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ORIGINAL PAPER

Preformed Amide-containing biopolymer for Improving the Environmental Performance of Synthesized Urea–formaldehyde in Agro-fiber Composites

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Abstract Investigations have continued for production high performance agro-based composites using environmentally acceptable approaches. This study examines the role of adding amide-containing biopolymers during synthesis of urea–formaldehyde (UF) on properties of adhesive produced, especially its adhesion potential. The environmental performance of UF-resin synthesized in the presence of modified amide-containing biopolymer was evaluated by evaluating the free-HCHO of both adhesive (during processing) and of the eventual engineered composite product. Also, the benefits of this synthesis-modified adhesive in enhancing the bondability of sugar-cane fibers used in engineered composite panels was evaluated and compared to using UF-resin. The results obtained show that, static bending of the produced composites varied from 27.7 to 33.13 N/mm^2 of modulus of rupture (MOR) and from 2860 to 3374 N/mm^2 of Modulus of Elasticity (MOE); while for internal bond (IB) it's varied from 0.64 to 0.866 N/mm^2. Based on the ANSI and EN Standards modified UF-based agro composites produced meet the performance requirements for high grade particleboards with respect to static bending strength. These agro-based composite also tested out as having free-HCHO values of $\sim$13 mg/100 g board.

Keywords Modified-HCHO-based adhesive · Urea–formaldehyde · Biopolymers · Agro-based composite · Environment · Free formaldehyde

Introduction

Formaldehyde-based adhesives, especially urea–formaldehyde adhesives are used worldwide in manufacture lignocellulosic composites intended for interior applications. They are used because they have good adhesion properties and low cost. During the curing of formaldehyde-based adhesives, especially urea–formaldehyde adhesives in the hot press, some of the free formaldehyde reacts with various chemical constituents of the lignocelluloses, some is incorporated into the adhesive polymers, some is off-gassed into the air, and some is destroyed via the Cannizzaro reaction (a chemical reaction that converts formaldehyde into methyl alcohol and formic acid). During storage or in-service use of lignocellulosic composites, especially when exposed to elevated humidity or temperatures, measurable levels of free formaldehyde can also be generated due to hydrolysis, isomerization and decomposition of formaldehyde-resin [1].

Numerous investigators [2–4] studied the health effects of formaldehyde. Epidemiology studies have inferred a possible association between formaldehyde exposure and increase risk of cancer. Exposure to extremely high concentrations of HCHO in air can produce spasms and edema of the larynx. Individual susceptibility to the irritating effects of airborne formaldehyde can increase with repeated exposures [5, 6].

Attempts have been made to protect the environment or to minimize gaseous toxicants resulting from utilizing phenolic or amino resins as wood-product adhesives. Numerous

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studies have dealt with using formaldehyde-free adhesives, namely; thermosetting or cross-linked type of polymers, e.g., isocyanate binders and polyvinyl alcohol, or using natural products e.g., natural tannin and proteinaceous adhesives [7–19]. The isocyanates and phenol formaldehyde resins are reported to be good adhesive bonding agents for agricultural waste such as straw and rice husks [11].

Previous work by the two lead authors of this paper and their collaborators at NRC-Cairo have reported an improvement in the bondability of sugar-cane bagasse fibers with commercial UF when adding organic and inorganic materials, such as nitrogen-containing starch derivatives, as HCHO-scavenger [12, 14]. An even more effective derivative was the addition of an acrylamide-containing starch derivative [14]. Addition of small percentages of nano-clay has also been reported as successful additive to improve the performance of UF as adhesive for plywood and particle-boards [15].

This present work deals with preparation of newly synthesized urea formaldehyde adhesive incorporating a promising acrylamide-containing starch derivative during synthesis of UF-adhesive to achieve bonded composites that have little free-HCHO. Conditions of preparation of starch derivatives and synthesis of modified UF adhesive were optimized. The ability of this novel adhesive system to improve and replace environmentally unacceptable UF is also evaluated.

Experimental

Synthesis of Modified Urea–Formaldehyde Adhesives

In an attempt to improve the performance of urea–formaldehyde, an inexpensive and commercially accepted adhesive for wood composites, acrylamide containing starch derivatives were used to modify UF during its synthesis. Maize starch from Miser Co. and glucose were modified by acrylamide (AM) using previously developed method [13]. Prehydrolysis of the starch at different concentrations of hydrochloric acid, at different times and temperatures, and at differing AM-to-starch ratios provided a series of five starch derivatives [HSt (A), HSt(B) & HSt (C), HSt (D), HSt (E)]. These differing prehydrolysis processes resulted in a series of starch derivatives (as amide containing biopolymers) with different nitrogen content (195.7–554.0 m atom/100 g starch). The nitrogen content of these prepared biopolymers was determined by using Kjeldahl digestion method. The conditions of preparing these starch-based biopolymers are recorded in Table 1.

