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SYNTHESIS, CHARACTERIZATION OF UREA-FORMALDEHYDE (UF), MODIFIED UF AND GRAFTED UF RESIN AND ANTIBACTERIAL STUDY OF UF RESIN AFTER MODIFICATION AND GRAFTING

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ABSTRACT

Urea-formaldehyde (UF) resins are polycondensation resins that attracting considerable interest today, in manufacturing particleboards. UF resins possess some advantages such as fast curing, good performance in the panel, water solubility and low price over others. This paper incorporates initial results that have been achieved by modifying and grafting a UF resin by utilizing p-phenylenediamine (PPDA) and vinyl acetate (VA) respectively. These modifications also reduced the tendency of the resin to crack and facture and substantially improved the resistance of bonded joints. In this study, three UF resins (such as unmodified, modified and grafted) were analyzed for their specifications and characterized with FTIR measurements and antibacterial activities. The antibacterial tests evaluated and compared the inhibition zone of S. aureus and E. coli with antibiotic Gentamycin.

KEYWORDS: Antibacterial properties, Grafted Urea-Formaldehyde (GUF) resin, Modified Urea-Formaldehyde (MUF) resin, Urea-Formaldehyde (UF) resin.

INTRODUCTION

As the most important type of amino resin is so-called amino plastic resins, UF resins attract lots of interest because they have great commercial importance and are easy to be manufactured at low cost, especially as adhesives for metal, plastic and wood products[1-8]. UF resins are polymeric condensation products of formaldehyde and urea. The synthesis of a UF resin is commonly performed by a two-step procedure i.e. addition and condensation. The addition reaction or so-called methylolation reaction leads to the formation of monomethylol urea, dimethylol urea and trimethylol urea under alkaline conditions. The condensation reaction under acidic conditions produces methylene or dimethylene ether linkage[9].

UF resins possess some advantages such as fast curing, good performance in panels, water solubility etc. Drawbacks of UF resins are low water resistance and tendency to emit formaldehyde from bonded wood composite boards[10-11]. Lower resistance to water limits the use of wood-based panels bonded with UF resin to interior applications. Free formaldehyde present in UF resins and hydrolytic degradation of UF resins under moisture conditions are known to be responsible for FE for wood-based panels[12]. UF resins are light colored largest class of amino resins that are predominate adhesives for interior grade plywood and particleboard. UF resins have been known for many decades[13-14] and are currently used worldwide as thermosetting wood adhesive in manufacturing particleboard (PB) and medium-density fiberboard[15].

