

Blocking of PMDI Resin and Mixed Phenol Blocked PMDI/Phenol Cardanol Formaldehyde Hybrid Resin for Plywood

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ABSTRACT

PMDI (Polymeric diphenylmethane diisocyanate) resins cannot be used for plywood, as these resins, after spreading on veneer will lose -NCO by reacting with moisture in air and wood. In this study for plywood manufacturing, the -NCO group is blocked using phenol and imidazole and the cost of the resin is reduced by mixing with phenol-cardanol formaldehyde resin. The FTIR (Fourier Transform Infrared) studies confirm NCO blocking. For phenol blocked PMDI resin studied using DSC (Differential Scanning Calorimetry) analysis the deblocking of NCO group started at 160° C. For imidazole blocked PMDI resin, even though the deblocking of NCO group started at 125°C, curing is only achieved at a pressing temperature of 170-180°C. For getting Boiling Water Resistant (BWR) grade as per IS-848:2006-Specification for Synthetic Resin Adhesive for plywood, a press temperature of 180°C is required. The addition of DBTL (Dibutyltin dilaurate) catalyst to phenol blocked PMDI resin improved the bond strength of plywood. The Phenol cardanol formaldehyde resin combined with phenol blocked PMDI resins, when used to make BWR grade plywood has confirmed to Boiling Water Proof (BWP) grade plywood as per IS-848:2006.

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INTRODUCTION

In order to use the available timber resources in an efficient manner, new types of adhesives which provide improved performance of wood panel products with low formaldehyde emission have to be developed. However formaldehyde based adhesive are being phased out gradually in many countries due to emission of formaldehyde from panel products⁹. When the formaldehyde emission of wood panel products are restricted by laws and regulations, various studies has been conducted to reduce the

emission by several options which include employing scavenger resins, controlling manufacturing variables, post treatments and using resin additives like masking agents, scavengers and inhibitors⁹. The formaldehyde emission however cannot be eliminated altogether as long as the resins are based on formalin as the reactant. Hence, there is a need to employ “no added formaldehyde” resin. This objective has been achieved by using isocyanate based adhesives. Isocyanate resins are

formaldehyde free resins and are highly reactive compared to formaldehyde resins. Aliphatic isocyanates like HDI (Hexamethylene Diisocyanate) are hazardous and are mainly used in coating formulation. Aromatic isocyanate are less hazardous compared to aliphatic isocyanate⁷. TDI (Toluene diisocyanate) and MDI (Diphenylmethanediisocyanate) are the commonly used aromatic isocyanates⁷. MDI has lower vapour pressure and are less reactive than TDI and it provides higher tensile strength, greater toughness and heat resistance⁷. Hence due to toxicological concerns, MDI resins are appropriate for bonding wood panel products. MDI is an aromatic isocyanate derived from aniline and is a solid at room temperature⁷. Polymeric MDI is a liquid at room temperature and provides a low freezing point and storage stability than pure MDI⁷.

Polymeric MDI (PMDI) resins are costlier compared to conventional formaldehyde resins like phenol and urea formaldehyde. But they provide efficient bonding even at low resin consumption. PMDI resins easily react with the moisture present in the atmosphere and these resins also adhere strongly to press plates while pressing the boards. To avoid these drawbacks, the NCO group present in the resin should be blocked using suitable blocking agents. The NCO groups can be blocked with a compound containing active hydrogen atom and at elevated temperatures these blocked NCO groups are deblocked⁴. Aromatic MDI resins can be deblocked at lower temperature when compared to aliphatic isocyanates.

The reaction of isocyanate resin with the hydroxyl groups present in wood resulting in urethane formation are already studied and proven using different techniques¹². Urethane bonds are formed in the Southern Pine modified with methyl isocyanate¹². The N in the bonded urethane was used as a tracer to determine the distribution of reacted chemicals in the wood holocellulose and lignin fractions¹². The degree of substitution was higher in the lignin fractions than in the holocellulose¹².

Using solid state NMR studies of PMDI reaction in wood, it is claimed that the major component formed from the curing of PMDI in wood are urea structures arising from the reaction with water¹³. At higher temperature and

low moisture content PMDI can react with urea NH's to form crosslinking biuret and/or dimer and trimer structures¹³.

Typical blocking agents used to block MDI resins include malonates, triazoles, ε-caprolactam, sulfite, phenols, ketoxime, pyrazoles and alcohols¹⁸.

Imidazole-, 2-methylimidazole- and benzimidazole blocked hexamethylene diisocyanate and isophorone diisocyanate have been prepared and characterized by elemental analysis, IR and NMR spectroscopy². The structural property relationship of these adducts has been established by reacting with hydroxyl-terminated polybutadiene². The cure rate of the adduct increases from the imidazole to 2-methylimidazole and to benzimidazole blocked adduct².

Imidazole and 1-methylimidazole react with isocyanate in boiling nitrobenzene or phenyl ether to form N-substituted imidazole-2-carboxamides in good yield⁸.

