Improving Indoor Air Quality: Using Polymate-777A as a formaldehyde scavenger to Decrease Formaldehyde emission in Plywood Panels.

Abstract

Formaldehyde emissions from wood composite products is a big concern for the environment and people's health. This study focused at how effective a product called Polymate-777A, the additive used as a formaldehyde scavenger is in reducing the formaldehyde emissions from plywood. This study was carried out by taking different concentration of Polymate-777A with urea formaldehyde resin for manufacturing of plywood. The study was also checked how Polymate-777A affected the properties of this resin, like its viscosity and gel time etc. The study also carried the mechanical properties and formaldehyde emission of the plywood made by using Polymate-777A . The Results revels that when 1.5% or more Polymate-777A was used as scavenger for plywood manufacturing, the plywood met the emission standards set by Japan and Europe for formaldehyde emissions. This study suggests that using Polymate-777A could be a good way to reduce formaldehyde emissions from wood products, which would be better for the environment and people's health.

Keywords: wood composite products, Formaldehyde emission, environment and people's health, Polymate-777A. Emission standards.

1. INTRODUCTION

Low cost and proven performance have made urea formaldehyde (UF) resins the most important wood adhesives for interior applications. However, the formaldehyde emission from UF-bonded wood products has been recognized as a potential source of indoor air pollution leading to inhabitant discomfort and possible health problems. The practical concern over formaldehyde emissions has elicited a great deal of research since the 1970s. Recent studies" stipulate these major sources of formaldehyde emission from UF-bonded wood products are (1) starting material as formaldehyde in the UF resins; (2) liberated formaldehyde during the condensation reaction between methylol groups; and (3) emitted formaldehyde from the hydrolytic degradation of the cured resin. Over the past two decades, great progress has been made in improving the formaldehyde emission from such wood products as particleboard, hardwood plywood, and medium-density fiberboard. Beneficial steps have included reducing the formaldehyde/urea (F/U) molar ratio, synthesizing UF resin with acidic catalysts without first using an alkaline catalyst, (6) impregnating the wood furnish with a formaldehyde scavenger: and treating boards with formaldehyde scavengers or a barrier coating (or both) after manufacture. The effect of the UF resin hydrolysis on formaldehyde emission from boards is not a trivial one, despite this practical progress.

The production of particleboards (PB) and medium density fiber boards (MDF) consumes a large fraction of UF resins produced worldwide. The industrial success of these resins can be attributed to their high reactivity, excellent adhesibility to wood and affordibility (Dunky,1998). In 1992, the California Air Resource Board (CARB) identified formaldehyde as a toxic air contaminant (CARB, 1992). In 2006 the International Agency for Research on Cancer (IARC) reclassified formaldehyde from "probable human carcinogen" (Group 2A) to "carcinogenic to humans" (Group 1), aimed at compelling producers to reduce formaldehyde release to lower levels (IARC, 2004; SCOEL, 2016). Formaldehyde emission from wood-based panels is debased on several external (exogenic) and internal (endogenic) factors.

Many countries have enacted strict regulations to address the environmental and human health concerns stemming from formaldehyde emissions in finished wood-based panels (Ulker et al., 2021). Various studies and reviews have explored methods to mitigate formaldehyde emissions, with the most effective approach involving the use of formaldehyde scavengers, also known as formaldehyde catchers (Bertaud et al., 2012; Mantanis et al., 2018; Hemmilä et al., 2019). These scavengers, chemicals capable of bonding with free formaldehyde, can be applied post-production or incorporated into the resin during mixing to reduce emissions

In this work two commercial scavenger named Polymate-777A andPolymate-777P supplied by Patina Chemicals was studied its effectiveness and potential of scavenging properties of formaldehyde scavenger as well as bonding and mechanical properties and hence its suitability as a scavenger for wood composite products.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Technical-grade urea granules (99%), formaldehyde (37% HCHO), Phenol (99%), formaldehyde (37%), Sodium hydroxide (96%), and aqueous solutions of both formic acid (HCOOH) and sodium hydroxide (NaOH) were used for the synthesis of UF resins. Wood veneer used for manufacture of plywood belongs to Eucalyptus as core and Gurjan as face veneer.

