SYNTHESIS AND PROPERTIES STUDY OF THE UREA FORMALDEHYDE RESIN MODIFIED WITH PMDI USED FOR MANUFACTURING OF WOOD COMPOSITE PRODUCTS.

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Article History: **Received: 05.05.2023** **Revised: 06.06.2023** **Accepted: 29.07.2023**

Abstract:
Urea formaldehyde adhesives are widely used in wood composite industries to make wood based panel products, However to achieve better bonding strength and low VOC emission panel products the modification of resin further required. The objective of the study was to manufacturing of modified urea formaldehyde resin with polymeric isocyanate (pMDI) for manufacturing of better water resistant wood composite and resin properties study for manufacturing of wood composite products. In order to improve the water resistance properties, urea –formaldehyde resin are commonly modified with melamine or phenol. In this study water resistance properties of urea formaldehyde resin was enhanced by using Yamandur R-11(polymeric isocyanate (PMDI) having terminal isocyanate –CNO group appx. 12,5 %) with urea –formaldehyde resin . A typical composite adhesive was manufactured by mixing emulsifiable polymeric isocyanate with urea formaldehyde resin at a different concentration starting from 1%, 2.5%, 5.0%, 7.5% and 10% on the basis of liquid Urea Formaldehyde resin. Adhesive properties of UF /pMDI hybrid resin like viscosity, gel time ,FTIR spectroscopy, free formaldehyde of the resin and other resin property like formaldehyde emission of the board were analyzed. The results showed that the hybrid adhesive consisting of UF resin and emulsifiable polymeric isocyanate has shown better adhesive properties than the conventional Urea formaldehyde resin for manufacturing of wood composite products and reduces formaldehyde emission to maintain better indoor airquality for safer environment.

Keywords: - modify urea formaldehyde resin, polymeric isocyanate (PMDI, UF /pMDI hybrid resin, formaldehyde emission, safer environment.

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DOI: - 10.48047/ecb/2023.12.10.699

1.0 INTRODUCTION

In order to improve water resistance of the plywood made with urea-formaldehyde resin (UF), an adhesive, commonly used in the manufacture of wood-based materials, is modified first with water resistant melamine-formaldehyde (MF) or phenol-formaldehyde (PF) adhesives. Despite their obvious advantages, a combined melamine-urea-phenol-formaldehyde (MUPF) resin does not completely exhibit the advantageous properties of its individual components, particularly in terms of resistance to the action of variable ambient conditions. As a result, wood based materials manufactured with its use have lower water resistance than when produced using pure PF resin Hence Effort for lowering of energy consumption, for improving of environment and better exploitation of raw materials will be new technologies.

The (pMDI) resins have already been successfully used to create wood panel goods such as particle board and medium density fiberboard. However, due to a number of factors, its use as an adhesive for the production of plywood is restricted. According to analyses, adding 40% more isocyanates to UF resin enables the production of plywood with water resistance that is even better than that stipulated in the corresponding standard binding for MF resin (Pizzi et al., 1993). Lei et al. (2006) claimed the opposite, claiming that while adding pMDI to MUPF resin significantly increased the board's water resistance, it generally had no effect on mechanical qualities. . These researchers showed that, when pMDI is added to MUPF resin at as little as 5 % tensile strength of particleboards, after 2 h boiling the water resistance increases from 0.09 to 0.21 N/mm^2

The presented modification method of amine resins, apart from an increase in water resistance, also contributes to a reduction of costs associated with pMDI use. According to reports, adding isocyanate to PF resin or UF resin adhesives cause s the methylol group and NCO group of each adhe sive to react, forming urethane bonds with relative ly high bond strengths (Pizzi 1983, Pizzi and Walt on 1992, Pizzi etal. 1993, Pizzi et al. 1996)..). Chelak and Newman (1993) reported that existing formaldehyde-based resins condense while emitting water to serve their purpose as adhesives, whereas isocyanate reacts with to form a polyurea structure as the backbone of its adhesive bond formation