Amide-containing starch (AM-St.)-modified UF adhesive was synthesized by incorporating 5% AM-Starch derivative (based on urea), acquiring different nitrogen contents with paraformaldehyde (PF) and urea (U), and using 2-stage process (alkaline-acidic). An unmodified UF adhesive control was also prepared for comparison using a three-neck round bottom flask with a reflux condenser. In this process, the PF/U control with a PF/U-ratio of 1.7:1 was prepared in 120 mL H_2O adjusted to pH 8.0 with 50% NaOH solution. The mixture under continuous mechanical stirring was heated to 96 °C in 45 min, and was held at this temperature for 30 min. In the second stage, the pH of the mixture was adjusted to pH 5.5 with acetic acid and subsequently the mixture was boiled at 96 °C for 30 min. Finally the reaction mixture was concentrated by removing the water under vacuum and maintaining a pH of ∼8.0.

Characterization of Adhesive System

To evaluate the investigated modified UF adhesives the following characteristics was estimated: Free-HCHO, %

Table 1 Conditions of preparation of starch-based biopolymers

Starch-based biopolymer	Conditions of hydrolysis			AM/starch	Matom (N/100 g St.)
Biopolymer	HCl, M	Time, h	Temp.		
HSt (A)	0.5	2	60	–	–
HSt (B)	1	2	60	–	–
HSt (C)	1.5	2	60	–	–
HSt (D)	1.5	4	60	–	–
HSt (E)	1.5	2	80	–	–
AM-St (A)	–	–	–	0.5	196
AM-St (C)	–	–	–	1	441
AM-HSt (A)	0.5	2	60	0.5	237
AM-HSt (B)	1	2	60	0.5	294
AM-HSt (C)	1.5	2	60	0.5	377
AM-HSt (D)	1.5	4	60	0.5	460
AM-HSt (E)	1.5	2	80	0.5	487
AM-HSt (F)	1.5	2	60	1	554

(using sodium sulphite method), gel time (sec.), bond strength, and viscosity, in comparison with the properties of commercial UF [16, 17] Viscosity of the unmodified and modified UF adhesives were measured at 25 °C using a Brookfield Programable DV-II Viscometer, with spindle # 3.

Composites Preparation and Properties Tests

Bagasse composites were prepared by blending the ground raw Bagasse (3 mm diameter) with 12% (total dry weight) of the various modified UF-adhesives. Each resin system also contained a hardener at 0.12% (total dry wt.). These bagasse/resin mixtures were formed into composite boards by hot pressing at a pressure of 2.5 MPa and at platen temperatures of 140 °C for 8 min. The target thickness of the composite boards produced was ~4 mm.

All composites prepared using the various adhesives were subjected to mechanical and physical tests. The modulus of rupture (MOR), Modulus of Elasticity (MOE) and internal bond (IB) were estimated according to ASTM-D3039, [18] using universal Instron testing machine; while water absorption and thickness swelling percentages were estimated according to the GDR standard, TGL 11-373 [19]. Each result recorded in the following discussions is the average of four replicate measurements.

Results and Discussion

Characteristics of AM-Modified UF Adhesives

One of the major disadvantages of traditional urea–formaldehyde adhesives is the emission of the hazardous formaldehyde during cure, storage and use [20] Therefore, the development of new modified UF adhesives were assessed by comparing their physical/mechanical properties and free-CHO able to emit, in relation to both control and commercial UF. The data obtained are illustrated in Figs. 1 and 5.

Figure 1a shows free-HCHO of investigated modified synthesized UF adhesive in comparison to unmodified synthesized and commercial standard UF adhesives; while Fig. 1b shows the efficiency of amide-containing starch modifiers in reducing the CHO emissions when compared directly to the UF control. It is clear that, incorporating starch-based biopolymer during synthesis of UF showed major advantages in reducing the environmental impact,

