang, X.; Jia, X. R.; Li, Z. C.; Ji, Y.; Yang, L.; Wei, Y. *J Am Chem Soc* 2004, 126, 15180.
18. Yang, Z.; Zhang, W.; Liu, J.; Shi, W. *Colloids Surf B* 2007, 55, 229.
19. Farlow, M. W. In *Organic Synthesis: Collective*; Rabjohn, N., Ed.; Wiley: New York, 1963; Vol. 4.
20. Scott, R. W. J.; Wilson, O. M.; Crooks, R. M. *J Phys Chem B* 2005, 109, 692.
21. Essawy, H. A.; Moustafa, A. B.; Elsayed, N. H. Presented at the Proceedings of the 3rd International Conference of Chemical Industries Research Division; National Research Center: Cairo, Egypt, December 16–18, 2008.
22. Essawy, H. A.; Moustafa, A. B.; Elsayed, N. H. *J Appl Polym Sci* 2009, 114, 1348.
23. Essawy, H. A.; Moustafa, A. B.; Elsayed, N. H. Presented at the Proceedings of the 1st International Joint Conference on Material Science, Nanotechnology and Biotechnology; National Research Center: Cairo, Egypt, January 4–6, 2009.
24. Essawy, H. A.; Moustafa, A. B.; Elsayed, N. H. *J Appl Polym Sci* 2010, 115, 370.
25. Ritacco, H.; Kurlat, D. H. *Colloids Surf A* 2007, 218, 27.
26. Glazkov, S. S. *Russ J Appl Chem* 2004, 77, 1711.
27. Mansouri, H. R.; Thomas, R. R.; Garnier, S.; Pizzi, A. *J Appl Polym Sci* 2007, 106, 1683.
28. Maminski, M. L.; Pawlicki, J.; Zado, A.; Parzuchowski, P. *Int J Polym Mater* 2007, 56, 1.