Antibacterial Study of Melamine-Formaldehyde (MF), Modified MF and Grafted MF Resin

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ABSTRACT

Condensation product of melamine and formaldehyde is used in large amounts as resins and binders for industrial applications. Melamine-formaldehyde resins are more widely used. Coatings made with MF resins have better chemical resistance and demonstrate better exterior durability. In addition to the coating applications listed for UF resins, MF resins can be used in container, automotive, and appliance coatings. Even though MF resins provide better stain and water resistance in coatings versus UF resins, UF resins are used in wood coatings because they can be cured with little or no heat. They also are generally less expensive than MF resins. This paper incorporates initial results that have been achieved by modifying and grafting a MF 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 MF 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 property, Grafting, Melamine-Formaldehyde (MF) resin, Modification.

INTRODUCTION

Amino, or aminoplast, resins are an important class of cross-linkers for industrial coatings.[1–8] Amino resins are usually water-white, viscous materials that may contain added solvent to reduce viscosity for ease of handling. The first amino resins used in coatings were made from the reaction of urea or melamine with formaldehyde followed by butanol (either *n*- or iso-). They were essentially polymeric and therefore were offered at 50 to 60% solids in butanol/xylene mixtures. These have been commercially available for nearly 70 years.[9] In the polymeric age, it is essential to modify the properties of a polymer according to tailor-made specifications designed for target applications. There are several means to modify polymers properties, viz. blending, grafting and curing. 'Blending' is the physical mixture of two (or more) polymers to obtain the requisite properties. 'Grafting' is a method wherein monomers are covalently bonded (modified) onto the polymer chain, whereas in curing, the polymerization of an oligomer mixture forms a coating which adheres to the substrate by physical forces. Actually there is no time scale for the process of grafting which can take minutes, hours or even days, whereas curing is usually a very rapid process, occurring in a fraction of second. Graft copolymerization of vinyl monomers on to substrate polymers is generally considered to involve the generation of reactive sites on the polymer followed by the addition of monomer, which propagates in a conventional manner. This can be achieved by several methods, i.e. high-energy radiation[10], low-energy radiation in the presence and absence of sensitizers [11-12], and chemical methods [13-16]. Modification of protein by a number of chemical methods has been studied extensively. However in recent years attempts are being made to modify fibrous proteins by graft co-polymerization. Among fibrous proteins, collagen and polymers have received considerable attention. However, very little alten has been paid towards graft copolymerization onto polymer [17]. Graft copolymerization [18-24] on to polymers can be achieved by generating free radicals, on backbone of polymer, which are capable of initiating grafting.

