DOI:10.7598/cst2019.1534
ISSN:2278-3458

Chemical Science Transactions
2019, 8(**1**), 36-42

RESEARCH ARTICLE

Synthesis of PUMF Resin for the Manufacture of Plywood

B. S. MAMATHA*, D. SUJATHA and D. N. UDAY

Scientist, Indian Plywood Industries Research and Training Institute, Post Box No 2273, Bangalore-22, India
mamatha@pirti.gov.in

Received 27 April 2018 / Accepted 15 May 2018

Abstract: Phenol urea-melamine formaldehyde (PUMF) resin adhesive was prepared by using phenol, urea and melamine in two different molar ratios. The effects of the molar ratio of formaldehyde, phenol, urea, melamine on performance of PUMF resin adhesive were studied. The resin developed was characterized by differential scanning calorimeter (DSC) and Fourier transform infrared spectroscopy (FTIR). Plywood was manufactured using the developed resin and bonding properties were evaluated as per IS: 848-2006. The results indicated that the plywood made using PUMF resin of the molar ratio (phenol: urea: melamine): Formaldehyde 1:0.79:0.38:2.15 at pH 9.0 yield best result. The studies indicate that the PUMF can be used make wood-based panels of boiling water resistant grade.

Keywords: Adhesive, Plywood, Phenol, Melamine, Urea, Spectroscopy

Introduction

In India, almost all exterior grade plywood is made with phenol formaldehyde (PF) resins. Many formulations are available which can satisfy a wide range of working and performance according to the demands of the users. PF resins require very high temperature with longer pressing time for curing than amino resins. And the dark brown color in the cured glue line is also a disadvantage of PF resin. Due to day to day rising cost of phenol, there is a need to substitute phenol to reduce the cost of the resin and which makes the resin lighter with reduced curing temperature.

Modification of PF resins with several different chemical groups has been tried to reduce or remove the drawbacks associated with PF resin. Few studies have been done to manufacture resin with replacement of phenol with material which is easily available and gives good bond quality. Addition of acid catalysts in PF resin systems to enhance the cure rate of PF resin was tried earlier but durability of the product were decreased due to accelerated hydrolysis of structural wood components[1]. Phenol melamine formaldehyde (PMF) resins have been synthesized by incorporating melamine in the PF resin system with the resin cured at lower temperature. PMF resins in combination with Urea Formaldehyde (UF) resins have been used for the manufacture of concrete form plywood[2] . Sidhu Avtar *et al.*,[3] evaluated that the resin PMF produced at a pH of 7.5 outperformed those resins produced at a pH of 9.0. Phenol modified melamine urea formaldehyde (MUF) resins have been used for the production of exterior grade particleboard and oriented strand board (OSB) in Europe. It was reported that the PMUF resin can reduce the content of free formaldehyde and can make wood-based panel with high water resistance and weather ability by Zhen *et al.*,[4] . Hence in this study urea and melamine was partially replaced for phenol in the manufacture of PUMF resin for plywood.

Experimental

Raw materials used for the resin manufacture were phenol (98.89%), urea and melamine (46% and 67% nitrogen content respectively), formaldehyde (36.85% by mass). Different molar ratios of phenol:urea:melamine:formaldehyde formulations namely A and D were manufactured by using the formulation as given in Table 1. The moles of formalin added on the total moles of amino and phenol has been tabulated.

Table 1. Raw material (in moles) used for the manufacturing of PUMF resin

Sample	Phenol	Urea	Melamine	Formalin
A	1	0.09	0.12	3.81
D	1	0.79	0.38	2.15

Manufacturing process of the resin and the plywood

Phenol, formalin and the required amount of caustic solution (33% w/w) to maintain pH 9.0 was charged into the kettle. After 10 minutes of stirring at 40 °C and 80 °C melamine and urea were added slowly and the temperature was maintained at 80 °C till precipitate formation was observed. The adjustments need to be made to maintain pH and temperature throughout the resin cooking. Urea and melamine were added once at 40 °C is termed as A1/D_1 respectively and the process where urea and melamine added at 80 °C is termed as A2/D_2 respectively. The resin was cooled when requisite water tolerance of 1:4 was achieved. After cooling to ambient temperature the resin was discharged and sample was taken to further check the properties of the resin at ambient temperature.

The PUMF resin was admixed with fillers/extenders and spreaded onto the veneers (silver oak) having a moisture content of 6%. Panels of 8ft x 4ft at pilot scale were manufactured. The adhesive formulation for various resin system and the pressing condition are as given in Table 2. Plywood was also made using PF and MUF resin as per the standard procedure. After hot pressing the panels were downloaded and stacked horizontally for a period of 24-48 h for stabilization. The panels were then trimmed to required size, conditioned before testing.