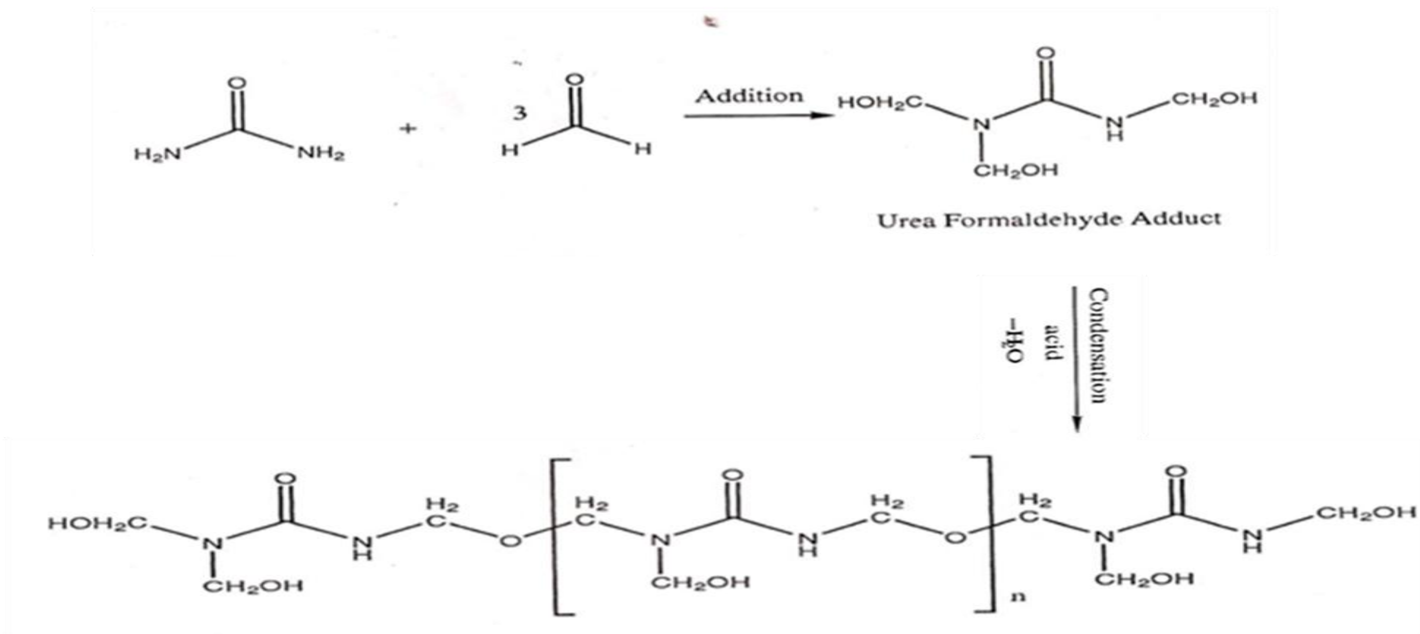
MATERIALS & METHODS

All chemicals and reagents were of analytical grade and used without further purification. Formaldehyde was purchased from Aldrich Chemical Co., Milwaukee, W.C. Urea (the contents of NE 46.0%) was purchased from J.T. Baker Chemical Co., Phillipsburg, NJ. p-Phenylenediamine was purchased from Du Pont Petrochemicals, Wilmington, DE. Azo-bis-isobutyronitrile (AIBN) and vinyl acetate were purchased from Sigma-Aldrich. Urotropin and oxalic acid were purchased from J.T. Baker Chemical Co., Phillipsburg, NJ. N, N – Dimethylformamide (DMF) and Dimethylsulphoxide (DMSO) solvents were purchased from Sigma-Aldrich.