2.1.2. Scavenger (Polymate-777A)

Polymate-777P is a commercial brand additive used as a formaldehyde scavenger supplied by M/S-Patina Chemicals, Kolkata, India. This scavenger is formulated by mixing some speciality chemicals to achieve the E_1 and E_0 emission levels of the wood-based composite board manufactured by Phenol formaldehyde resin.

2.2. Methods

2.2.1. Physical and chemical properties study of the scavenger: -

The physical and chemical properties like colour, odour,solubility, pH, moisture content, solid content, chemically compatibility with the resin was tested .

2.2.2. Urea Formaldehyde (UF) resin manufacturing: -

500 gms formalin (formaldehyde content 37%) was taken in a three necked round bottom flask and made alkaline with 50% sodium hydroxide solution to pH 7.5-8.0. 200gmsof urea was gradually added to the three necked round bottom flask and stirring started. Stirring continued till the reaction ends. Temperature was raised by heating and then maintain temperature at 92±2ºC and keep at this temperature under agitation for 2 hours. pH was checked time to time and maintained at 7.5-8.0. In the second stage,50% solution of formic acid was added to maintain the pH to 5.0-5.5 and continue the reaction under agitation at the same temperature. The progress of the reaction was followed by measurement of flow time and water tolerance. When the flow time in B_4 flow cup is 13-14 secs and water tolerance 1:5 or 6 then pH was adjusted to 8.0 to 8.5 by adding 33% caustic solution and cooling was started. Pre-mixedPolymate-777A and water at a proportion 1:1was added @ temp. 75-80^{0}C and continue the cooling. Second urea 15gms was added @60^{0}C, cooling continued up to 40^{0}C and maintain the pH 8.0-8.5 by adding caustic solution. The above resin was kept overnight for conditioning. The synthesized urea formaldehyde (UF) resin was taken for plywood manufacturing, shelf life, free formaldehyde determination and other properties. The Urea formaldehyde resin was prepared in above procedure by using scavenger Polymate-777A at various concentrations starting from 0.0%,0.5%,1.0%,1.5%,2.0% and 3.0% of total resin named as UF_0, UF_1, UF_2, UF_3, UF_4, $UF_5$and UF_6.

2.2.3. Manufacturing of Plywood

Plywood with a size of 600mm×600mm×9mm was manufactured by using eucalypatus.as core and gurjun as face veneer and by using UF. The amount of glue spread used was appx.280-300 g/m^2 for manufacturing 6mm plywood. The plywood was hot-pressed at 110-115°C for UF and 11-12 kg/cm^2 specific pressure for UF_0, UF_1,UF_2 ,UF_3,UF_4,$UF_5$and $UF_{6,}$.Two numbers of ply board samples having dimension 600mm×600mm×9 mm were prepared for each concentration to carry out the expt. Total 24 numbers of samples were prepared to design the expt.

Table 1 The concentration of Polymate-777A adopted for the experiment.

Treatments	Scavenger Concentration (%)
UF0	0.0
UF1	0.5
UF2	1.0
UF3	1.5
UF4	2.0
UF5	3.0

2.2.4. Properties of Resin

The prepared resins were characterized according to gel time, solids content, viscosity, and free formaldehyde *etc.*

Table. 2: Typical glue formulation and panel manufacturing parameters

----

Resin:	200parts
Wheat flour:	16parts
Hardener:	0.8parts
Liq. Ammonia:	1.6 ml
Veneer Moisture:	6-8%
Spread Rate:	2.8- 3.0 m^2/kg
Open Assembly Time:	30 minutes
Pressing Temperature:	110 ±5^0C
Specific Pressure:	12-14 kg/cm^2
Pressing Time:	12minutes for 9 mm plywood.

2.2.5 Viscosity: -

A shift in glue viscosity can have significant ramifications on glue spreader rates. Glue with high viscosity poses challenges in spreading and results in excessive glue application, which is unfavorable both in terms of quality and cost-effectiveness. Viscosity serves as a crucial indicator for evaluating the polymerization progress and extent of resin, whether in manufacturing or application. Within the plywood industry, the viscosity of adhesive is typically assessed using a standard flow cup. This study utilized the B6 (IS:3944-1982) flow cup to analyze the flow time of the adhesive mix and the B4 cup for the resin.