Resin characterization

The properties of resin such as viscosity, pH and solid content were determined and the values are tabulated in Table 2. The curing of these resins in DSC was examined using a TAQ1000. Prior to performing a DSC scan, the cell temperature was equilibrated at 25 °C and the samples including the reference pans were heated from 25 °C to 200 °C at a constant rate of 10 °C/min using nitrogen as a purge as at a flow rate of 50 mL/min.

The sample chamber of FTIR was continually purged with nitrogen while the spectra were obtained. The IR spectra of PUMF-A was carried out using liquid resin**.** The IR spectra of PUMF-D, PF and MUF are of partially cured samples. The spectra obtained are given in Figure 1-4 respectively.

Table 2. Adhesive formulations and pressing parameters used for the manufacturing of boards

PUMF resin	100 parts
GNCP	4 parts
Maida	4 parts
Species	Vellapine, Poplar, Silver oak
Construction	5 ply
Moisture content of veneer before coating	6% - 8%
Glue spread	300-340 g/sqm
Open assembly time	30-60 min.
Moisture content of glued veneers before pressing	14% - 16%
Hot press temp	140 ± 1 °C
Sp. Pressure	14-16 kg/cm^2
Pressing time	3 mins + thickness

Testing of plywood

For each of the plywood made the samples were subjected for testing to find the wood failure values as per IS: 848-2006 (Specification for synthetic resin adhesives)[1]. The test condition for BWR GRADE (Boiling water resistant) consists of three cycles. Each cycle consisting of 8 hours boiling in water and thereafter drying at 65±2 °C for 16 hours. After the completion of three cycles the percentage wood failure of samples were visually observed and recorded in Table 3.

Results and Discussion

PUMF resins with different formulations were manufactured to study the bonding properties of the resin suitable for the manufacture of plywood. PUMF resin cooking of any molar ratios was found very sensitive to both the temperature and the addition of alkali percentage. Accordingly proper control of the resin cooking conditions and time, to achieve the desired viscosity were optimised. Monitoring of the resin was done at every stage as the reaction is found to be very sensitive to pH as well as for the temperature due to the addition of two different moiety amino and phenolic group. It was observed that resin batch (A), requires more percentage of alkali than resin batch (B). Mole percentage of Amino group is more than phenol hence the percentage of alkali requirement was less so as to maintain the pH 9.0 in Resin B. All the PUMF resin successfully synthesized showed lower viscosity than comparing to the conventional phenolic and amino resins as displayed in Table 3. Even after cooking the resins for longer time, viscosity could not be developed ultimately leading to the failure of the resin. Hence water tolerance of 1:4 at hot conditions was kept as criteria to determine for stopping the reaction which would give a water tolerance of 1:2.5 in cold condition at 25 °C. The properties of the resin were as tabulated in Table 4.

As the specific gravity of the resin was very low, it necessitated to add the extenders to get requisite viscosity of the adhesive so as to achieve good bonding. Adhesion of an adhesive depends on the viscosity of the resin, if the resin is very thick, penetration of the resin will not takes place leading to starved joint. At the same time if the viscosity of the resin is very thin, resin penetrates to the cell cavities leading to starved joint. Hence the required viscosity of the resin was improved by the addition of groundnut cake powder and Maida during the adhesive formulation. The resin solids of all the formulations were approximately 50%.

Table 3. Bond quality of plywood

Test	Results					
	D1	D2	A1	A2	PF	MUF
Wood failure	80% Good bond	85% Excellent Bond	60-70 % Pass standard	50 % Pass standard	90-95% Excellent Bond	20% Failed

Table 4. Properties of resin

S. No.	Particulars	A1	A2	D1	D2	PF	MUF
1	Solid content %	49.86	50.11	50.19	50.43	48.91	51.86
3	pH of the resin	8.92-9.0	8.92-9.0	8.92-9.0	8.92-9.0	9.81	9.0
4	Flow time (s)	16-18	16-18	16-18	16-18	22	19
5	Free formaldehyde	0.58	0.51	0.52	0.63	0.71	1.01