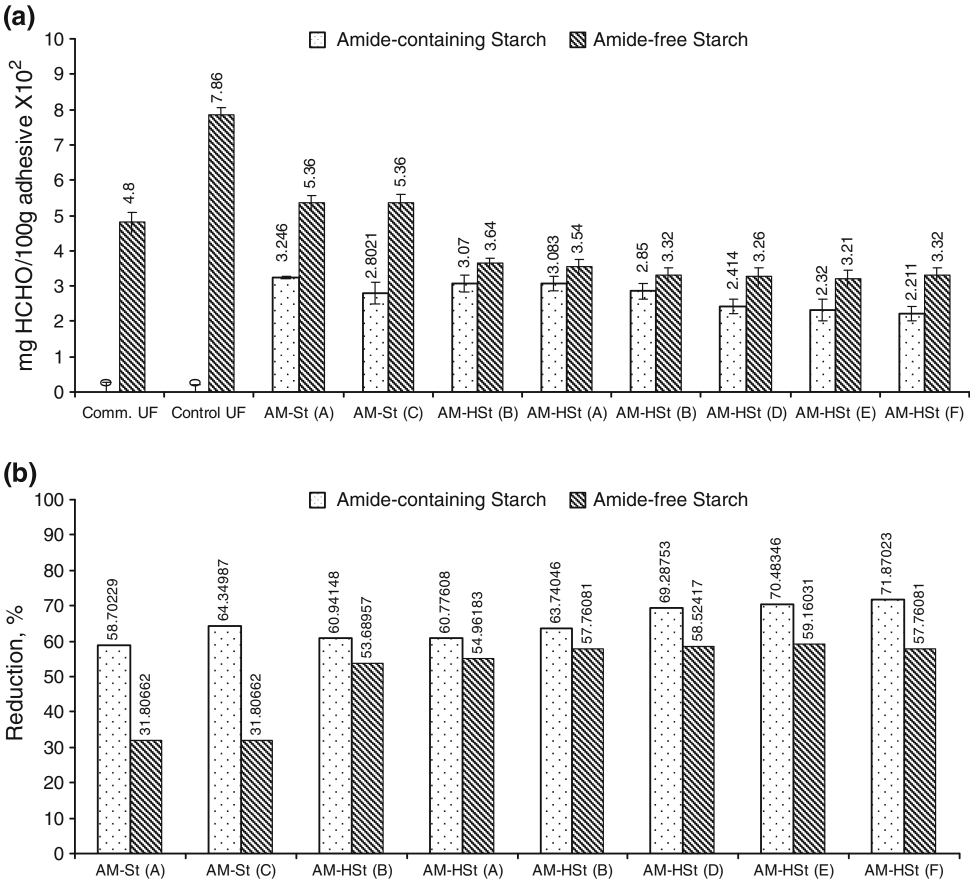

Fig. 1 Effect of modified UF by starch- based biopolymers on free-HCHO of produced adhesives. **a** Free-HCHO of unmodified and modified UF adhesives, and **b** Reduction of free-HCHO of modified UF/unmodified one

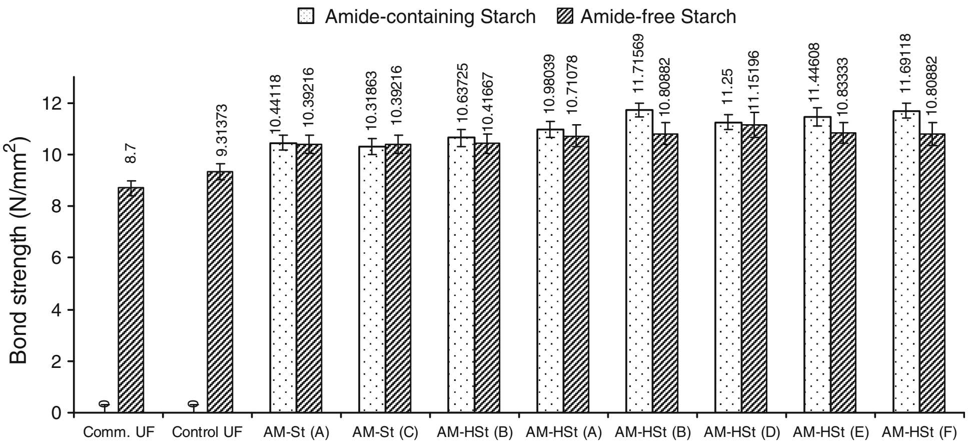

Fig. 2 Effect of modified UF by starch- based biopolymers on bond strength of modified UF—adhesives