2.2.6 Solid content: -

A resin sample weighing between 3.0 to 5.0 grams was placed into an evaporating dish (W1), and its exact weight was recorded (W2). The sample was evenly dispersed throughout the dish and then subjected to drying in a hot air oven set at 105°C for a duration of 3 hours. Subsequently, the dried sample was transferred to a desiccator to cool down to room temperature. The dish containing the dried resin was then weighed (W3). The percentage weight by weight of the resin's solids content was determined using the following simple relation

:% solid content = W3-W1(g) x 100/ W2(g) .

2.2.7. Measurement of gelation time: -

About 5 gm of the resin mix was placed into a test tube and a thin wire spring was placed in the tube to manually mix the contents. The test tube was placed in an oil bath at constant temperature of 100 and 120^0C and the container were mixed until liquid resin transferred to gel. The gelation time was recorded.

2.2.8 pH-value - The pH is monitored automatically in a pH meter.

2.2.9 Free Formaldehyde content of resin

A solution of 50ml of 1 mole of pure sodium sulfite was prepared in 500ml flasks. Thymolphthalein indicator was added with care, about 3 drops, and the mixture was meticulously neutralized by titration using 0.1N hydrochloric acid until the indicator's blue color vanished. To this solution, 5 grams of the resin sample was added along with crushed ice to maintain the temperature. The resultant mixture was titrated with 1N hydrochloric acid until complete decolorization was achieved. The percentage of free formaldehyde (%CH2O) content was calculated using the formula:

%CH2O = [Net ml. of acid X Normality of acid X3.0]/(weight of sample)

The free formaldehyde content of the resin was analyzed for all six samples with varying concentrations, in addition to the control sample UF0, UF1, UF2, UF3, UF4, UF5, and UF6.

2.2.10 Measuring Formaldehyde emission

Perforator method

The formaldehyde emission perforator value was assessed using the DIN EN 120 method (European Committee for Standardization, 1991). Initially, approximately 110 grams of the test piece were precisely weighed to an accuracy of 0.1 gram and deposited into a round-bottom flask. Subsequently, 600 milliliters of toluene were added to the flask. In the perforator attachment, one liter of distilled water was placed and brought to a boil. The boiling toluene was then passed through the distilled water for a duration of two hours. During this process, the distilled water effectively absorbed the formaldehyde and other volatile organic compounds (VOCs) stripped by the boiling toluene. The formaldehyde trapped by the water was subsequently quantitatively determined utilizing a UV spectrophotometer after treatment with acetyl acetone and ammonium acetate solution at 412 nanometers.

Fig:-1 1Perforator equipment setup used in EN 120 method

2.2.6.1 Desiccators' method

The measurement of free formaldehyde emission was conducted using the desiccator method outlined in the standard JIS A 1460:2015. This test aims to quantify the amount of formaldehyde emitted from plywood samples and absorbed within a specified volume of distilled water over a 24-hour period in a glass desiccator.

To begin the test, ten test pieces of each plywood type were prepared, each measuring 150 ± 1 mm in length and 50 ± 1 mm in width, alongside a blank sample. These samples were then placed within a desiccator with a sealed volume of 11 liters, which contained a glass-crystallizing dish holding 300 mL of distilled water.

After the 24-hour period elapsed, the samples were removed from the desiccators. The formaldehyde solution obtained from the distilled water was then prepared for spectroscopic analysis.

Figure. 2 Apparatus of desiccator set up testing, according to JIS A 1460

2.2.7 **Evaluation of plywood properties: -**

The plywood properties, including glue shear strength in both dry and wet conditions, modulus of rupture (MOR), and modulus of elasticity (MOE), were evaluated according to IS 1734:1983 standards. Each plywood sample underwent testing to assess its water resistance properties in accordance with IS 848-2006 specifications, applicable to both MR and BWP grades of synthetic resin adhesives.