EXPERIMENTAL

Synthesis of Urea-Formaldehyde (UF) Resin

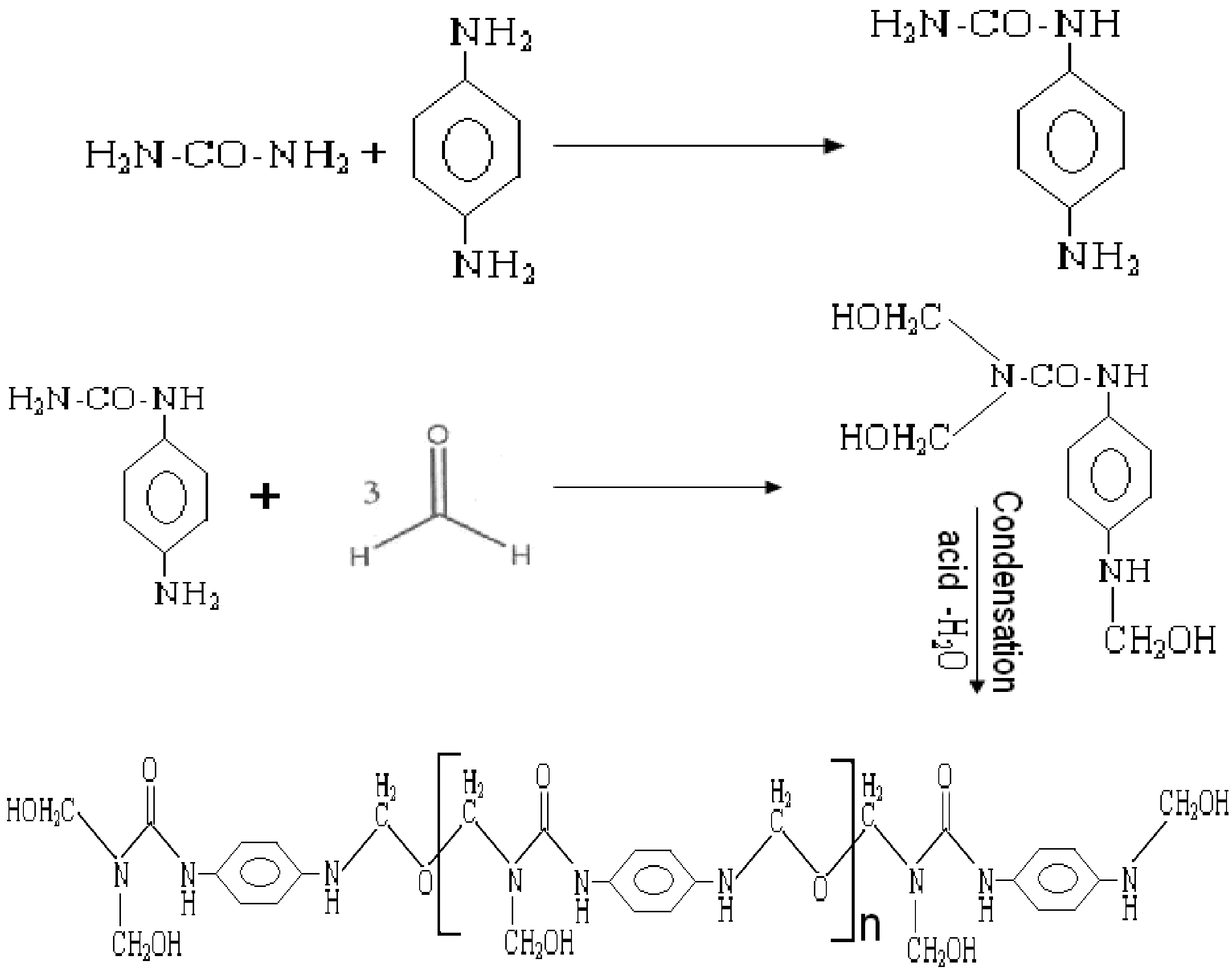
All UF resins used for this study were prepared in the laboratory. Three different procedures were used earlier under three pH conditions, i.e., alkaline, weak acid and strong acid. For the alkaline reaction, UF resins were synthesized according to traditional two-step procedure. The method involves formaldehyde (45%) was placed in the reactor and heated to 60°C and then the reaction was adjusted to pH 7.5-8 with urotropin (20% wt). Subsequently, urea was added in equal parts at 1 min intervals, and the mixture pH was adjusted to 4.5 with oxalic acid (20% wt), for the condensation. This product was cooled at room temperature and washed liberally with distilled water to remove impurities.