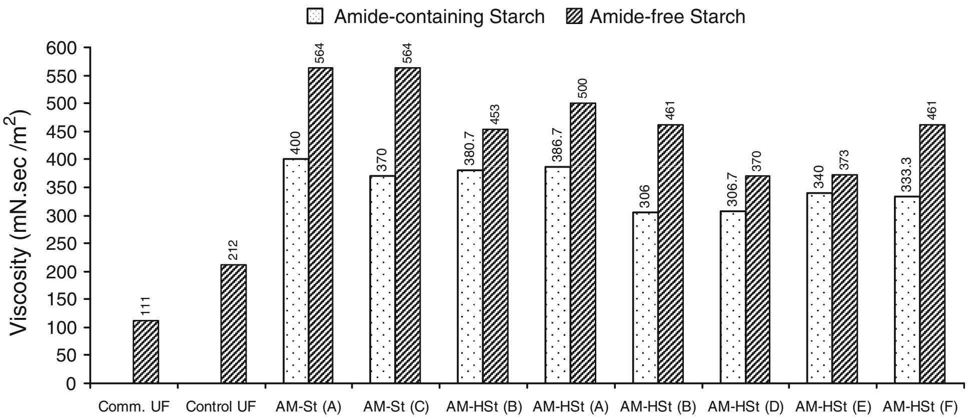

Fig. 3 Effect of modified UF by starch- based biopolymers on viscosity of modified UF—adhesive

through reducing the free-HCHO, which was able to emit from adhesive. The free-HCHO decreased with incorporating both amide-free and amide-containing starch. The efficiency of reducing the free-HCHO in adhesive system ranges from 32.8 to ~ 71.9%. The best reduction in free-HCHO is achieved when composites were made using modified UF-resin [AM-HSt (F)], whereas the amide-containing starch has higher level of nitrogen (554 m atom N/100 g).

From Fig. 2 it's clear that, the development biopolymer-based UF adhesives achieve higher bond strength values. The higher nitrogen content of amide-containing starch (AM-HSt(F)), achieves better bond strength 11.69 N/mm^2; with respect to both standard commercial UF and unmodified synthesized UF (bond strength ~8.7–9.3 N/mm^2, respectively).

For the viscosity performance of modified UF-adhesives, Fig. 3 shows that the amide-free starches provide adhesives with relatively higher viscosities compared to amide-containing starches despite variations in solids content between 59.5 and 63.4% for matched adhesive systems (Fig. 4). Increasing the nitrogen content of amide-containing starch from 196–554 m atom N/100 g starch, produced a decrease in UF viscosity from 400 to 330 mPa sec. This trend can be related to the values of free-HCHO of modified UF adhesives (Fig. 1).

For comparing the UF adhesives made from amide-free starches with those made from amide-containing starches (Figs. 3 and 5), the data show that there is clear relation between gel time and viscosity, whereas the increase in viscosity accompanied the decrease in gel time. This confirm finding of Osemeahon [21]. While, for amide-containing starch-UF adhesives, the viscosity and gel time values are not clear correlated. This is probably due to, in addition to the effect of viscosity, to the change in the content of amide groups, which influence it's chemically ability to catch the free-HCHO produced from condensation step of synthesis of UF. In other words, at relatively higher nitrogen content of amide-containing starch (e.g., 554 matom N/100 g St.), the amide groups may retarded the formation of free-HCHO in condensation step, consequently increased the gel time.

Mechanical and Physical Properties of Bagasse Composites Using Modified UF

The data obtained show that, the nitrogen content of AM-St. derivatives has a profound effect on physical and

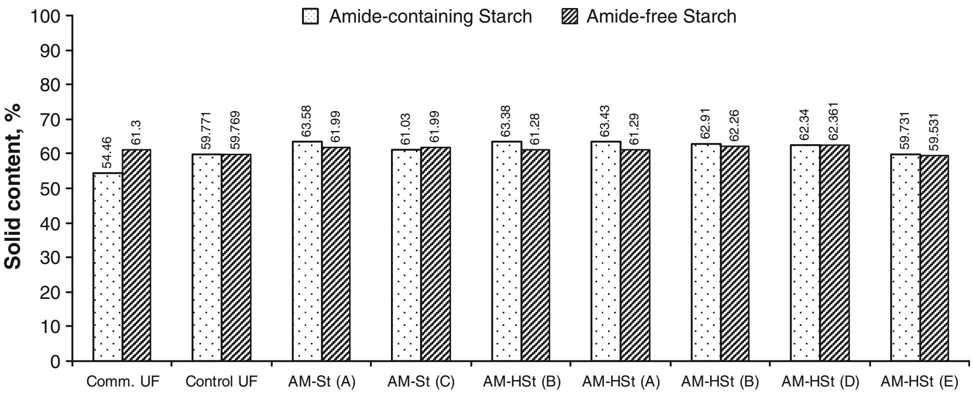

Fig. 4 Effect of modified UF by starch- based biopolymers on solids content of modified UF—adhesive