3 RESULT AND DISCUSSION

3.1 Typical properties of Polymate-777A andPolymate-777P

The physical and chemical properties of the additives Polymate-777A and Polymate-777P were assessed in accordance with IS 1508:1972 standards. The results indicated values within the acceptable criteria, demonstrating satisfactory performance. Furthermore, during manufacturing, Polymate-777A and Polymate-777P were found to be compatible with both amino and phenolic resins, without causing any adverse effects on the resin's qualities.

Table 3: Typical properties of Polymate-777A

Appearance: -	White free flowing powder
Odour: -	Characteristic. (Slight.)
Solubility: -	Soluble in water
pH (10%) :-	6 -7
% Ash content; -	<3.0
Flammability: -	Non-flammable.
% Solid: -	> 95

3.2 Effect of scavenger on resin properties: -

Based on the results, it was noted that there were no notable alterations in viscosity and solid content. However, there was a decrease in the gel time of the resin as the concentration of scavenger load increased, impacting the curing kinetics of the urea formaldehyde resin. Additionally, the free formaldehyde content of the resin decreased in all cases compared to the reference sample without scavenger. This reduction in formaldehyde content suggests that both the formaldehyde content and emission of the wood composite board will also decrease. Figure. 3 Scavenger concentration of free formaldehyde UF and PF resin

Table.4 Typical properties of resin (Urea Formaldehyde resin)

Sample name	Flow time (S)	Solid content (%)	Gel time (S)	pH	Free formaldehyde (%)
UF0	19	46.8	79	6.56	1.62
UF1	20	46.4	76	6.61	1.42
UF2	20	46.7	74	6.62	1.08
UF3	21	46.8	68	6.63	0.76
UF4	19	47.1	62	6.72	0.66
UF5	22	46.9	60	6.71	0.52

Mechanical Properties and bond quality: -

The static bending properties of the plywood board exhibit improvement with increasing scavenger concentration. The highest modulus of rupture (MOR) was observed in specimens with scavenger concentrations ranging from 0.5 to 3 wt% in the plywood board. Specifically, the MOR increased from 54.62 N/mm² to 58.61 N/mm² as the scavenger amount increased from 0.5 to 3%, and from 36.21 N/mm² to 39.16 N/mm² for PF and UF resin, respectively. However, no significant increase in MOR was observed when the scavenger concentration increased from 0.5 to 3.0%.

Regarding mechanical properties, the addition of scavenger noticeably enhances bond quality, as evidenced by the result of the glue shear strength (GSS). The GSS strength of the specimens remained above the minimum standard requirement. Additionally, results demonstrate that all resin-bonded plywood boards passed the standard during cyclic tests conducted according to MR and BWP grade specifications outlined in IS 848:2006. Fig. :-4 Mechanical properties of the plyboard

Table. 5 Urea Formaldehyde resin

Sample name	MOR Along (N/mm^2)	MOR Across (N/mm^2)	MOE Along (N/mm^2)	MOE Across (N/mm^2)	GSS (N) (Dry)
UF0	36.21	25.18	4518	2811	1128
UF1	37.18	26.11	4602	2861	1168
UF2	37.92	26.86	4611	2901	1206
UF3	38.16	27.11	4625	2972	1244
UF4	38.88	27.32	4688	2996	1272
UF5	39.16	27.86	4711	3011	1301

Tab. :-6 Resistance to water test (MR)

Test	Test Method	Criteria for conformity	Results
Three cycles: Each cycle consisting of 3 hours 60±2^{0}C in water and thereafter drying at 65±2^{0}C for 8 hours	Clause 4 and 7.3.2 of IS:848-2006(as per table -1)	No separation of plies at the edges and/or surface at the end of three cycles. On forcible separation of plies with knife, wood failure shall be predominant and shall be more than 75% for excellent bond and not less than 50% for pass standard. For less than 50% wood failure, the specimen shall be considered as failed	No separation of plies at the edges and /or surface at the end of three cycles. 60% Wood Failure Pass Standard