A novel blocked isocyanate adduct was synthesized from 2,4,6-trichlorophenol with polymethylenepolyphenylisocyanate. The Differential thermal analysis showed that the blocked adduct began to deblock at 70° C which were lower than that of commercial blocked isocyanate⁴.

Dibutyl tin dilaurate is considered as an effective catalyst in polyurethane industries. SobhanNiyogi, Sanjay sarkar and BasudamAdhikari, studied the catalytic activity of DBTL in polyurethane formation prepared from Neopentyl glycol (NPG) and toluene diisocyanate¹⁴. It was observed that the activity of catalyst is dependent on the sequence of addition of DBTL catalyst. Highest reaction rate was observed when the catalyst was added after the addition of TDI to diol¹⁴.

Blending of Formaldehyde resin like PF and UF resins with isocyanate to form a hybrid resin improved the characteristics of the resins. Addition of small amount of PMDI between 10 % and 15 % by weight, to UF resins for plywood considerably improve the UF glue line water resistance¹⁰. Introduction of PMDI to urea resin at 2.5 % made it possible to manufacture particle boards with better bending strength and internal bond⁶.

In PF-PMDI resin, Methylol carrying PF resols can undergo two reactions of almost equal rate³. One reaction is the standard condensation that PF resin undergo to crosslink through methylene (-CH₂-) bridges and the second reaction is the attack of the MDI on the hydroxyl of the methylol groups (-CH₂ OH) present on the PF resol³.

The UF resins have been shown to co-polymerize readily in water with PMDI. This reaction is based on the reaction of the isocyanate group (-NCO) with the methylol groups on the UF resins, which is much faster than the reaction of NCO with water³. The primary curing mechanism identified is identical to that identified for phenolic resin³.

Kinetic evidences in thermo-mechanical analysis experiments and carbon-13 nuclear magnetic resonance spectroscopy evidence indicates that the strength of a joint bonded with UF-pMDI mixes is improved by co-reaction of the methylol groups of UF resins with pMDI to form a certain number of methylene crosslinks⁵. The formation of these methylene crosslinks is predominant, rather than formation of urethane bridges⁵.

This research is conducted to develop a suitable blocked PMDI resin using phenol and imidazole and to study their bonding efficiency in plywood manufacturing. Phenol and imidazole blocked PMDI resin are characterized using FTIR and DSC studies. The blocked resins alone and in the combination of Phenol cardanol formaldehyde resin are studied.

MATERIALS AND METHODS

The MDI resin used for the research was supplied by M/s Bayer Material science. Desmodur 44V20L having a specified NCO content of 30 to 32.5% was used for the preparation of blocked MDI resin. Specification of these desmodur products¹⁶ are given in Table 1.

The blocking agents used were phenol and imidazole and the solvent was a mixture of xylene and m-cresol. Butanol is also used for facilitating the blocking reaction. Dibutyltindilaurate were used as a catalyst for urethane formation. Plywood boards are made using silver oak veneers.

Synthesis of phenol blocked PMDI resin

In a three necked reaction kettle equipped with a mechanical stirrer and a reflux condenser, 70g Xylene, 146g m-cresol and 65g of phenol are added while stirring and heating started in an oil bath. The temperature is raised to about 50°C and maintained for about 40 minutes. Add 60g of Desmodur44V20L. When temperature is about 80°C, Butanol is added. The solution is allowed to condense at 90°C until all NCO groups were blocked and then allowed to cool to room temperature. NCO content is determined frequently using standard dibutylamine back titration method.

Determination of NCO content

The NCO content was determined using a standard dibutylamine back titration method¹⁵. The Isocyanate is reacted with dibutylamine to form a urea. Unreacted (excess) amine is determined by backtitration with HCL¹⁵.

Synthesis of imidazole blocked PMDI resin

In a three necked reaction kettle equipped with a mechanical stirrer and a reflux condenser, 70g Xylene and 146g m-cresol and 50g imidazole are added. Imidazole is added slowly and dissolved in the solvents by stirring. The temperature is raised to about 50°C and maintained for about 40 minutes. Add 60g of Desmodur44V20L. At 80°C, Butanol is added and allowed to condense at 90°C until all NCO groups are blocked. Catalyst Dibutyltindilaurate, is added after cooling to 70°C and left for cooling to room temperature.

Synthesis of Phenol-Cardanol Formaldehyde (PCF) resin

A water soluble phenol-cardanol formaldehyde resin¹⁷ which was developed by IPIRTI, Bangalore are synthesized in laboratory. In a three necked reaction kettle equipped with a mechanical stirrer and a reflux condenser, 70 parts by weight of phenol and 30 parts by weight cardanol was charged while stirring followed by 60 parts by weight of formalin (37%). To the reaction mixture 6 parts of sodium hydroxide in 33 parts by weight of water was added and the mixture was heated to 90±2°C. The reaction mixture was kept at 90±2°C for about 2 hours. The novolac resin formed was cooled to 55°C and

10 parts by weight of sodium hydroxide in 45 parts of water was added to the reaction mixture followed by 100 parts by weight of formalin (37%). Then reaction was carried out at 70–72°C. Maintained the temperature at 70–72°C till the flow time when measured in B-4 cup of IS: 3944 gives 14–15 seconds in hot condition. Then started cooling to room temperature. Properties of the resin are given in Table 2.