Scheme for synthesis of Urea-Formaldehyde (UF) Resin

Modified p-Phenylenediamine-Urea-Formaldehyde (PUF) Resin

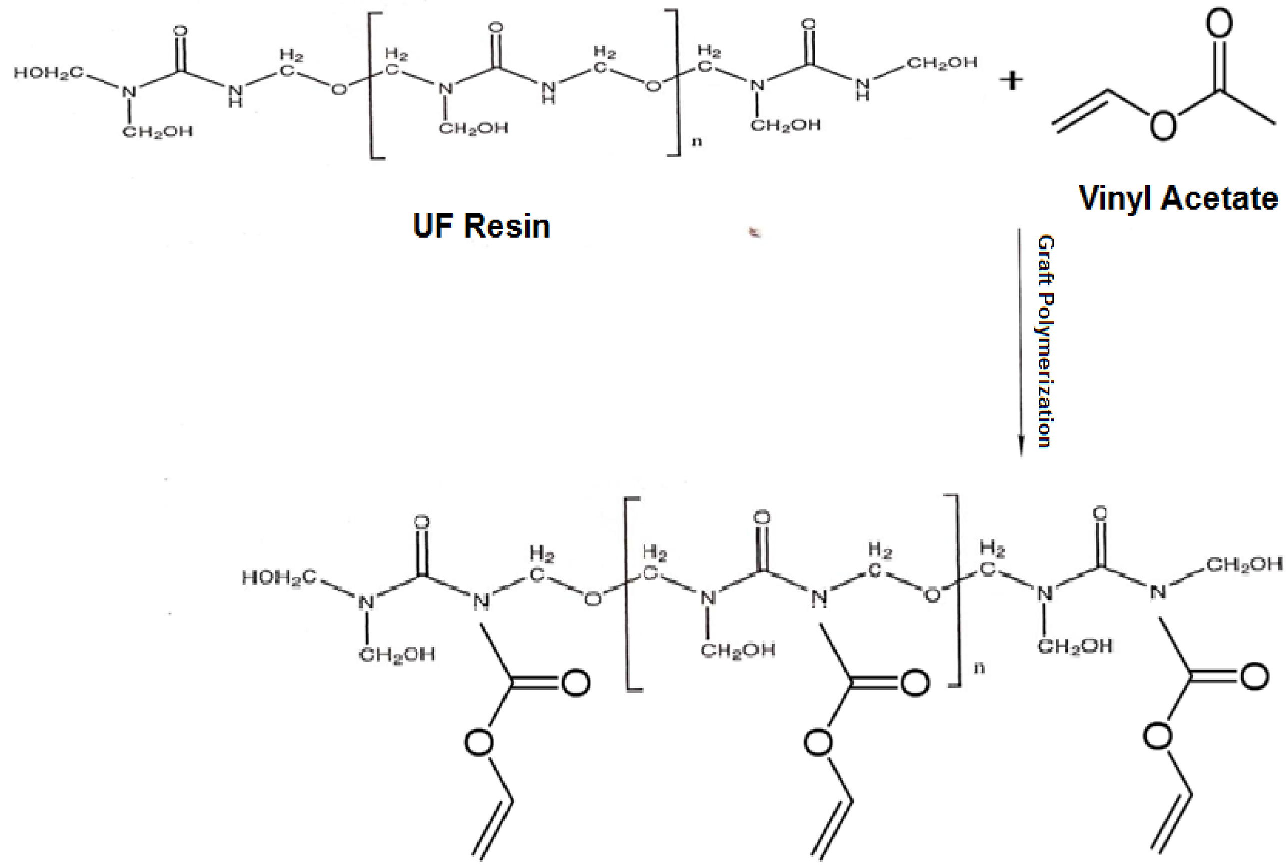
The required amount of formaldehyde was charged as an approximately 45% aqueous solution into a resin kettle previously heated to about 60˚C, and the pH was adjusted to 7.5 -8.0 with urotropin (20% wt). Then the modifier p-phenylenediamine was added slowly along with sufficient urea. In the urea and modifier solution the pH was adjusted to 7.5 – 8.0 with 20% of urotropin solution. The temperature was increased to 80-90^{0}C and the pH was adjusted to 4.5-5.0 with oxalic acid (20% wt) for the condensation. The mixture was cooled at room temperature and washed liberally with distilled water to remove impurities.



Scheme for synthesis of Modified Urea-Formaldehyde (MUF) Resin

Modification of UF Resin by Grafting with Vinyl Acetate

The prepared UF resin and azo-bis-isobutyronitrile (AIBN) [20% of UF resin] were dissolved in N,N-dimethylformamide(DMF) and vinyl acetate(VA) respectively . These two dissolved solutions were mixed in a reaction flask. After mixing, the resin-initiator solution appeared transparent. The transparent solution heated over waterbath at temperature 65^0C for 6 hrs. After heating, the solution becomes curdy. This grafted resin cooled to room temperature, decanted and washed several times with water.



Scheme of Grafted Urea-Formaldehyde (GUF) Resin

Characterization of Unmodified UF, Modified (MUF), Grafted (GUF) Resin

The infrared spectra were obtained on a Perkin Elmer Fourier Transform Infrared Spectroscope (FT-IR) BX Series using a KBr plate to identify the chemical structure of the sample. The specimen was prepared by coating the sample on the potassium bromide. The peaks appeared in FTIR spectrum as shown. The spectra of the unmodified , modified and grafted UF resins are almost identical and the peaks revealed could be attributed to the characteristic functional groups of the resins such as amide and C=O at 1650-1550 cm^{-1} and CH_2OH, CH_3 and CN at 1400-1360 cm^{-1}etc. The most characteristic difference between the unmodified UF resin and the modified and grafted UF resins were at the spectral area 3700-3000 cm^{-1}. The difference is due to the hydrogen bonding with the reactive functional groups such as CH_2OH, NH_2 and NH. The sharpening and the shifting at 3421.91 cm^{-1} of this band after grafted, indicate the formation of bonded NH group.