3.3Effect of the scavenger on Formaldehyde Emission

The formaldehyde emission of plywood, depending on scavenger type and content, is illustrated in Figures 5 and 6. The lowest formaldehyde emission was achieved in plywood specimens containing Polymate-777A for urea formaldehyde resin (0.36 mg/L), followed by Polymate-777P (0.22 mg/L), as tested according to JIS A 1460, and 7.86 mg/100 gm board and 2.96 mg/100 gm board when tested as per IS 13745 at a scavenger concentration of 3%. However, no significant decrease in formaldehyde emission values was observed with a one-step increase in scavenger content, with emissions increasing from 0.5 to 1.0 wt%. Yet, significant decreases in formaldehyde emission values were achieved when the ratio increased from 1.5 to 2.0% and from 2 to 3%.All plywood boards tested met the requirements of the E1 grade (max. 1.5 mg/L) specified in Japanese standard JIS A 5908 at all scavenger concentrations. Plywood boards containing 2% and 3% of both scavengers met the requirements of the E0 grade (max. 0.5 mg/L) specified in JIS A 5908.The addition of scavengers with aromatic rings decreases the density of methylene bonds in the urea formaldehyde resin chain, consequently reducing formaldehyde emission from the samples. This reduction is likely due to the high affinity of scavengers towards emitted formaldehyde molecules, facilitated by the presence of adjacent phenolic hydroxyl groups (-OH) on the aromatic ring, accelerating nucleophilic addition reactions. Specifically, the non-bonded electron lone pairs on the OH groups attack carbonyl groups (C=O) in formaldehyde, forming a methylol structure (RO-CH2-OH). Subsequently, the reaction proceeds through the attack of the other lone pair on the adjacent ring-OH to the methylol group via an intramolecular interaction

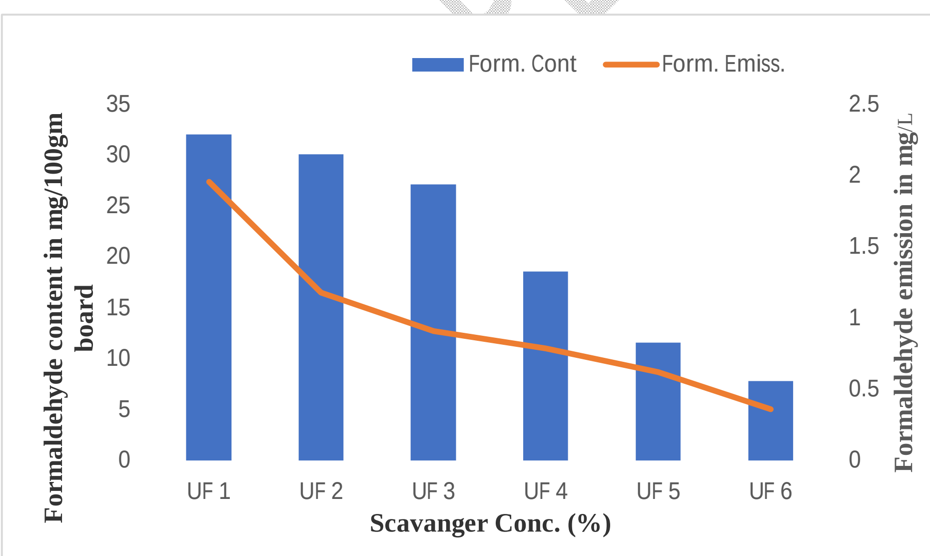

Fig.;-6 Formaldehyde emission at formaldehyde content (mg/L)

CONCLUSIONS

The study concludes that Polymate-777A is highly effective in reducing formaldehyde emissions in plywood production. Not only does it lower formaldehyde levels, but it also improves the quality of the panels. The study suggests that the best results are achieved when using Polymate-777A at concentrations between 1.5% and 2% with urea formaldehyde resin. This ensures that the plywood meets strict standards for indoor and outdoor use. Because Polymate-777A maintains material properties while reducing emissions, it's a promising option for industrial use. The researchers recommend further refining the concentration levels and incorporating Polymate-777A into manufacturing processes to meet even stricter emission standards. These findings contribute to making wood composite production more eco-friendly and health-conscious.