PCF-Phenol blocked PMDI Hybrid Resin

50g of Phenol blocked MDI resin was added slowly in to a 100 g of PCF resin while stirring. The solution is stirred for about 5 minutes till getting a homogeneous solution and used for spreading on veneers. The viscosity of the PCF resin was decreased after the addition of blocked MDI resin.

Expected Reaction Mechanisms

Isocyanate reacts with active hydrogen atom present in blocking agents, phenol and imidazole to form a weak bond¹¹ as shown in Figure 1. This results in the formation of phenol and imidazole blocked PMDI resin as shown in Figure 2 and Figure 3 respectively.

At elevated temperature, while pressing the board, these blocking agent regenerates and the NCO group become available for urethane formation. NCO group react with the butanol and the hydroxyl groups present in wood to form urethane. If dibutyltin dilaurate (DBTDL) is added to the blocked PMDI resin, it catalyses the reaction with butanol as shown in Figure 4¹⁴.

NCO group react with Butanol and the hydroxyl group present in wood components to form polyurethane linkages as shown in Figure 5.

Another possible reaction is the reaction of –NCO group with urethane to form allophanate as shown in Fig 6.

Characterization of Blocked resin

FT-IR (Fourier Transform Infrared) and DSC (Differential Scanning Calorimetry) method were employed to characterize the blocked resin. FT-IR spectra were recorded in the range of 400–4000 cm⁻¹ using Perkin Elmer Spectrum GX. The thermal properties of blocked resins are studied using DSC in the temperature range of 25–200°C using Mettler-Toledo DSC 1. Both FTIR and DSC

studies were carried out from Indian Institute of Science, Bangalore.

Plywood manufacturing and testing

The phenol and imidazole blocked MDI resin were coated on the Silver oak veneers having a moisture content of 6–8% and pressed in a hot press at specified temperature and pressure after different open assembly time (OAT) as given in Table 3. The plywood so produced were subjected to test as per IS: 848-2006¹. An attempt also made to form a hybrid resin by mixing the phenol blocked PMDI resin with Cardanol-phenol formaldehyde resin.

Three replicate boards were made for each board type. The pressing details for each type are as per shown in Table 3.

Three Boards each was made with phenol blocked PMDI resin, without the addition of catalysts and after adding catalyst, dibutyltin dilaurate and denoted as ‘BP’ and ‘BPC’ respectively. The bonding properties of plywood bonded with imidazole blocked PMDI resin are studied at two pressing temperatures. Three Boards each of ‘BI-1’ and ‘BI-2’ are pressed at 150°C and 180°C respectively using imidazole blocked PMDI resin. All the boards were tested for BWR grade as per IS:848-2006¹.

PCF-Phenol blocked hybrid resin were coated on veneers and pressed at the temperature and pressure as reported in Table 3. To compare the bonding strength, three boards were also made with PCF resin alone. Boards made with PCF-Phenol blocked resin were named as ‘CMDI’ and the other board made with PCF alone is named as ‘CPF’. The pressing details of all the boards are as per given in Table 3.

RESULTS AND DISCUSSION

FT-IR analysis

The FT-IR spectra of phenol and imidazole blocked MDI resin are shown in figs 8–9. The NCO group has characteristic absorption peak at 2285–2250 cm⁻¹ as shown in Figure 7. Figure 8 and Figure 9 shows that no characteristic peaks appear between 2285–2250 cm⁻¹ for both phenol and imidazole blocked PMDI resin. Hence all the NCO groups are blocked. Also all the spectra showed an absorption peak between 1280–1180 cm⁻¹ which shows the formation of C–N

stretch hence confirming the formation of blocked reaction product. The FTIR Spectra of CPF-blocked PMDI hybrid resin as shown in Figure 10 also showed no absorption peak around 2285-2250 cm^{-1} which proves that the phenol blocked PMDI resin has not reacted with PCF resin.

Differential scanning calorimetry

The DSC curve formed over a specified temperature range is showed in Figures 11 and 12. The phenol blocked PMDI resin started deblocking at around 160°C as shown in Figure 11 and the imidazole blocked PMDI resin started deblocking at 125°C as shown in Figure 12.

Bonding strength of plywood

The bond strength of the plywood is checked by knife test after required cyclic boil dry test as per IS 848:2006¹. Board BPC, BP, BI-1 and BI-2 were tested for BWR grade¹. The results were shown in Table 4.

Board 'BPC' in which 0.5% catalyst Dibutyltindilaurate (DBTL) were added at room temperature showed far better results compared to Board 'BP' without catalyst. Board 'BI-2' bonded at 180°C showed good bonding strength compared to 'BI-1' which are bonded at 150°C.

The board made with CPF alone and CPF-Phenol blocked resin was tested for BWP grade. Result as per Table 5 indicates that CPF resin mixed with blocked PMDI showed better results than CPF resin alone.

