



DIBUTYLTIN DILAURATE AND TRIETHYLAMINE CATALYZED PHENOL-CARDANOL FORMALDEHYDE/BLOCKED PMDI HYBRID RESIN FOR PLYWOOD

Ganesh Gopal T.M.*¹, S.K. Nath¹, Sujatha D¹ and Ramamurthinanda Kumar²

¹IPIRTI, Yeshwanthpur PO, Bangalore-560022, India

²Dept of Wood Science and Technology, Kannur University, India

Abstract: The organometallics and tertiary amines which can improve the polyurethane formation can be utilized in plywood manufacturing for the urethane formation from blocked PMDI resin to enhance the plywood bond strength. The catalytic activity of phenol blocked PMDI (Polymeric diphenylmethane diisocyanate) resins and Phenol cardanol formaldehyde (PCF)/phenol blocked PMDI hybrid resin with DBTL (Dibutyltin dilaurate) and triethylamine catalysts for the manufacture of plywood is studied using DSC and FTIR. The DBTL catalysts decreased the curing temperature of blocked resin. The FTIR analysis showed that DBTL enhances the urethane formation in PCF-PMDI resin. The addition of DBTL improved the bond strength of PCF/phenol blocked PMDI hybrid resin glued plywood. The decomposition temperature of resins is studied using TGA analysis. It showed that the blocked resin without any catalyst showed better thermal stability and also the PCF/phenol blocked PMDI resin is more thermally stable than blocked resin alone.

Keywords: Plywood, DBTL, Triethylamine, Phenol, Blocked PMDI resin.

Introduction: Polymeric diphenyl methane diisocyanate, which is an aromatic group of isocyanate used in the polyurethane formation, can be effectively used as an adhesive in wood panel industries as they have high reactivity and efficiency in bonding. Polyurethanes are polymeric materials formed by the reaction between an isocyanate and alcohols with two or more reactive hydroxyl group (OH). They are

excellent in adhesive properties, chemical resistance and heat resistance. The NCO group present in PMDI is highly reactive with hydroxyl group and the moisture present in the atmosphere which results in storage difficulties. This can be overcome by the blocking of NCO group using suitable blocking agents like phenol.

The reaction of NCO groups of MDI and the methylol groups of some formaldehyde based resins are studied by Pizzi *et.al*^{1, 2}. They found that the most relevant reaction occurring appears to be between the –NCO group of MDI and the methylol groups of formaldehyde based resins and this reaction is an order of magnitude faster than the deactivation of MDI by water¹. The

For Correspondence:

tmgg87@gmail.com

Received on: February 2015

Accepted after revision: March 2015

Downloaded from: www.johronline.com

second relevant reaction is the attack of the methylol group on the aromatic nuclei of MDI¹. Tertiary amines and organometallics such as tin compounds are most useful catalyst for the polyurethane formation. Dibutyltin dilaurate acts as a Lewis acid catalyst by complexing with isocyanate and are generally thought to function by interacting with basic sites in the isocyanate and polyol compounds^{3,4,5}. Catalytic activity of tertiary amine catalysts were proposed by Baker and Holdsworth in 1947 and Farkas and Strohm in 1965⁶. Baker *et.al* postulated the formation of a complex consisting of an isocyanate and a tertiary amine catalyst⁶. With the formation of this amine complex, the nitrogen atom of the isocyanate group is activated and readily reacts with hydrogen atoms from any water or polyol⁶. Farkas *et.al* proposed the involvement of an amine-active hydrogen complex followed by the reaction with isocyanate⁶.

A two stage cardanol-phenol formaldehyde resin (CPF) was developed by IPIRTI in which the first stage was carried out by reacting excess of phenol with formaldehyde to get the novolak and in the second stage this novolak resin is reacted with excess of formaldehyde in presence

of alkali to form resol resin⁷. This type of resin synthesis confirmed the involvement of cardanol in the methylol formation reaction⁷. If pure PMDI with free NCO group is added to this CPF resin to fortify the polymerization reactions, the resin will cure fast before coating on veneers. Hence blocked PMDI resin is used. In this study the catalysis of blocked PMDI resin and the bond strength of Blocked PMDI-PCF hybrid resins are studied. The thermal decomposition of the blocked resin is also studied. Since PMDI is a costly adhesive the admixing of this resin with CPF resin can minimize the cost and improves the bond strength of plywood. The NCO group in blocked PMDI resin is not reacted with water while mixing with aqueous dispersion of PCF resin.