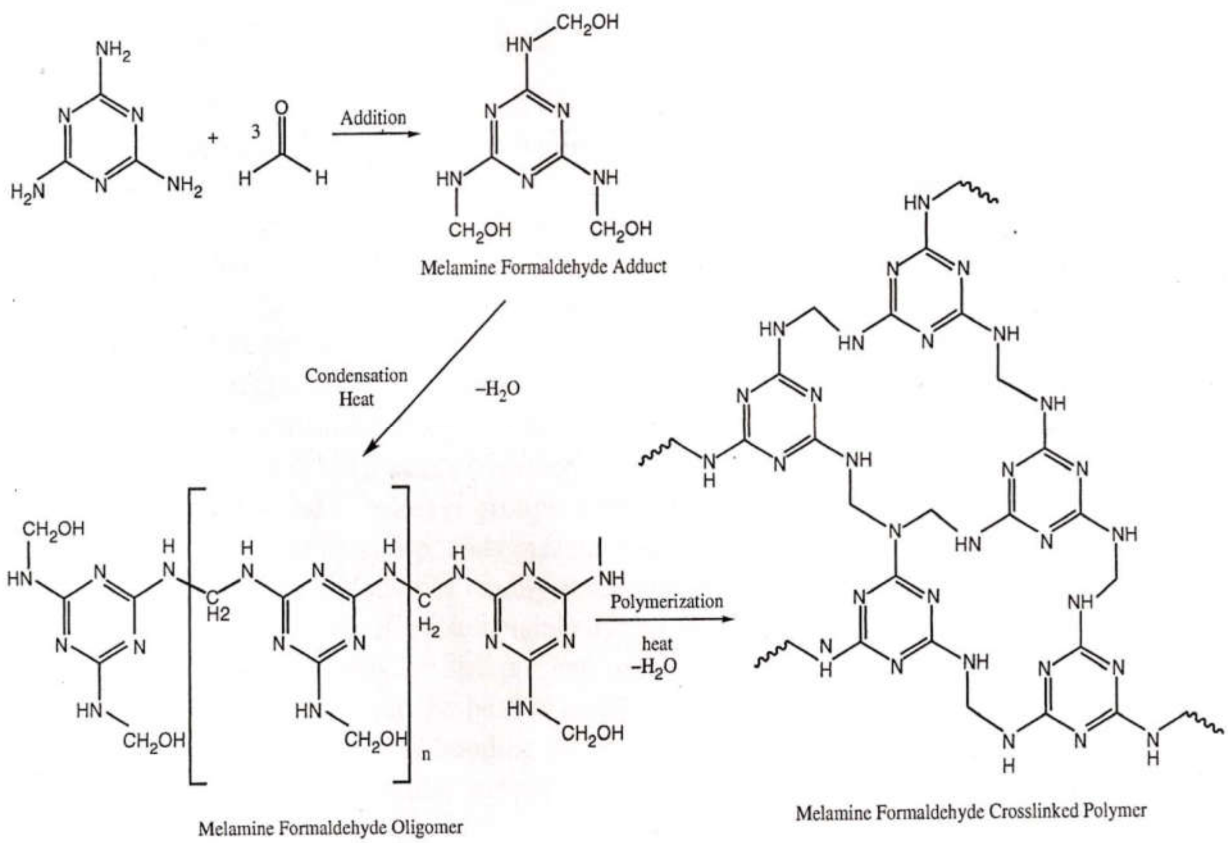
MATERIALS & METHODS

All chemicals and reagents were of analytical grade and used without further purification. Formaldehyde was purchased from Aldrich Chemical Co., Milwaukee, W.C. Melamine (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 Melamine-Formaldehyde (MF) Resin

All MF 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, MF 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 NaOH (10% wt). Subsequently,12.6 gm melamine was added and heated to boiling for 40 minutes 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 Melamine-Formaldehyde (MF) Resin

Modified p-Phenylenediamine-Melamine-Formaldehyde (MUF) 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 NaOH (20% wt). 12.6 gm melamine powder and 10-15% p-phenylenediamine (modifier) are added slowly in round bottom flask and heated to boiling for 40 minutes. In the melamine and modifier solution the pH was adjusted to 7.5 – 8.0 with 10% of NaOH 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.

Modification of MF Resin by Grafting with Methyl Acrylate

The prepared MF resin and azo-bis-isobutyronitrile (AIBN) [20% of MF resin] were dissolved in N,N-dimethylformamide(DMF) and methyl acrylate (MA) 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^{0}C for 6 hrs. After heating, the solution becomes curdy. This grafted resin cooled to room temperature, decanted and washed several times with water.

Characterization of Unmodified MF, Modified (MMF), Grafted (GMF) 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 MF resins are almost identical and the peaks revealed could be attributed to the characteristic functional groups of the resins such as amide, CH_2OH, CH_3 and CN at 1500-1340 cm^{-1}etc. The most characteristic difference between the unmodified MF resin and the modified and grafted MF 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.