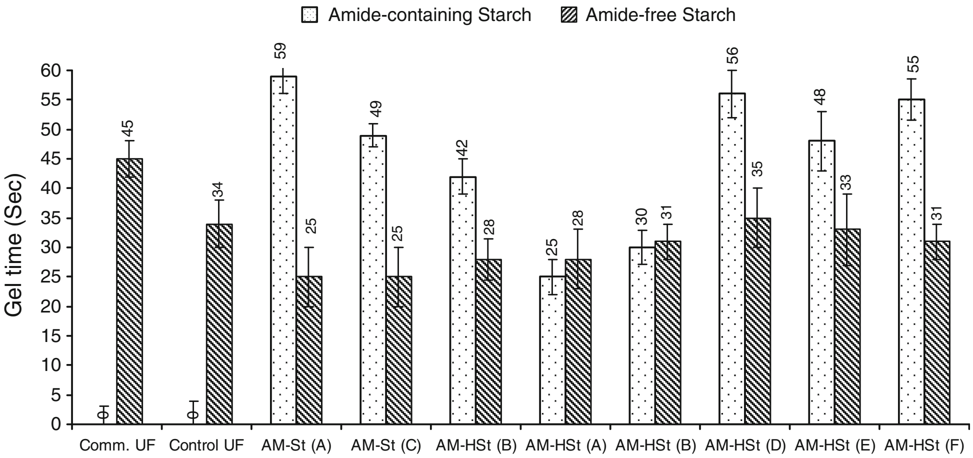

Fig. 5 Effect of modified UF by starch- based biopolymers on gel time of modified UF—adhesives

mechanical properties of final board. From Fig. 6 it is clear that, the investigated modified UF-adhesives exhibited an advantage in reducing the environmental impact, by reducing the free-HCHO emitted from sugar-cane fiber bagasse composite boards. The perforated-HCHO values (PV) of boards resulted from amide-free starch- UF adhesives are in the range 93.5–31.2 mg/100g board; while those from amide-containing starch-UF adhesives are in the range 57.3–13.57 mg/100 g board. The optimum reduction value is achieved on using AM-HSt(F) with the highest nitrogen content (~554 m atom/100g St), where the reduction in the PV- value of this board is reached 68%; while that of composite boards made of commercial UF is 42.43 mg/100 g board..

The static bending (MOR and MOE), internal bond (I.B), and water swelling properties of the composites made using the foregoing modified UF adhesives are illustrated in Figs. 7, 8and 9. For static bending properties (MOR & MOE), Fig. 7 shows that, the two types of UF resins synthesized using either amide-free or amide-containing starches, tended to increase the static bending properties of sugar-cane fiber bagasse composites when compared with UF resins from unmodified synthesis or commercial standard UF adhesives. The modified UF synthesized using amide-containing starches resulted composite with better static bending properties than UF resins using amine-free starch modifiers. The MOR and MOE of composites made by using amide-containing starch-UF adhesives varied from 28 to 33.1 N/mm^2 and from 2850 to 3374 N/mm^2, respectively. When using amide-free starches-UF adhesives the values for MOR and MOE varied from 27.7 to 30.9 N/mm^2 and from 2810 to 3250 N/mm^2, respectively. The values of MOR and MOE of composites resulted from unmodified synthesized UF and commercial UF are 25.51 and 2850 N/mm^2 and 22.07 and 2459 N/mm^2, respectively. The MOR and MOE of composites panels made using modified UF which was synthesized using amide-containing starches tended to be about 10 ± 3% higher than the other UF resin system evaluated in this study.

The explanation of this observation is probably related to the viscosity values of modified UF adhesives. Low viscosity UF gives rise to lower molecular weight which favors molecular chain mobility that enhances flexibility of polymer network in composite produced [21]. This view was emphasized from the values of free-HCHO of boards, whereas the flexibility reduces stress during hot pressing the board and resin cure. The reduction of stress reduces