CONCLUSION

Phenol and imidazole blocked PMDI resin were manufactured and confirmed the blocked NCO groups using FTIR studies and DSC studies. Plywood was manufactured at laboratory scale using these resin systems. For the Phenol blocked PMDI resin, the addition of catalyst DBTL, is required for getting better results. Even though the imidazole blocked PMDI resin containing DBTL catalyst started deblocking at 125°C, they required 180°C for achieving good bonding. The addition of Phenol blocked PMDI resin to PCF resin improved the bond strength of plywood and the PCF resin is not reacted with blocked PMDI resin at room temperature.

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Table 1: Properties of Desmodur®44v20 L.

Property	Required value	Units
NCO content	30.5-32.5	% by weight
Viscosity	160-240	mPa.s
Phenyl isocyanate content	≤50	Ppm

Table 2: Properties of the Resin

Properties	Phenol blocked MDI	Imidazole blocked MDI	PCF resin
pH	4	10	10
Flow time (sec) (B4 cup of IS:3944)	20	20	28
Viscosity (cp)	~60	~60	~90
Shelf life (Days)	>60	>60	10-15

Table 3: Pressing Details of Plywood

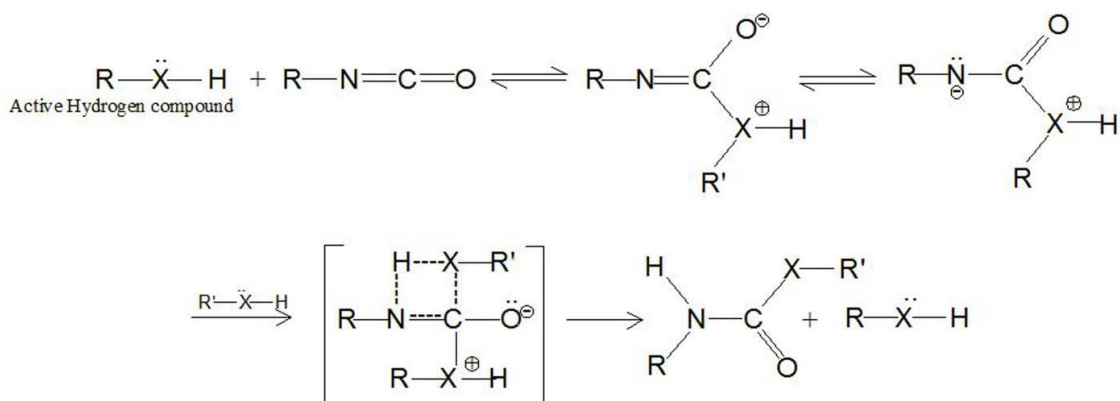
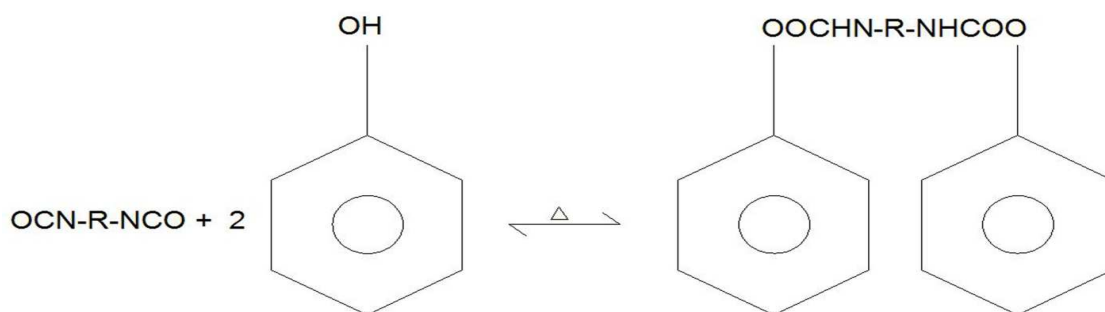
Board Type	Open Assembly Time (OAT) (h)	Temperature (° C)	Pressure (Kg/cm ²)	Pressing time (min)
BP	3	180	16	7
BPC	3	180	16	7
BI-1	3	150	16	7
BI-2	3	180	16	7
CMDI	2	180	16	7
CPF	2	180	16	7