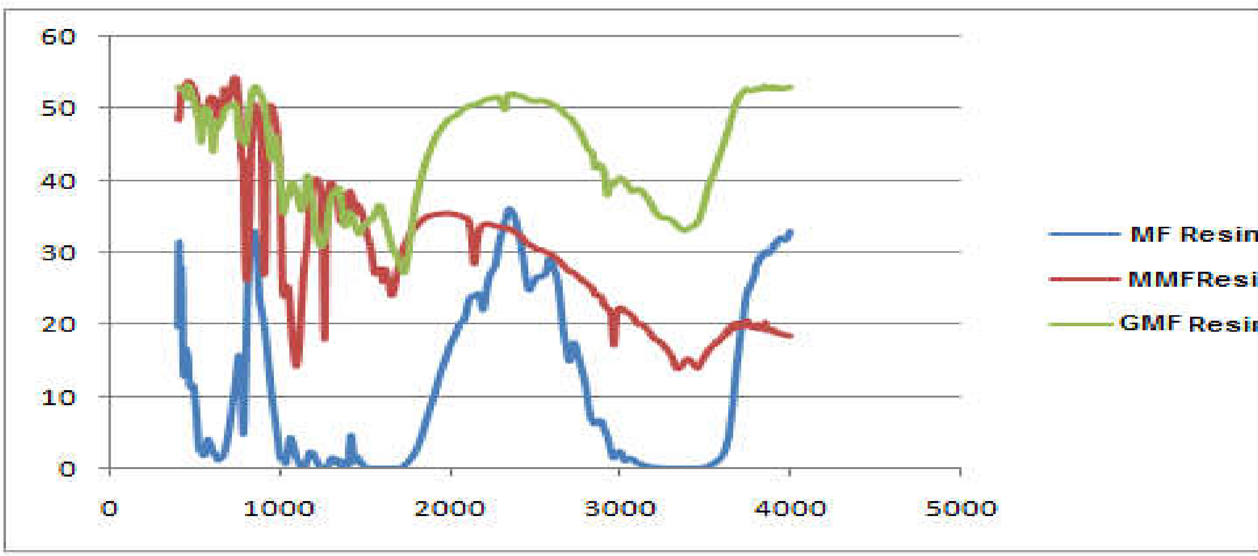


FIGURE 1. FTIR spectra Unmodified Melamine-Formaldehyde (MF), Modified Melamine-Formaldehyde (MMF) & Grafted Melamine-Formaldehyde (GMF) Resins in the region 400- 4000 cm^{-1}.

Antibacterial Activities of Unmodified, Modified and Grafted MF 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 MF Resins

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

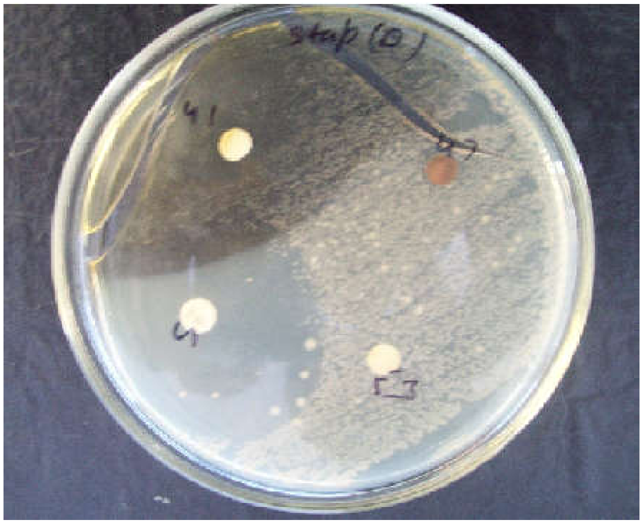


Plate A: Bacterial effect of unmodified, modified & grafted MF Resin against *Staphyllococcus aureus (S. Aureus)*

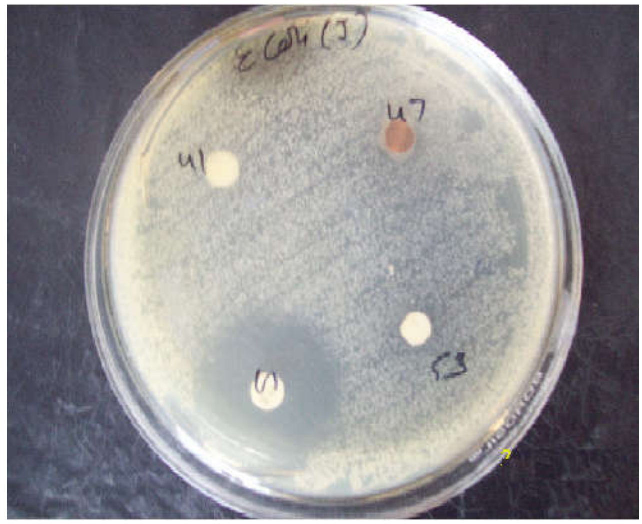


Plate B: Bacterial effect of unmodified,modified & grafted MF Resin against *Escherícha Coli (E.Coli)*

Compound	Conc. of Compound	Zone of Inhibition	
		Staphylococcus aureus	*Eschericha coli*
VP-41	1000 ppm	25 mm	0.0 mm
VP-47	500 ppm	0.0 mm	0.0 mm
VP-53	250 ppm	0.0 mm	7 mm
Gentamycin (G)	120 mcg/disc	25 mm	25 mm

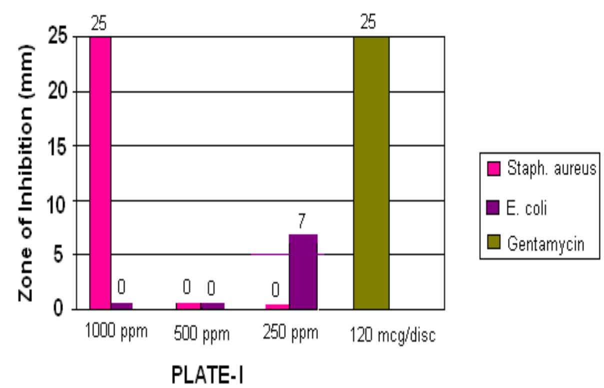


TABLE 1. Effect of concentration (ppm) of various resins on the size of inhibitory zone (mm) (mean of six replications) for various micro-organisms

Results and discussion

In previous work[25], formaldehyde was used to synthesize MF resin and the reaction was performed in aqueous solution. Here in order to improve the yield and the stabilization of MF resins, PPDA and MA were used as the modified and grafted MF resins. Figure 1 shows a comparison of FTIR spectra from 400 to 4000 cm^{-1} between unmodified, modified and grafted MF resins. We have characterizes already these resins. All these changes of amine stretching vibration frequency indicate the formation of MF resin, which is consistence with previous work[26].