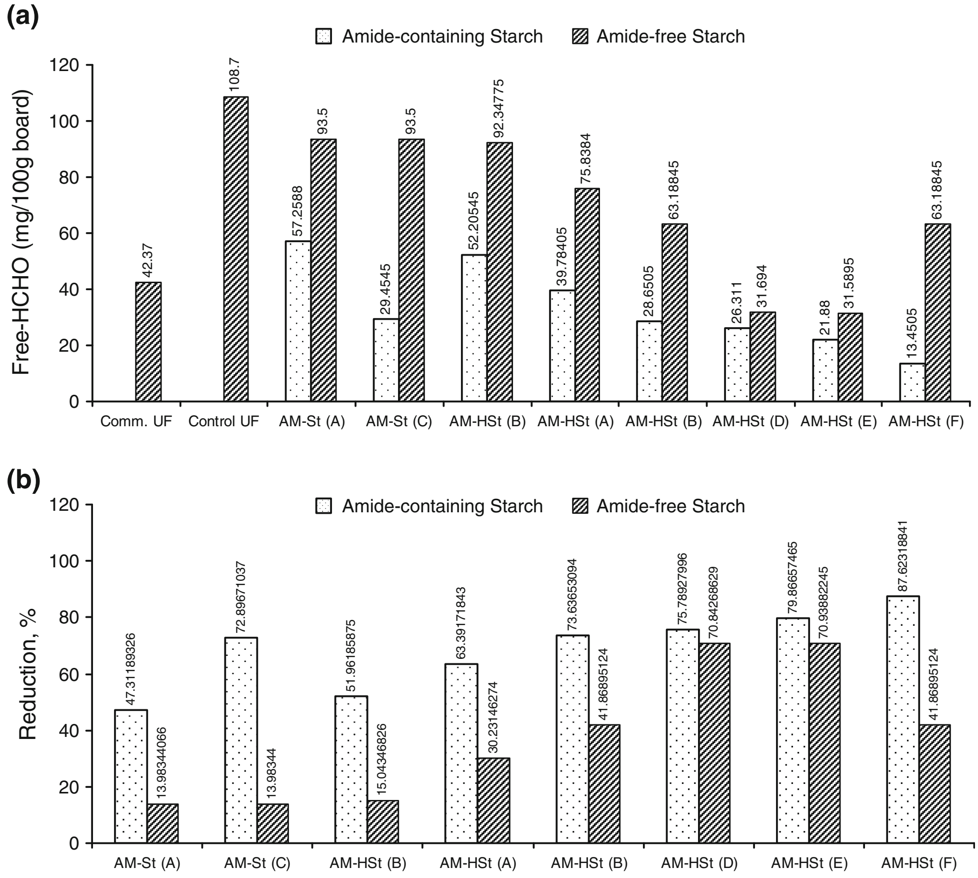

Fig. 6 Effect of modified UF by starch- based biopolymers on free-HCHO emitted from bagasse composites

the contact temperature to fibers and emission of HCHO. As there is a good relation between the increase of hot pressing temperature with increasing volatile organic compound (VOC) emissions during board formation [22].

Similar to the trend noted for MOE property, the internal bond (IB) of modified-UF is affected by nitrogen content of amide-containing starch modifier (Fig. 8). Incorporating of high-nitrogen AM-HSt (F) starch greatly improved IB (0.866 N/mm^2), when compared with a nitrogen content of other modifiers (0.64–0.73 N/mm^2). In general, amide-free starches have little effect in improving the internal bond of modified UF (0.67–0.704 N/mm^2), compared to unmodified ones (0.63 N/mm^2). All modified UF adhesives provided composites with relatively high internal bond strength, compared to that produced from commercial UF (0.51 N/mm^2).

According to particle board grade requirements from NPA (ANSI A208.1) [23] modified UF-based agro-fiber composites that meet or superior the requirements of high grade particleboards (H-3), especially with respect to static bending values) MOR 23.5 N/mm^2 & MOE 2,750 N/mm^2) can be produced.

Water swelling properties (SW) of the produced modified UF-based composites varied from 20.7 to 26.2% (Fig. 9). Sugar-cane fiber bagasse composites bonded using amide-free or amide- containing biopolymers generally tended to exhibit less water resistance (increased SW) when compared with commercial UF or the unmodified UF control (SW = 17.4%). Variations in the water swelling resistance between UF resins made with amide-containing starch and amide-free starches were noted. This, may be ascribed to the competing reaction of amide groups (hydrophilic side) of biopolymer's and urea with formaldehyde, during adhesives synthesized. Still, the water swelling results of most board meets the requirement of standard specifications ($\leq$25% % by ANSI).

Summary

Based on the results of the perforate free-HCHO, static bending and internal bond tests, a modified UF adhesive resin synthesized with a high amide-containing starch modifier (AM-St (F)), can be used successfully to produce an environmentally preferable adhesive for the production of lignocellulosic composites. These composites had satisfactory strength properties ($\sim$33 N/mm^2 MOR, 3195 N/mm^2 MOE & $\sim$0.9 N/mm^2 IB), and lowered free-HCHO values of about 30% (13.45 mg HCHO/100 g board) when compared to matched boards made from commercial UF