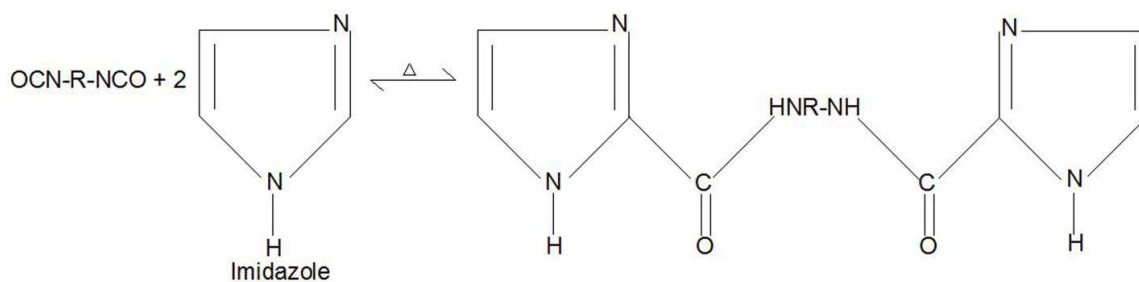
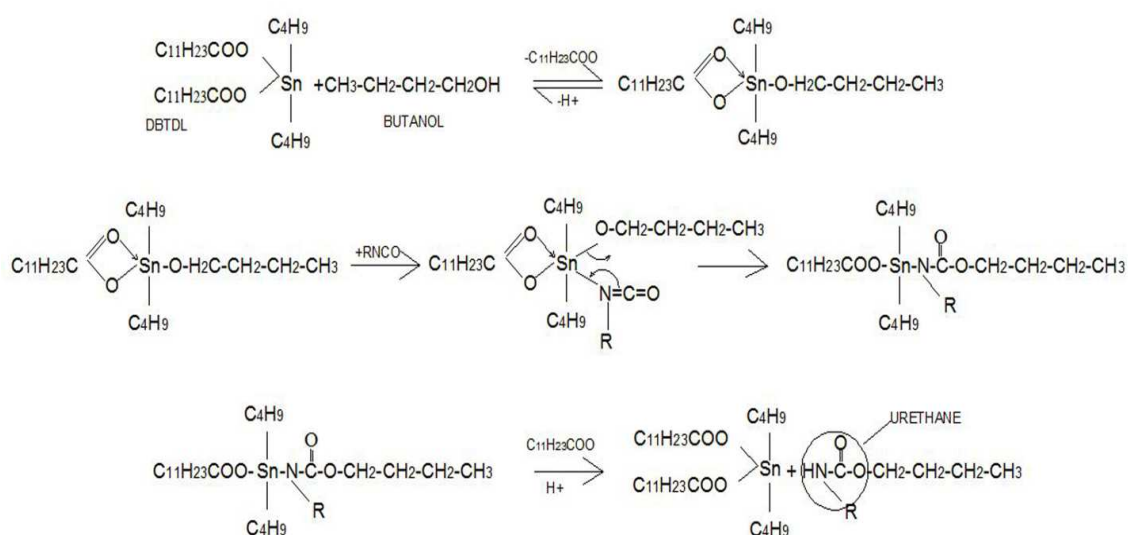
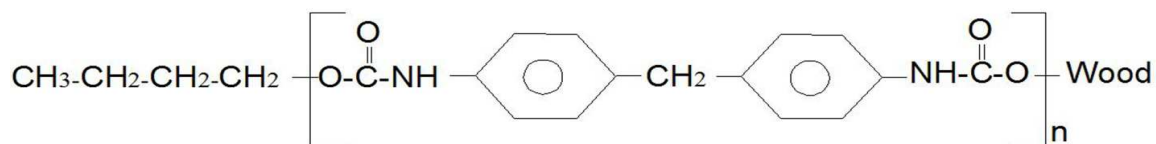
Table 4: Cyclic Test Result as Per IS: 848-2006 (BWR Grade)

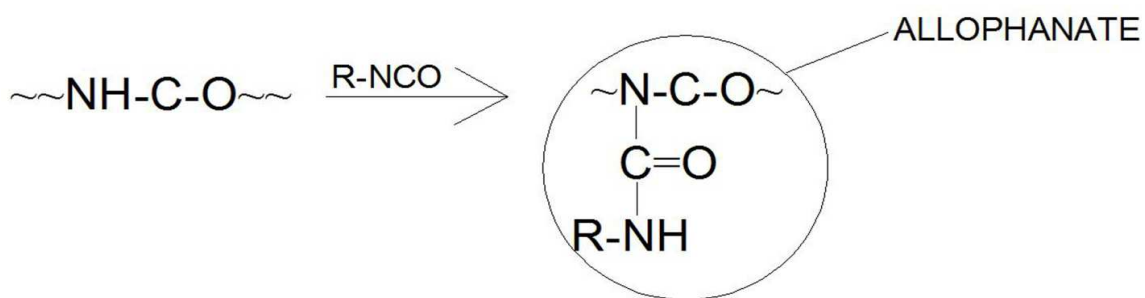
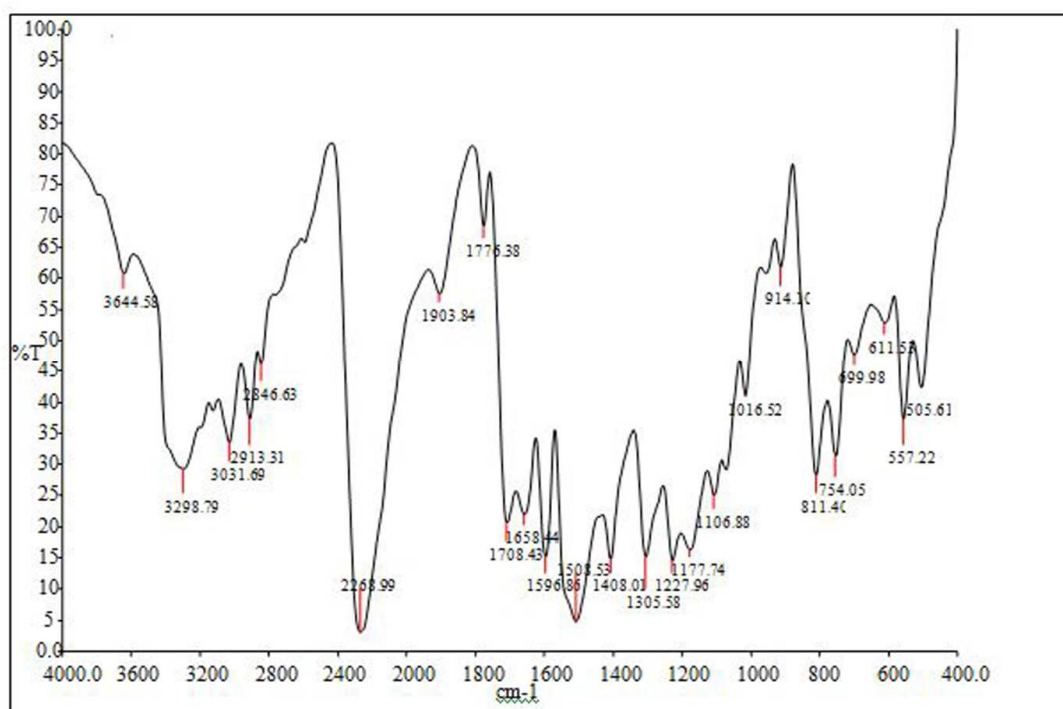
Sample	Wood failure (%)
BPC	80 %
BP	60%
BI	40-50%
BI-2	60 %