Materials & 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 products are given in Table 1⁸.

Table 1: PROPERTIES OF DESMODUR®44V20 L⁸

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

Preparation of blocked PMDI resin⁹

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 and 60g of Desmodur44V20L are being added. When temperature is about 80°C, 20g of 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.

Preparation of phenol cardanol formaldehyde resin⁷

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 novolak 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.

Differential Scanning Calorimetry (DSC)

The catalysis of deblocking mechanism of blocked resin is studied using DSC in the temperature range of 25-200°C using Mettler-Toledo DSC 1 from Indian Institute of Science, Bangalore. Dibutyltin dilaurate and triethylamine are used as catalysts. The DSC analysis of blocked resin is carried out by adding 0.5% of catalysts The DSC of blocked resin without any catalyst is also studied.

Fourier Transform Infrared Spectroscopy (FTIR)

The pure PMDI resin without blocking is allowed to react with PCF resin. PMDI is slowly added in to PCF resin in the ratio 1:1. The same ratio of hybrid resin after adding about 0.25% of DBTL is also prepared. Both are allowed to react at 102°C. The resulting sample is analyzed through FTIR. FT-IR spectra were recorded in

the range of 400-4000cm⁻¹ using Perkin Elmer Spectrum GX from Indian Institute of Science, Bangalore.

Thermo gravimetric analysis (TGA)

The thermal stability of resins is studied by TGA analysis. The thermal decomposition were analyzed upto a temperature of 800°C using Perkin Elmer, Diamond TG/DTA from SAIF, Cochin university, Kerala.

Plywood manufacturing and testing

Blocked PMDI resin was added in to PCF resin in the ratio 1:1, while stirring. 6% of coconut shell powder is added slowly and stirring is continued till getting a homogeneous solution. To this solution 0.25 % catalysts are added. The plywood coated after the addition of dibutyltin dilaurate is denoted as ‘CD’ and the plywood coated after the addition of 0.25% triethylamine is denoted as ‘CT’. To compare the bonding strength, three boards were also made with PCF resin alone and denoted as ‘CMD’. The Silver oak veneers having a moisture content of 6-8% are used and pressed in a hot press at specified temperature and pressure as given in Table 2. Three replicate boards were made for each board type. The plywood so produced was subjected to BWP grade test as per IS: 848-2006¹⁰.

Table 2: PRESSING DETAILS OF PLYWOOD

Board Type	Open Assembly Time (OAT) (h)	Temperature (°C)	Pressure (Kg/cm ²)	Pressing time (min)
CD	2	180	16	7
CT	2	180	16	7
CMD	2	180	16	7

Expected Reaction mechanism

The phenol cardanol formaldehyde resin is made in a two stage process. In the first stage an excess phenol is allowed to react with formaldehyde to form a novolak resin. Hence formation of methylene linkages will be predominant (Figure 1). In the second stage when this novolak resin is allowed to react with excess formaldehyde, ortho and para substituted

methylols are formed (Figure 2). These resol resins, after admixing with blocked PMDI resin, and after coating on veneers, when pressed at elevated temperatures, the NCO groups are deblocked and reacted with hydroxyl groups of wood, butanol, and methylol to form urethane (Figure 4). The presence of dibutyltin dilaurate (DBTL) will catalyze the urethane formation (Figure 3).