REFERENCES

Ko K (1976) How to control pollution of formaldehyde for formaldehyde series thermosetting resin adhesives (m Japanese). Settyaku Kyokaishi 12:160-166

Tomita B (1980) How chemical structure of UF resin affects formaldehyde emission (in Japanese). Mokuxai Kogyo 35:193199

Washington State University, Pulhnan, WA, pp 3-20 Myers GE (1984) How mole ratio of UF resin affects formaldehyde emission and other properties: a literature critique. For Prod J 34(5):35-41

Antov, P.; Mantanis, G.I.; Savov, V. (2020a): Development of Wood Composites from Recycled Fibres Bonded with Magnesium Lignosulfonate. Forests, 11, 613.

Sahoo, S.C., Amitava, Sil., & Dharm, Pal. (2020). Effect of Nano-additive on the Bonding Strength and Formaldehyde Emission of the Plywood Adhesive during Manufacturing of Wood Based Panel Products. *International Journal of Innovative Technology and Exploring Engineering, 10*(2), 158–161. doi:10.35940/ijitee.b8306.1210220

Boran, S.; Usta, M.; Gümüskaya, E. (2011): Decreasing formaldehyde emission from medium density fiber board panels produced by adding different amine compounds to urea formaldehyde resin. International Journal of Adhesion and Adhesives 31(7):674–678.

Boran, S.; Usta, M.; Ondaral, S.; Gümüskaya, E. (2012): The efficiency of tannin as a formaldehyde scavenger chemical in medium density fiberboard. Composites Part B, 43, 2487–2491.

Sahoo S.C., Sil, A., Riya, R., & Solankip, T. (2021). Synthesis and properties of UF/pMDI hybrid resin for better water resistance properties of interior plywood. *International Journal of Innovative Science, Engineering & Technology, 8*, 148-158

Costa, N.: Pereira, J.: Martins, D.; Martins, J.; Ferra, J.; Cruz, P.; Magalhães, F.; Mendes, A.; Carvalho, L. (2011):Innovative catalysts for urea-formaldehyde resins. In: Caldeira F (ed) Minimizing the environmental impact of the forest products industries. University Fernando Pessoa, Porto.

Costa, N.; Pereira, J.; Ferra, J.; Cruz, P.; Martins, J.; Magalhães, F.; Mendes, A.; Carvalho, L. (2013a): Sodium metabisulphite as a scavenger of air pollutants for wood□based building materials. International Wood ProductsJournal. 4. 242-247.

Costa, N.; Pereira, J.; Ferra, J.; Cruz, P.; Martins, J.; Magalhães, F.; Mendes, A.; Carvalho, L. H. (2013b): Scavengers for achieving zero formaldehyde emission of wood-based panels. Wood Science and Technology, 47, 1261–1272.

Sahoo, S.C.Amitava Sil,Annesha dutta (2023). Synthesis and Properties Study of The Urea Formaldehyde Resin Modified With Pmdi Used For Manufacturing Of Wood Composite Products. *European Chemical Bulletin*, *12*(10), 9875-9880.

Costa, N.; Pereira, J.; Martins, J.; Ferra, J.; Cruz, P.; Magalhães, F.; Mendes, A.; Carvalho, L. (2012): Alternative to latent catalysts for curing UF resins used in the production of low formaldehyde emission wood based panels. International Journal of Adhesion and Adhesives 33:56–60.

Eom, Y-G.; Kim, J-S.; Kim, S.; Kim, J-A.; Kim, H-J. (2006): Reduction of formaldehyde emission from particleboards by bio-scavengers. Mokchae Konghak 34:29–41.

European Panel Federation (2018): Autonomous agreement on a European Action Guide regarding the prevention of formaldehyde exposure in the European panel industry and compliance with the occupational exposure limits,

Ghani, A.; Bawon, P.; Ashaari, Z.; Wahab, M.W.; Hua, L.S. (2017): Addition of propylamine as formaldehyde scavenger for urea formaldehyde-bonded particleboard. Wood Research, 62 (2), 329-334.

Sahoo, S.C.., Tudu, R., Pandey, C.N., & Khatua, P.K. (2015). Green Adhesive-Using Glyoxalated Lignin and Hydrogenated Resin as Ecologically Safe Wood Adhesive for Interior Plywood. *International Journal of Prevention and Control of Industrial Pollution, 1*(1), 11-15.