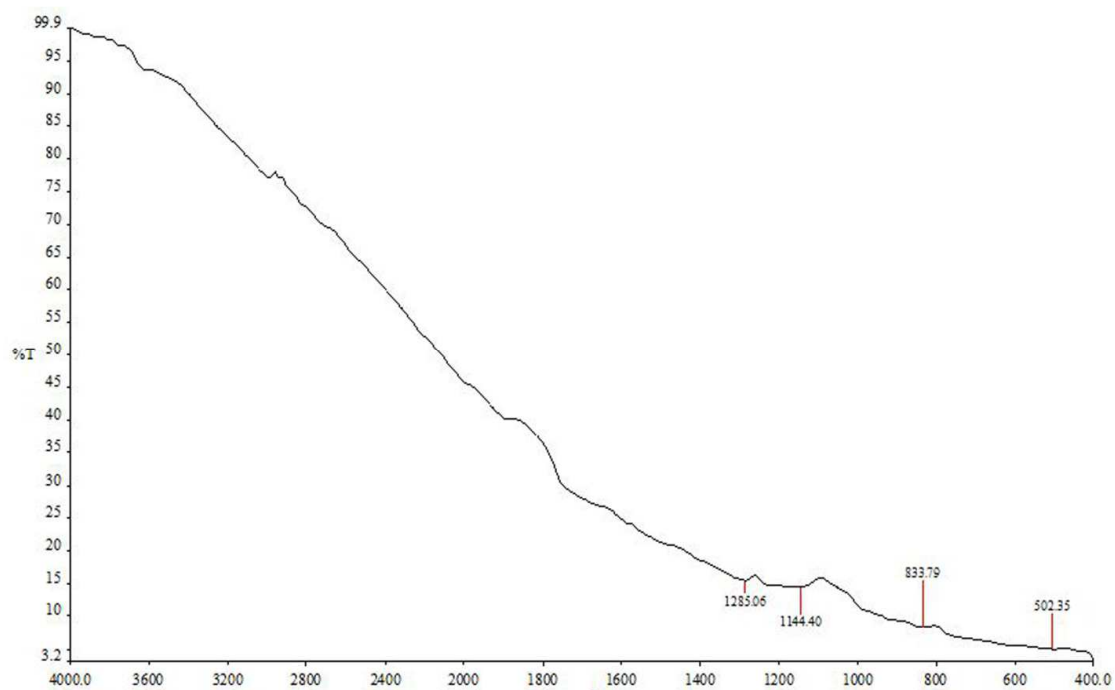
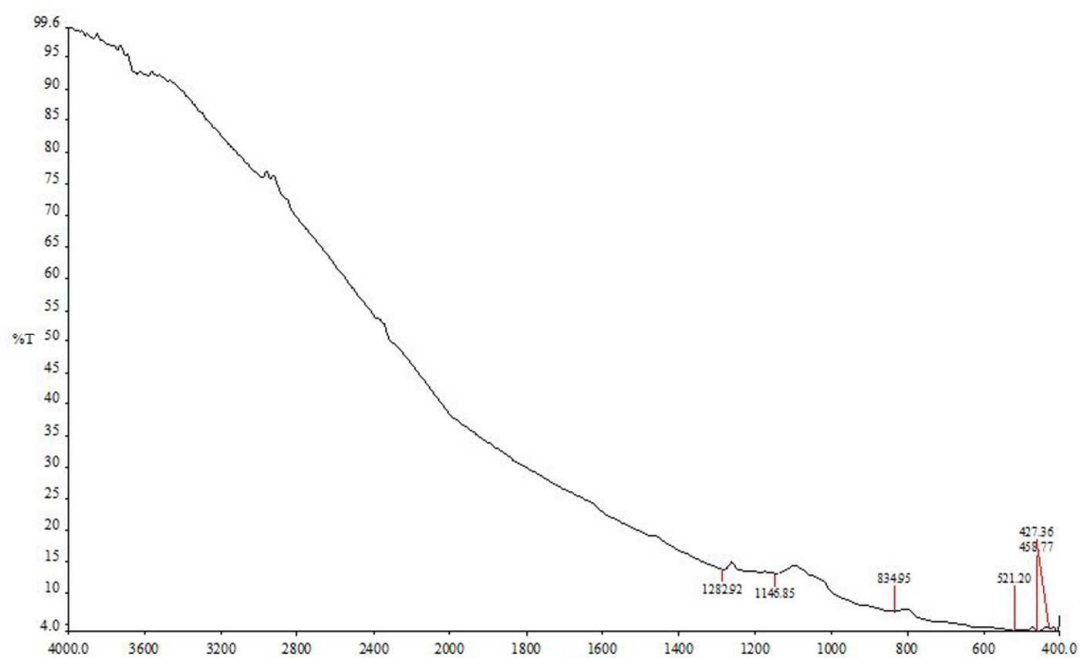
Table 5: Cyclic Test Result As Per Is: 848-2006 (BWP Grade)