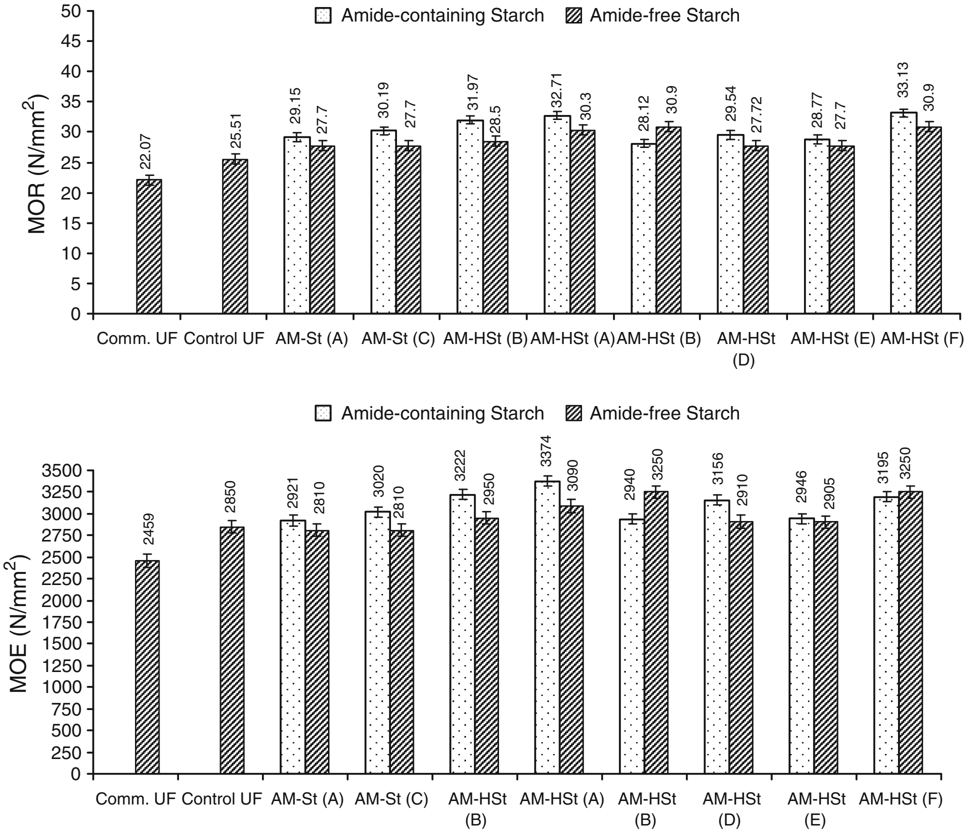

Fig. 7 Effect of modified UF by starch- based biopolymers on static bending properties (MOR & MOE) of sugar cane fiber bagasse composites produced

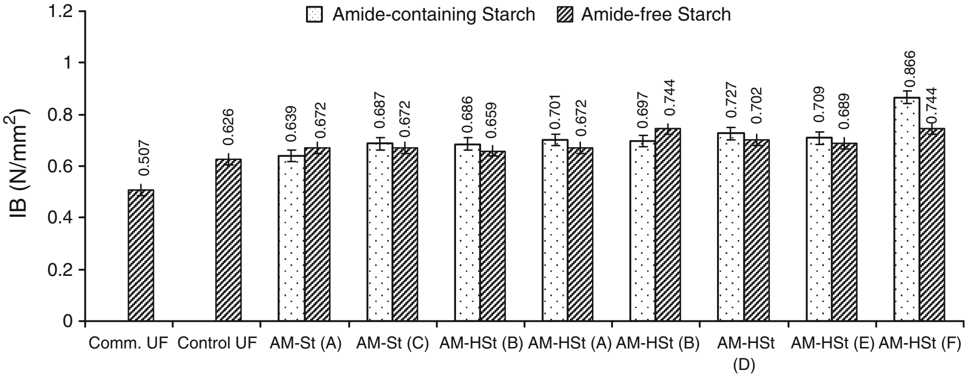

Fig. 8 Effect of modified UF by starch- based biopolymers on internal bond (IB) strength of sugar cane fiber bagasse composites

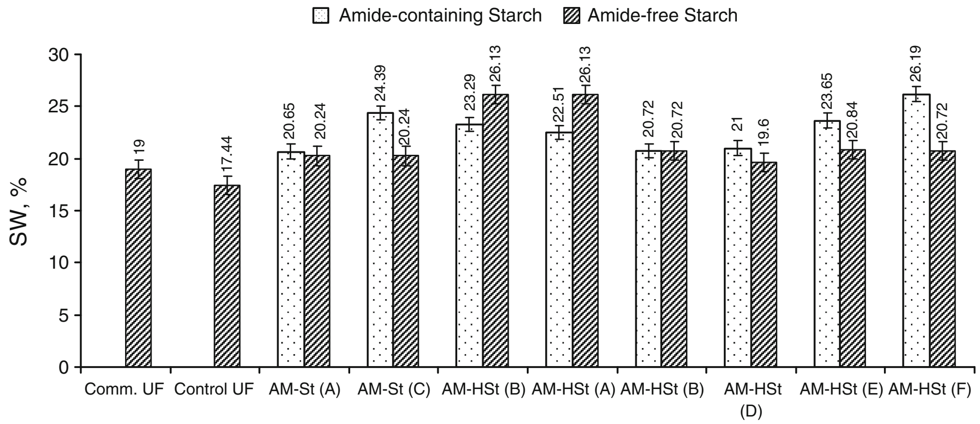

Fig. 9 Effect of modified UF by starch- based biopolymers on water swelling performance of sugar cane fiber bagasse composites