Spectroscopic study

Figure 1-3 are the dried resin samples; Figure 4 is the spectra of liquid resin. Figure 3, 4 shows the spectral of PUMF resin made using different proportion of phenol and amino group. The IR spectra of PF resin is as shown in Figure 1. The peak at 3459 cm^{-1} is of OH^{-}, at 2890 cm^{-1} is in phase stretching vibration of CH_2 alkane. 2824 cm^{-1} is out of phase stretching vibration of-CH_2-alkane, 1627 cm^{-1} is of C=C aromatic ring, 1467 cm^{-1} is of C-H aliphatic, 1230 cm^{-1} is asymmetric stretch of phenolic C-C-OH, 1150 cm^{-1} and 1007 cm^{-1} was of C-O stretch asymmetric stretching, aliphatic hydroxyl, NCN stretching of methylene linkages, 864 cm^{-1} CH out-of -plane, isolated H, 762 cm^{-1} is CH out of plane, ortho substituted[5]. In the spectra of MUF resin the peak at 3367 cm^{-1} is due to an NH stretching of primary aliphatic amine. Bands at 1560 cm^{-1} and 1671 cm^{-1} peak indicates the C=O stretching of primary amide C-N stretching of secondary amines. 812 cm^{-1} indicates triazine rings[6]. In the Figure 3, the peak at 3320 cm^{-1} is due to an NH stretching of primary aliphatic amine. Sharp and long bands at 1503 cm^{-1} and 1600 cm^{-1} peak indicates the shifting of C=O stretching of primary amide C-N stretching of secondary amines. Stable triazine rings at 812 cm^{-1} indicates the behavior of resin much as amino resin than as phenolic resin. The spectra of Figure 4, the peak at 3410 cm^{-1} is of OH indicating the presence of phenolic group and shows C-H aliphatic at 1482 cm^{-1}. A very small peak at 1160 cm^{-1} of C-O stretch asymmetric stretching was lowered and aliphatic hydroxyl shifted to 1006 cm^{-1}, peak at 1655 cm^{-1} indicating the NH stretching of primary aliphatic amine without change in band was observed, -O-CH_3, aliphatic ethers and C=O stretching of primary amide respectively. The absorption peaks at 1560 cm^{-1} of C-N stretching of secondary amines was narrowed and C-H mode in CH_2 and CH_3 respectively slight decreased the band at 1360 cm^{-1}. C-O stretching of aliphatic ether at 1163 cm^{-1} is almost negligible. 812 cm^{-1} of triazine ring structure was reduced to 803 cm^{-1}. It is assumed that in PUMF resin, the triazine rings might be connected by di methylene ether bridges hence have shown lower proportion of di methylene ether bridges indicating the mole proportion of phenol more than melamine in the resin. Spectra of Figure 3 and 4 indicates the presence of peaks that were present in the individual PF and MUF resin spectra as well as additional peaks possibly pertaining to the co condensed resin.

The IR can give only the qualitative indication of the structure of the resin. From the spectra it clearly indicates that the amount of co-condensation in these resins is possible. As many wave lengths were overlapped, the linkages between phenol, urea, melamine and formaldehyde could not exactly deduce. But it clearly indicates that the resin reactivity is very complex which may need other instrumental study for the co-condensation in the resin.