The adhesives used in plywood are mostly aqueous based. However, due to the PMDI's high reactivity with water, it cannot be combined with water.The disadvantage of employing Polym eric Methyl Diphenyl Diisocyanate (PMDI) as an adhesive for plywood using standard techniques is that it has a high reactivity with water. In this study attempt was made to manufacture water resistance plywood using Urea –Formaldehyde resin modified with polymeric isocyanate (pMDI)and resin properties. The majority of the adhesives used in plywood have an aqueous foundation. However, due to the PMDI's high reactivity with water, it cannot be combined with water. The disadvantage of employing Polymeric Methyl Diphenyl Diisocyanate (PMDI) as an adhesive for plywood using standard techniques is that it has a high reactivity with water. This study attempted to produce plywood that was water-resistant using urea-formaldehyde resin that had been modified with polymeric isocyanate (pMDI), and it examined the resin's performance in wood-based composites.

2.0 MATERIALS AND METHOD

2.1 Materials

Technical-grade urea granules (99%), formaldehyde (37% HCHO) and aqueous solutions of both formic acid (HCOOH) and sodium hydroxide (NaOH) were used for the synthesis of UF resin. The polymeric isocyanate (pMDI) was Yamandur R-11,M/s – Chandra chemicals ,west Bengal ,an isocyanate-terminated Prepolymer containing 12.5 % free isocyanate groups having viscosity 15-25 Cps @30^{0}C and appearance of dark brown colour emulsified liquid. Wood Veneer used for manufacture of plywood belongs to *Dipterocarpussp.* (Gurjan) as core and face veneer .

2.2 Methods

2.2.1Preparations of the Urea- formaldehyde resin

230-250 parts by weight of formalin (Formaldehyde content 37%) was charged into resin kettle and made alkaline with 50% sodium hydroxide solution to pH 7.5 -8.0. 100 parts by weight of urea was gradually added to the kettle and stirring started. Stirring continued till the end of the reaction. Temperature was raised by passing steam and then set at 92º±2ºC and kept at this temperature under agitation for 1½ - 2 hours. pH were checked time to time and maintained at 7.5 – 8.0. In the second stage, the pH of the solution was lowered to 5.0 – 5.5 by adding 50% solution of acetic acid and reaction was continued under agitation at the same temperature. The progress of the reaction was followed by measurement of viscosity and water tolerance. For ready result, instead of viscosity, flow time of the reaction mixture was measured in B_4 cup. Water tolerance was a measure of the number of times of weight of water which can be mixed with resin before incipient precipitate is formed. The resin was ready when a flow time of 14-15 seconds had in B_4 flow cup and water tolerance of 3-4 times. The reaction was arrested by raising pH to 7.5 – 8.0 by adding 50% alkali and then resin was cooled to ambient temperature.

2.2.2 Preparation of UF/pMDI resins Hybrid

UF/pMDI resins were prepared in the laboratory by adding polymeric isocyanate (pMDI) with different concentrations starting from 1%,2.5%,5%,7.5% and 10% into the liquid UF resin. Five different above UF/pMDI resins were prepared by adding polymeric isocyanate (pMDI) during cooling of the resin when the temperature was at 60 ± 2^0C . Finally, the resin mixture was agitated at high rpm using a laboratory stirrer until a homogenous solution was obtained and cooled to room temperature. Properties of these UF/pMDI resins were presented in Table 1.

2.2.3Characterization of the resin UF/pMDI

All manufactured UF, UF/pMDI resins as well as pure pMDI have Fourier transformation infrared (FTIR) spectra that were captured at room temperat ure in the 400–4000 cm-1 range. A cone-plate viscometer (DVII+, Brookfield, Middleboro, MA, USA) with the No. 2 spindle at 60 rpm and 26 °C was used to measur e the UF/BpMDI resins' viscosity.A gel time metr e was used to gauge the neat and hybrid resins' gel times at 100 °C. P^H of the resin was checked in a digital P^H meter at 27^0C after calibration.