Sample	Wood failure (%)
CMDI	80-90%
CPF	60 %

**Fig. 1:** Reaction of Isocyanate with Active Hydrogen Atom**Fig. 2:** Phenol Blocked Pmdi Resin

**Fig. 3:** Imidazole Blocked Pmdl Resin**Fig. 4:** DBTL Catalytic Activity**Fig. 5:** Formation of Urethane Linkages

**Fig. 6:** Formation of Allophanate**Fig. 7:** FTIR Spectra of Desmodur 44V20L

**Fig. 8:** FTIR Spectra of Phenol Blocked PMDI Resin**Fig. 9:** FTIR Spectra of Imidazole PMDI Resin

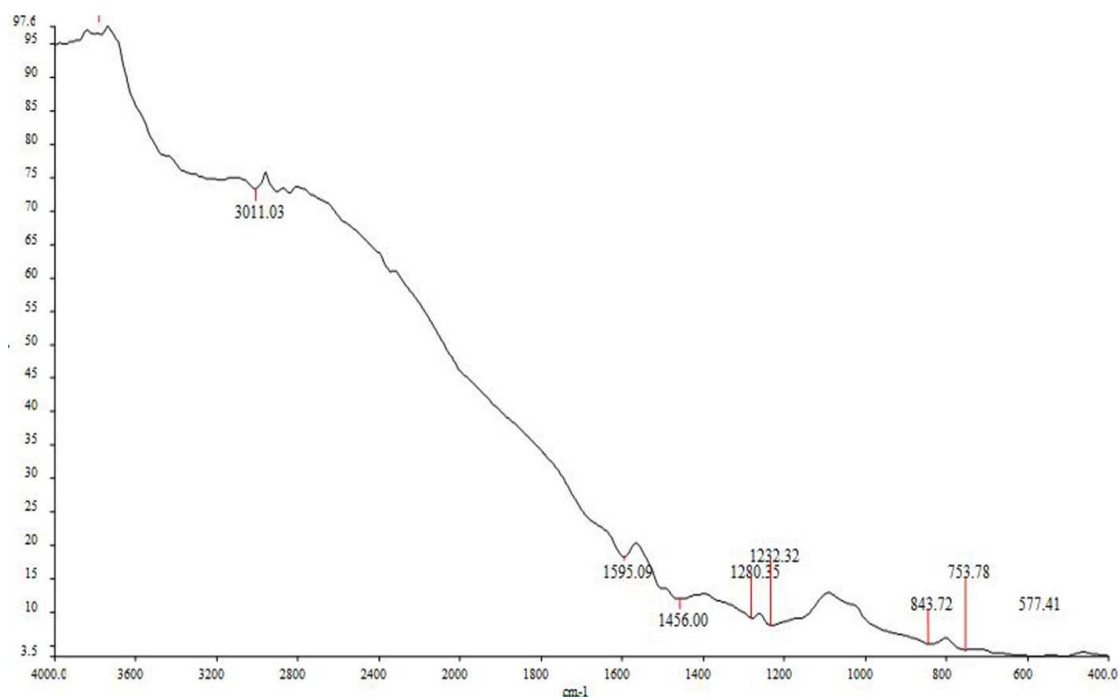


Fig. 10: FTIR Spectra of Phenol Cardanol Formaldehyde-Phenol Blocked PMDI Hybrid Resin