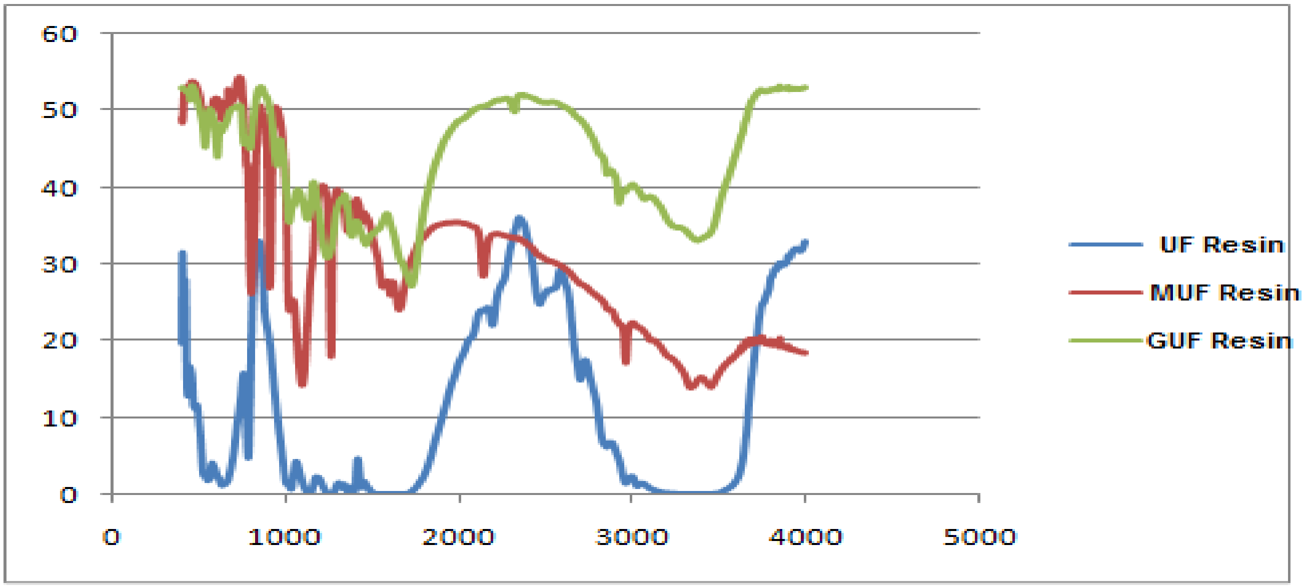


FIGURE 1. FTIR spectra Unmodified Urea-Formaldehyde (UF), Modified Urea-Formaldehyde (MUF) & Grafted Urea-Formaldehyde Resins in the region 400- 4000 cm^{-1}.

Antibacterial Activities of Unmodified, Modified and Grafted UF Resins

Evaluation of Antibacterial activity was done by the paper disc method by employing the Müller-Hinton agar (beef infusion, casein hydrolysate, starch, and agar) and 5 mm diameter paper discs of Whatman No.1. The compounds get dissolved in DMSO. The filter paper discs were soaked in different solutions of the compounds, dried and then placed in the petriplates previously seeded with the test organisms E.coli and S.aureus and are compared with antibiotic Gentamycin. The plates were incubated for 24-30 hours at 28 ± 2^{0}C and the inhibition zone around each disc measured.