2.2.4Total solids content

A resin sample weighing 3.0 to 5.0 gms was place d into an evaporating disc (W1 g).The sample was accurately weighed (W2g).The resin sample was spread out uniformly around the dish, keptd in a h ot air oven set at 105°±20°C, and allowed to dry f or three hours. When the sample became cooled to room temperature and keptin a desiccators. Weighing the dry resinW3g).From this the solids c ontent of the resin was determined as a percentage of its weight in weight: % solid content= (W3-W1)/ W2 * 100

2.2.5Determination of free formaldehyde content of the resin

50 ml solution of one mole of pure sodium sulphit e was taken in a 250 ml flask and 2 to 3 drop Thymolphthalein indicator was added.By carefull y titrating the mixture with 0.1N hydrochloric acid , the mixture was neutralised until the indicator's b lue colour vanished and then 25 gms of resin sample was Added .

The resulting combination underwent a series of ti trations with 1N hydrochloric acid to achieve total decolorization. The following formula was used to determine the amount of free formaldehyde (%):%CH2O = [Net ml. of acid * Normality of acid * 3.0]/(weight of sample).

3.0 RESULTS AND DISCUSSION

3.1 Properties of UF/B-pMDI resins

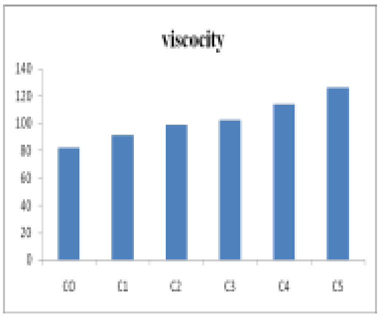
The gel time of hybrid UF/pMDI resins and control samples was determined to compare their activity and the results obtained are displayed in Fig-1. Adding 10% polymeric isocyanate (pMDI) reduced the gel time from 124 seconds (for the control) to 92 seconds.The data demonstrated that the gel time was affected by the addition of 1% to 10% polymeric isocyanate (pMDI) resin to the UF resin..Adding pMDI generally resulted in an incre ase in resin viscosity.With the addition of pMDI r esin in varied percentages, the viscosity rose from 82 to 126cp.Increase in percentage implied linearl y increasing viscosity.The viscosity of the UF resi ns was raised to 126cp by 10% addition of pMDI. As anticipated, the amount of pMDI resin added t o the UF resin had a substantial impact on the hyb rid resin's viscosity.

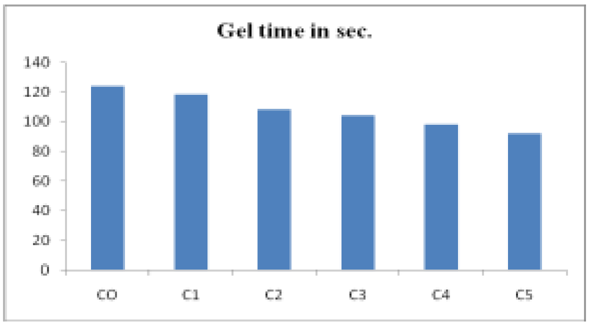
TABLES:-

TABLE -1 Properties of UF/pMDI resin

Sl.no	Type of resin	Viscocity (cp)	Gel time(S)@100^0C	Solid content(%)	p^H	Freeformaldehyde (%)
01	UF(Control)-C0	82	124	48.5	8.5	0.42
02	UF+1% Pmdi-C1	91	118	48.8	8.2	0.30
03	UF+2.5% Pmdi-C2	99	108	49.1	8.2	0.26
04	UF+5% Pmdi-C3	102	104	49.4	8.1	0.20
05	UF+7.5% Pmdi-C4	114	98	49.5	8.1	0.18
06	UF+10% Pmdi-C5	126	92	49.5	8.1	0.12

FIGURES: -





3.2Formaldehyde emission

Analysis of the data showed that the formaldehyde emission of plywood bonded with UF/pMDI hybrid resins with the addition of 1% and 10% pMDI resin at different concentration of addition of polymeric isocyanate with UF resin had a significant action of reducing formaldehyde emission when tested as per IS 137459(Table -8).The plywood bonded with conventional UF resin resulted in a formaldehyde emission of 44.4 mg/100 gm board(perforator value). The results show that the addition of pMDI resin into the UF resin greatly decreased the formaldehyde emission from the plywood. The addition of 10% to 7.5% pMDI resin reduced the emission by40% and 32%, respectively. This was probably due to the lower concentration of –NCO groups in the UF/PMDI resin with 1% pMDI resin compared with the case of 10% pMDI. The –NCO groups probably could react with the free formaldehyde (HCHO) and formed HNCO. Thus, the UF/ pMDI resins with the addition of 7.5 to 10% pMDI resin had more opportunity to reduce the formaldehyde emission. It is a well-known fact that free formaldehyde is released as a result of hydrolysis of hydroxymethylene bonds in resin. Blockage of these groups, either through their reaction with NCO groups or by direct substitution to the aromatic ring, will result in its lower content in resin.