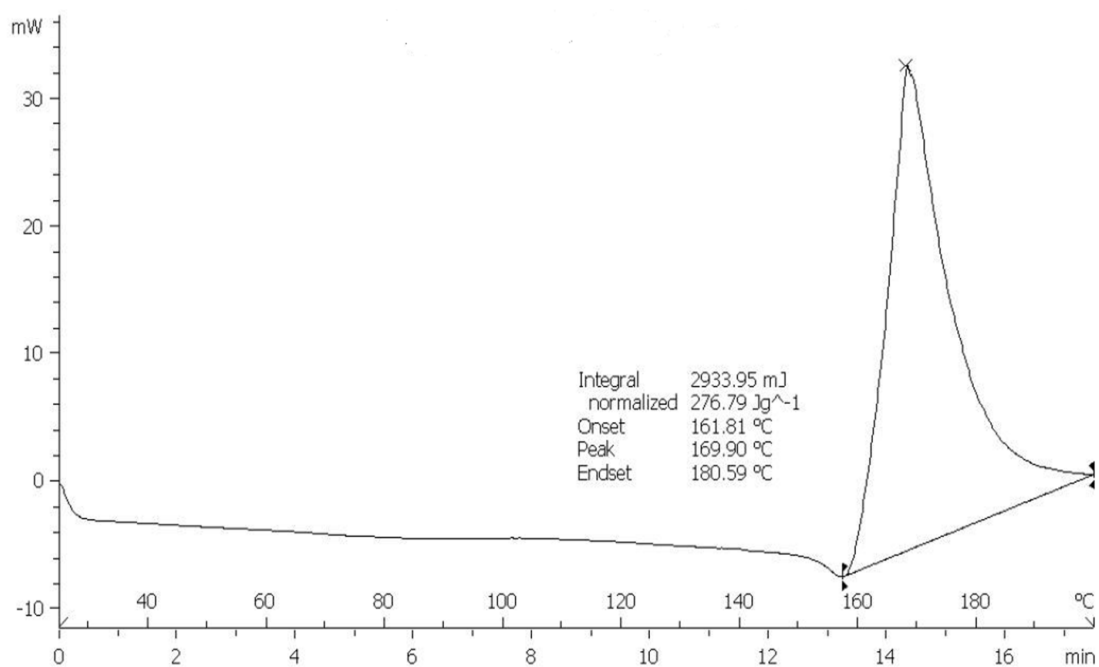
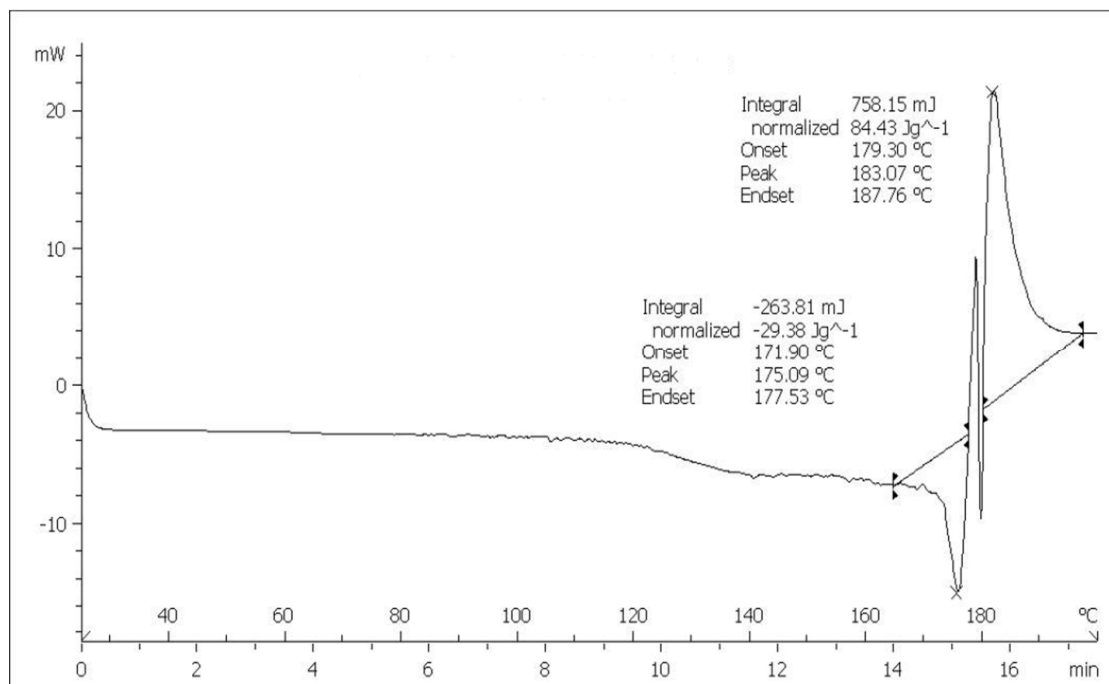


Fig. 11: DSC of Phenol Blocked PMDI Resin

**Fig. 12:** DSC of Imidazole Blocked PMDI Resin