The spectra of the unmodified , modified and grafted MF resins are most identical and the peaks revealed could be attributed to the characteristic functional groups of the resins such amide, CH_2OH, CH_3 and CN at 1400-1360 cm^{-1}etc. The most characteristic difference between the unmodified MF resin and the modified and grafted MF 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. 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 MF resins and antibacterial activities by *S.aureus* and *E coli.* We observed the followings:

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

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REFERENCES

1. *F.N. Jones and P.S. Ramchandran, Polym. Mater. Sci. & Eng., 77, 389 (1997).*
2. *D.E. Erickson and T.P. Golden, Paint & Coat. Ind., August, 50 (1995).*
3. *P. Swaraj, Ed., Surface Coating: Science and Technology, 2d ed. Chichester: John Wiley, 1997, pp. 861-865.*
4. *G.D. Vaughn, Paint & Coat. Ind., August, 58 (1998).*
5. *J. O. Santer, Prog. In Org. Coat., 12, 309 (1984).*
6. *Colak S, Colakoglu G (2004) Volatile acetic acid and formaldehyde emission from plywood treated with boron compound. Build Environ 39: 533-536.*
7. *Dessipria E, Minopoulou E, Chryssikos G, Gionis V, Paipetis A (2001) Use of FT-IR Spectroscopy for on-line monitoring of formaldehyde-based resin synthesis. Proceeding of the Fifth Panel Products Symposium, Landudno, Wales, 10-12 oct.*
8. *Kelly TJ, Smith DL, Satola J (1999) Emission rates of formaldehyde from materials and consumer products found in California homes. Environ Sci Technol 33, 81-88.*
9. *J.L. Williams and V. Stannell, Teintex, 10, 719, (1971).*
10. *H. Ishibashi and M. Oku, Proc. Int. Wool. Text. Res. Conf. Paris, See. III, (1965).*
11. *H.L. Needles and W.L. Wasley, Text Res. J., 39, 97, (1969).*
12. *M. Negish, K. Arai, and S. Okada, J. Appl. Polym. Sci., 11, 115, (1967).*
13. *A. Kantauch, A. Hebeish, and A. Bendak, Eur. Polym. J., 7, 153, (1971).*
14. *A. Bendak, A. Kantauch, and A. Hebeish, Kolarisztikai Ertesite, 13, 106, (1971).*
15. *P.L. Nayak, S. Lenka, and N.C. Pati, Angew. Makramol. Chem., 67, (1977).*
16. *M.K. Mishra, J. Macromol. Sci. Rev. Macromol. Chem., C19(2), 193, (1980).*
17. *P.L. Nayak, Ibid, C14(2), 193, (1976).*
18. *P.L. Nayak, S. Lenka, M.K. Mishra, J. Appl. Polym. Sci., 25, 63, (1980).*
19. *P.L. Nayak, S. Lenka, M.K. Mishra, Ibid, 26, 733, (1981).*
20. *S. Lenka, P.L. Nayak, M.K. Mishra, Angew. Macromol. Chem., 84, 183, (1980).*
21. *P.L. Nayak, S. Lenka, M.K. Mishra, Ibid, 90, 155, (1980).*
22. *S. Lenka, P.L. Nayak, M.K. Mishra, J. Polym. Sci. and Polym. Chem. Ed., 18, 22-47, (1980).*

23. *S. Lenka, P.L. Nayak, M.K. Mishra, J. Mishra, J. Macromol. Sci. Chem., A16(4), 843, (1981).*
24. *Dessipri E, Minopoulou E, Chryssikos GD, Gionis V, Paietis A, Panayiotou C (2003) Use of FTIR spectroscopy for on-line monitoring of formaldehyde based resin synthesis. Eur Polym J , 39 : 1533-1540.*
25. *Chris Tijanson P, Siimer K, Pehk T, Lasbn I (2002) Structural Changes in UF resins during storage. Holz Roh Werk 60: 379-384.*
26. *S S Jada, J App Polym Sci, 35,1988, 1573.*