Table - 2 Formaldehyde emission (perforator value) of the plywood testes as per IS 13745:1993

Sl. No.	**Type of resin used**	**Tests**	**Clause No**	Test Method	**Requirement as per IS 3087:2005**	**Results**
	2	**3**	**4**	5	**6**	**7**
1	C0	Perforator value (mg formaldehyde/100gm dry board.)	Clause 9.7	IS 13745:1993	8mg/100gm For E1 Class	44.44
2	C1				$8 \geq f_c \leq 30$mg/100gm For E2 Class	38.6.
3	C2					32.7
4	C3					32.6
5	C4					29.8.5
6	C5					26.5

Formaldehyde emission (mg/100gm)

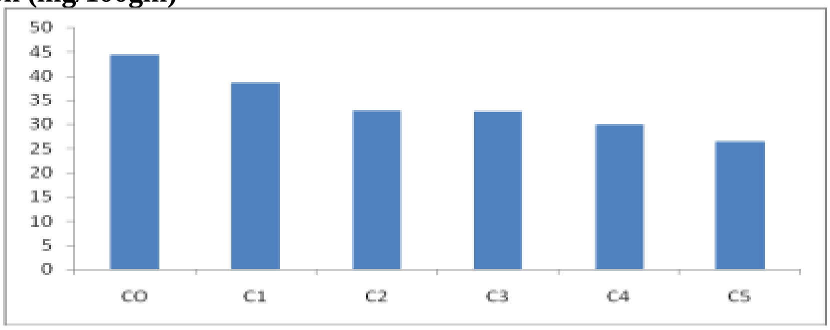


Figure -4 Formaldehyde emission of the UF/PMDI hybrid resin

3.3FTIR analysis

In order to confirm the UF/PMDI hybrid resin the FTIR spectroscopy analysis was conducted for the for UF,UF/PMDI and pure pMDI resin and the results are presented in Fig. 1,2,3. The NCO group has a characteristic absorption peak at 2285–2250 cm-1. The neat pMDI spectrum shows that the NCO peak appeared at 2250 cm-1. An absorption peak between 1770 and 1700 cm-1 was observed in the pure pMDI spectrum, which was assigned to the C=O group. Furthermore, strong absorption peaks between 3401 and 3195 cm-1 (N-H stretching) were detected in the spectra . One of the characteristic bands at a wavelength of 1700 cm-1 is ascribed to vibrations of the carbonyl group of C=O in the multi substituted urea. It may originate both from the cured UF resin [-CH2 -NHCON(-CH2 -)2] and polyurea formed as a result of reactions of MDI with -CH2 OH, -NH2 or -NH- groups of UF resin, or even from the carbonyl group of urethane bridges as a result of reactions between –N=C=O and -CH2 OH groups

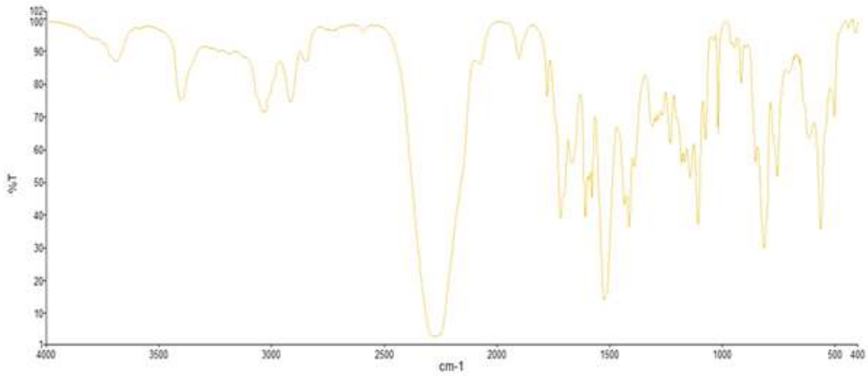


Figure -1 FTIR specta of polymeric Isocyanate (PMDI)