(42.37 mg/100 g board), i.e., reducing the free HCHO by about 68%. The modified UF-based agro-fiber composites that meet the requirements of high grade particleboards ANSI A208.1, especially with respect to static bending values and water swelling property that meet also the requirements of ANSI can be produced.

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References

1. H.-J. Deppe 1982 Emission von Organischen Substanzen aus Spanplatten. In; Luftqualitat in Innenraumen. K.Aurand, B. Seifert and J. Wegner (Eds.), Stuttgart, Fischer.: pp. 91
2. Blair A, Stewart P, M.O'Berg, Gaffey W, Walrath J, Ward J, Bales R, Kaplan S, Cubit D (1986) Mortality among Industrial Worker exposed to formaldehyde. J Natl Cancer Inst 76:1071
3. Collin JJ, Caporossi JC, Utidjiam HMD (1988) Formaldehyde exposure and nasopharyngeal Cancer: re-examination of the National Cancer Institute study and an update of one plant. Natl. Cancer Inst 80:376–377
4. R.E. Gosselin, R.P. Smith, H.C. Hodge (1984) "Clinical toxicology of commercial products 5th ed., PP. II-196-III-198-William and Wilkins, Baltimore
5. Proceedings of the world consultation on wood based panels, (1975) New Delhi, India
6. Beane Freeman L, Blair A, Lubin JH et al (2009) Mortality from lymphohematopoietic malignancies among workers in formaldehyde industries: the National Cancer Institute cohort. J Natl Cancer Inst 101(10):751–761
7. Dix B, Marutzk R (1988) "Tannin formaldehyde resin". Holz Roh-Werkt 46((1):19
8. Pizzi A (2000) Tannery row – The story of some natural and synthetic wood adhesives. Wood Sci Technol 34:277
9. Tomita B (1999) "Trend and future of wood adhesive". Mokuzai Kenkyu Shiryo 25:1
10. Tohmura S-I, Li G-Y, Qin T-F (2005) Preparation and characterization of wood polyalcohol- based isocyanate adhesives. Appl Polym Sci 98(2):791
11. Pan Z, Cathcart A, Wang D (2006) Properties of particleboard bond with rice bran and polymeric methylene diphenyl diisocyanate adhesives. Ind Crop Prod 23:40–45
12. Basta AH, El Saied H, Gobran RH, Sultan MZ (2004) Polym-Plast Technol Eng 43:819
13. Basta AH, El Saied H, Gobran RH, Sultan MZ (2006) Pigment Resin Technol 34:12
14. Basta AH, El Saied H, Gobran RH, Sultan MZ (2006) Design Monomers Polym 9(4):325
15. Lei H, Du G, Pizzi A, Celzard A (2007) Influence of nanoclay on urea-formaldehyde resins for wood Adhesives and It's Model I. Appl Polym Sci 106:3958
16. The European Standard, Determination of free formaldehyde in amino and amidoformaldehyde condensates,EN 1243 (1999)
17. Cetin NS, Ozmen N (2002) Int J Adhesion and Adhesives 22:481–486
18. ASTM D1037—06a Standard test methods for evaluating properties of wood-base fiber and particle panel materials
19. German Democratic Republic Standard, (1961) TGL 11–373
20. Km GM (2001) Examination of selected synthesis parameters for wood adhesive-type urea-formaldehyde resins by CNMR Spectroscopy. J Appl Polym Sci 80:2800–2814
21. Osemeahon SA, Barminas JT (2006) Properties of a low viscosity urea-formaldehyde resin prepared through a new synthetic Route. Bull Pure Appl Sci 250:67–76
22. Wenlong W, Gardner DJ, Melissa MGD (2002) Volatile organic compound emissions during hot-pressing of southern pine particleboard: panel size effects and trade-off between press time and temperature. J Forest Products 52(4):24–30
23. J.A. Youngquist, Chapter 10, Forest Products Laboratory, 1999, Wood handbook-Wood as an engineering material. Gen Tech Rep FPL-GTR-113. Madison, WI: US. Department of Agriculture, Forest Services