Results of Antibacterial Activities of Unmodified, Modified and Grafted UF Resins

The data in table show zones of inhibition of the resins along with Gentamycin against the bacterium *S. aureus*, *E. coli*. Unmodified and modified Urea-Formaldehyde resins were found to be of weak activity against *S. aureus* and *E.coli.* Highest antibacterial potential was observed with grafted UF resin against both bacteria *S. aureus* and *E.coli.*

Plate A: Bacterial effect of unmodified, modified & Plate B: Bacterial effect of unmodified, modified & grafted UF Resin against *Staphyllococcus aureus* grafted UF Resin against *Eschericha Coli (E.Coli)*

(S. Aureus)

Compound	Conc. of Compound	Zone of Inhibition	
		Staphylococcus aureus	*Eschericha coli*
UF Resin	1000 ppm	0.0 mm	7 mm
MUF Resin	500 ppm	7 mm	7 mm
GUF Resin	250 ppm	10 mm	10 mm
Gentamycin (G)	120 mcg/disc	25 mm	25 mm

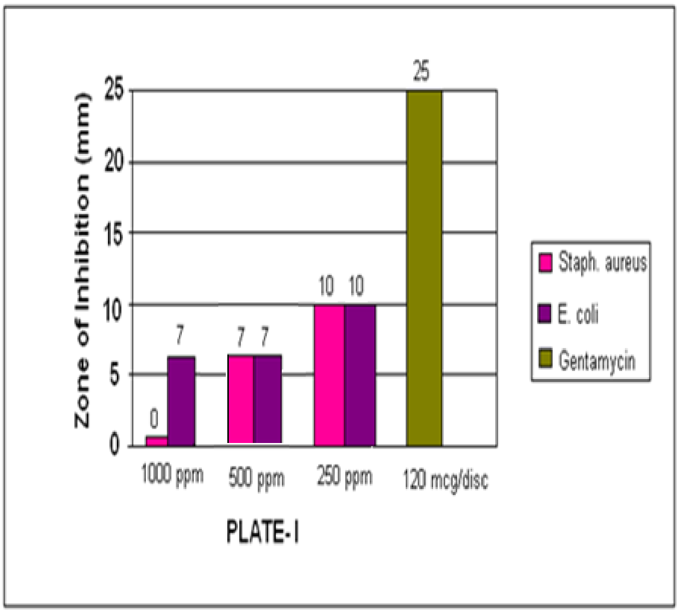


TABLE 1. Effect of concentration (ppm) of various resins on the size of inhibitory zone (mm) (mean of six replications) for various micro-organisms

Results and discussion

In previous work[16], formaldehyde was used to synthesize UF resin and the reaction was performed in aqueous solution. Here in order to improve the yield and the stabilization of UF resins, PPDA and VA were used as the modified and grafted UF resins. Figure 1 shows a comparison of FTIR spectra from 400 to 4000 cm^{-1} between unmodified, modified and grafted

UF resins. We have characterizes already these resins. All these changes of amine stretching vibration frequency indicate the formation of UF resin, which is consistence with previous work[17].

The spectra of the unmodified , modified and grafted UF resins are most identical and the peaks revealed could be attributed to the characteristic functional groups of the resins such amide and C=O at 1650-1550 cm^{-1} and CH_2OH, CH_3 and CN at 1400-1360 cm^{-1}etc. The most characteristic difference between the unmodified UF resin and the modified and grafted UF resins were at the spectral area 3700-3000 cm^{-1}. The hydrogen bonding with the reactive functional groups represent such as CH_2OH, NH_2 and NH[18]. The sharpening and the shifting at 3421.91 $cm^{-1}$of this band after grafted, indicate the formation of bonded NH group.

CONCLUSIONS: The work reported here focused on unmodified, modified & grafted UF resins and antibacterial activities by *S.aureus* and *E coli*. We observed the followings:

1. 1.Grafted UF resin by adding vinyl acetate directly attached to urea formaldehyde resin main chain and improved resin cure activity.
2. Unmodified UF resin was modified by p-phenylenediamine. The unmodified UF resin was less stable than modified UF resin.
3. Consequently, it can be inferred that affected zone of inhibition against the bacterium *S. aureus, E. coli* when compared with Gentamycin, the unmodified and modified UF resins are not much effective whereas grafted UF resin was observed of significant antibacterial potential.

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