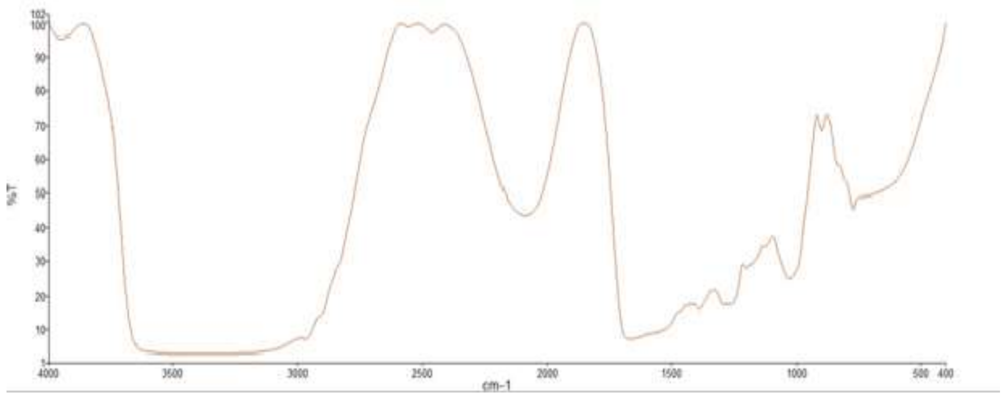


Figure -1 FTIR specta of UF Resin

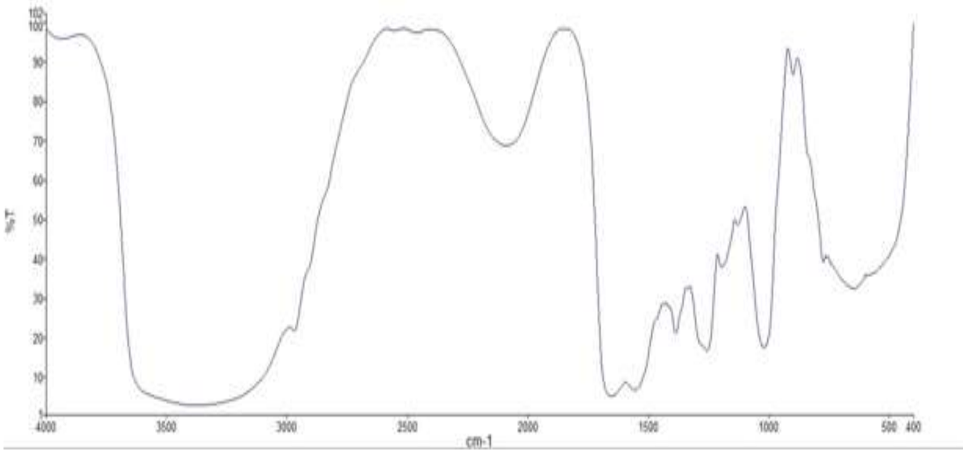


Figure -3 FTIR spectra of UF/pMDI resin

4.0 CONCLUSION

The results and analysis of studies leads to the conclusion that there is a rapid change in gel time of the UF/pMDI hybrid resin decreases as the concentration of incorporated pMDI increases from 1 to 10% . Based on the results of this studies it can be suggested that the modification of UF resin with pMDI is a way of enhancing to manufacture of better quality wood composite products in terms of the bonding quality .On the basis of IR spectrum it can be concluded that the addition of Polymeric isocyanate (PMDI) did not considerable effect the chemical structure of UF resin. The formaldehyde emission values reduces to 20 to 30% and meets E_2 emission classes which may also further achieved E_1 emission classes by incorporating scavenger to maintain the better indoor air quality for creating a safer environment.

5.0 Acknowledgement:

The authors expresses its deep sense of gratitude to the Director, IPIRTI Bangalore for the timely encouragement, guidance ,funding and advices rendered during the course of the study.

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