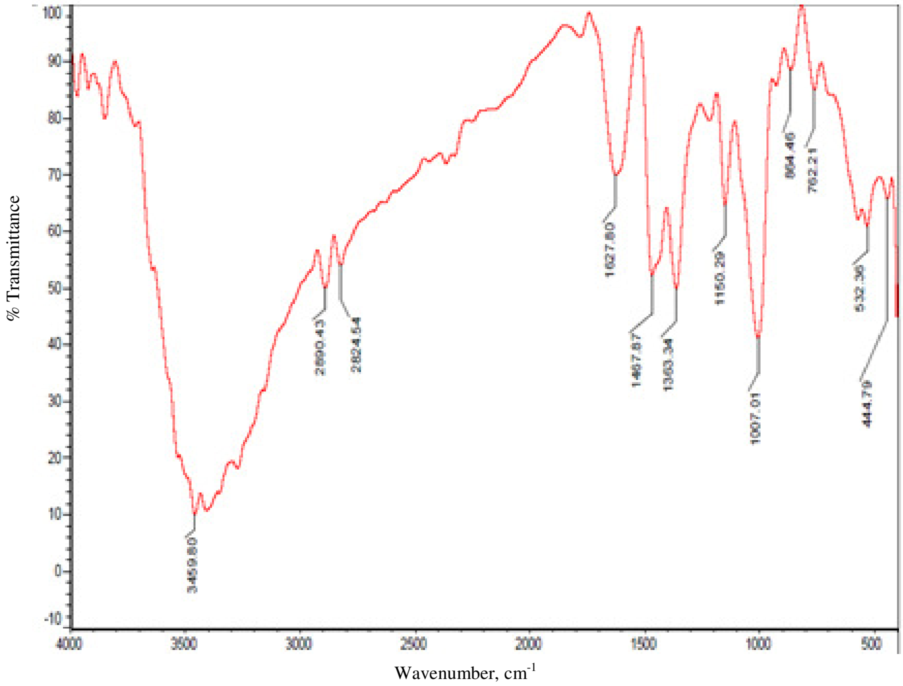

Figure 1. IR spectra of PF resin

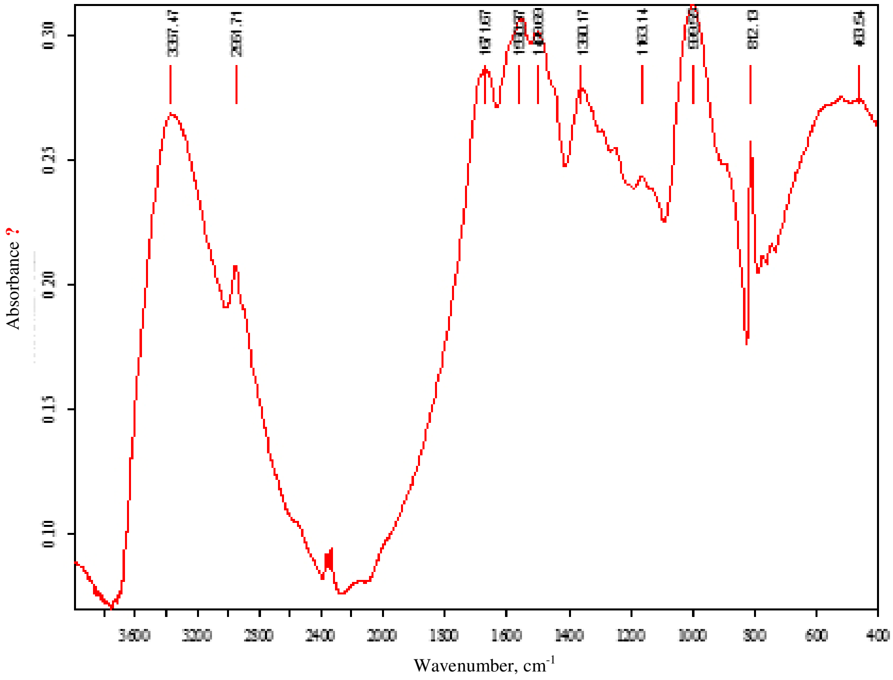

Figure 2. IR spectra of MUF resin

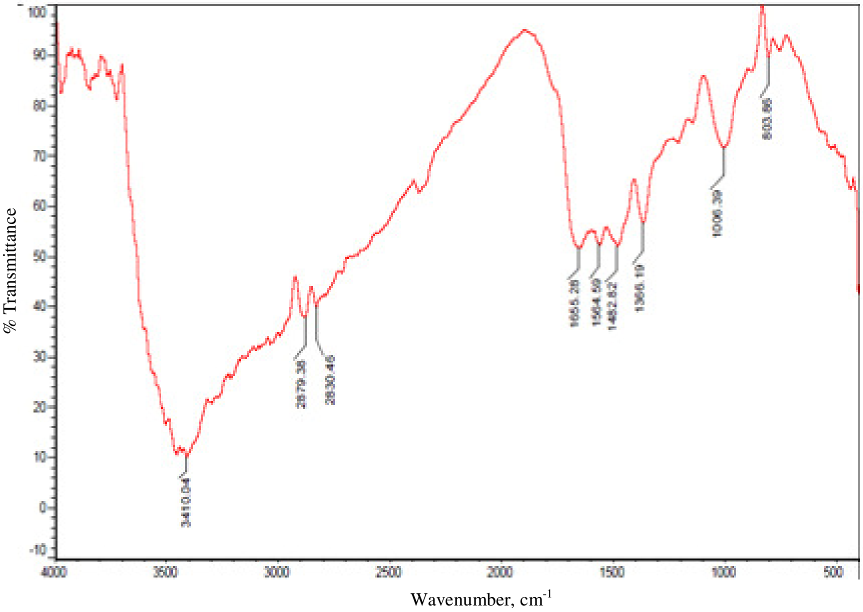

Figure 3. IR spectra of PUMF resin A

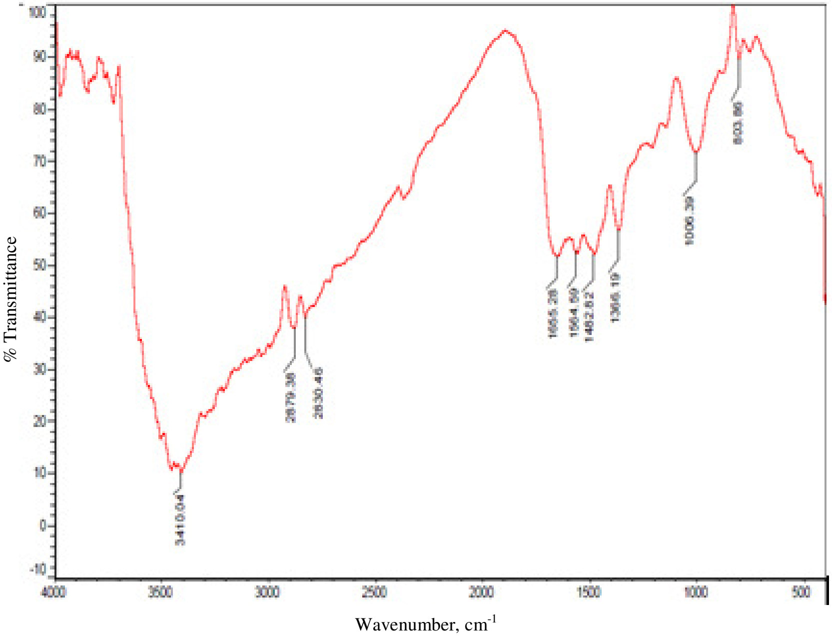

Figure 4. IR spectra of PUMF resin D

Curing characteristics of the resin

The maximum peak is the indirect indication of cure temperature. The peak temperature of the PUMF resins was (139 ^{o}C) were higher than the MUF resin (131 ^{o}C) and slightly lower than the PF resin (149 °C). The copolymerization that occurs between the methylols of phenol urea and melamine would have influenced in the resin curing at lower temperature. The heat of reaction of PF and MUF resin was 158.6J/g and 98J/g. However the heat of reaction of PUMF resins were in the range of 102-110 J/g indicating crosslinking density was inferior to PF resin.

Bond quality of the plywood

The plywood made at plant scale of 8ft by 4ft was subjected for testing for BWR grade. All the panels were so intact that no separation of plies at the edges and/or surface at the end of three cycles was observed. From Table 3, it can be observed that all the boards except the plywood made using MUF resin satisfy the requirements as per IS: 848-2006 for BWR grade. However Plywood made using PUMF resin has showed lower wood failure than conventional PF resin. Though copolymerisation would have occurred, the bonding of wood adhesive depends on the amount of methylene ether bridges formed rather than on the amount of copolymerisation occurred. It can be noticed that the formulation D has shown excellent bond properties than the boards made using A formulations.D2 has shown 85% wood failure with D1 of 80% wood failure.A1, A2 has shown a pass standard of 50-70%. This shows that the ratio containing molar percentage of amino group more than number of moles of phenol have given better bonding properties.

Conclusion

PUMF resin were manufactured were found to be of low viscosity, light coloured with low formaldehyde .The resin formulation with the molar ration of phenol and amino together to formaldehyde of 1:2.15 was the best suitable to satisfy the properties of plywood as per IS: 848-2006.It can be concluded that single stage PUMF resin can be successfully manufactured at plant scale. The boards manufactured at plant scale satisfy the properties as per IS: 848-2006 for BWR grade.

References

1. Clad W and Schmidt-Hellerau C, Particleboards for the building Industry: Performance and Suitability Test. Proc. 11th WSU Particleboard Symp., Pullman, Washington, 1977, 33-61.
2. Gao Zhenzhong, Liao Feng, Deng Shibing and Zheng Zhenjie, *Scientia Silvae Sinicae*, 2009, **45(8),** 124-128; DOI:10.11707/j.1001-7488.20090822
3. Ida Poljanšek and Matjaž Krajnc, *Acta Chim Slov.,* 2005, **52,** 238-244.
4. Pizzi A, Advanced Wood Adhesives Tech. Marcel Dekker, Inc: New York.1984, 67-87.
5. Sidhu, Avtar S, Ellis and Simon C, *Forest Prod J.,* 2007, **57(10),** 58-63.
6. Tamura Y, Yamada T, Hasegawa Y and Fukazawa A, *Mokuzai Kogyo*, 1981, **36(42),** 315-320.