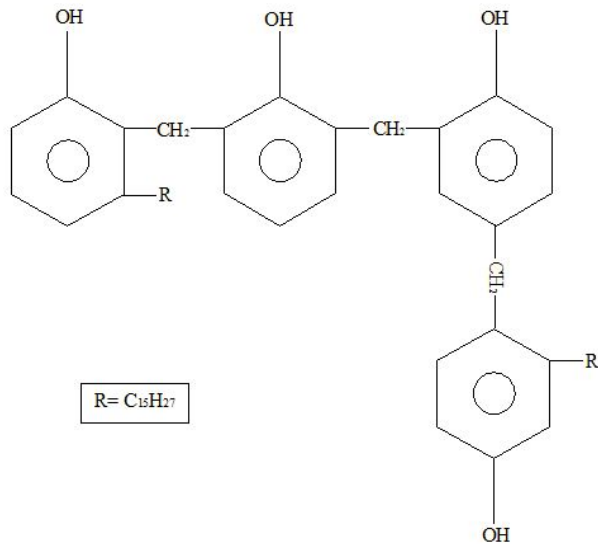


Figure 1: The first stage reaction in PCF resin

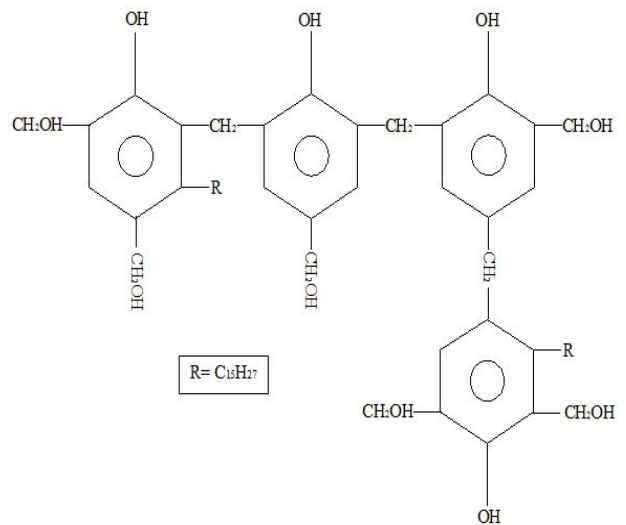


Figure 2: The second stage reaction in PCF resin

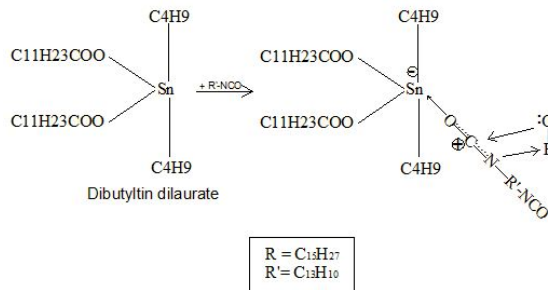


Figure 3: DBTL catalysis of urethane formation

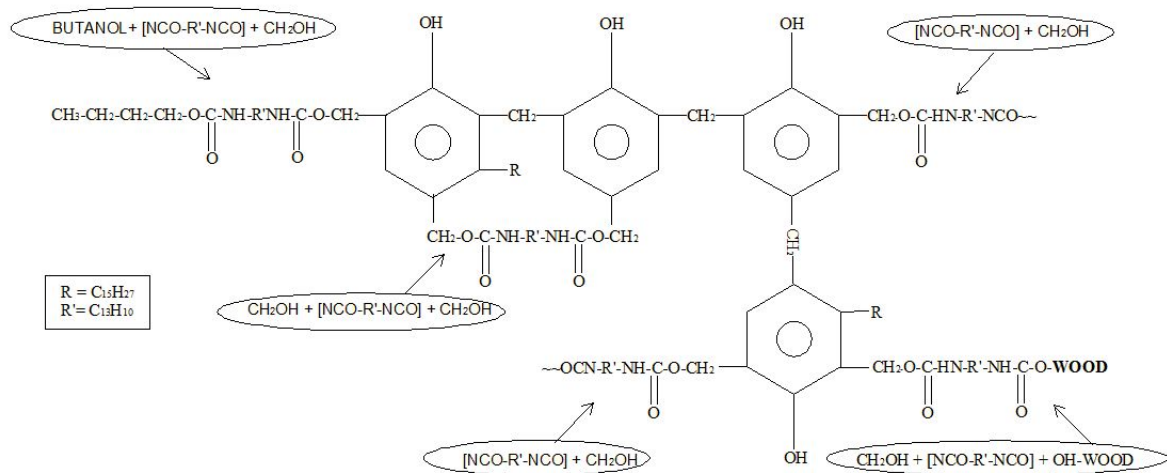


Figure4: Formation of urethane group

Results and discussion

Differential Scanning Calorimetry

The addition of catalyst reduced the curing temperature. For blocked PMDI without any catalyst the curing started at 161.81°C and the peak is obtained at 169.90°C and the reaction completed at 180°C as shown in Figure 5. When 0.5% triethylamine is added the curing started at

158.71°C and peak is obtained at 165.03°C as shown in Figure 6 and when 0.5 % DBTL is added, the curing started at 153.53°C and the peak is obtained at 160.12°C as shown in Figure 7. DSC studies showed that DBTL catalyst is more effective than triethylamine catalyst for the blocked resin prepared.

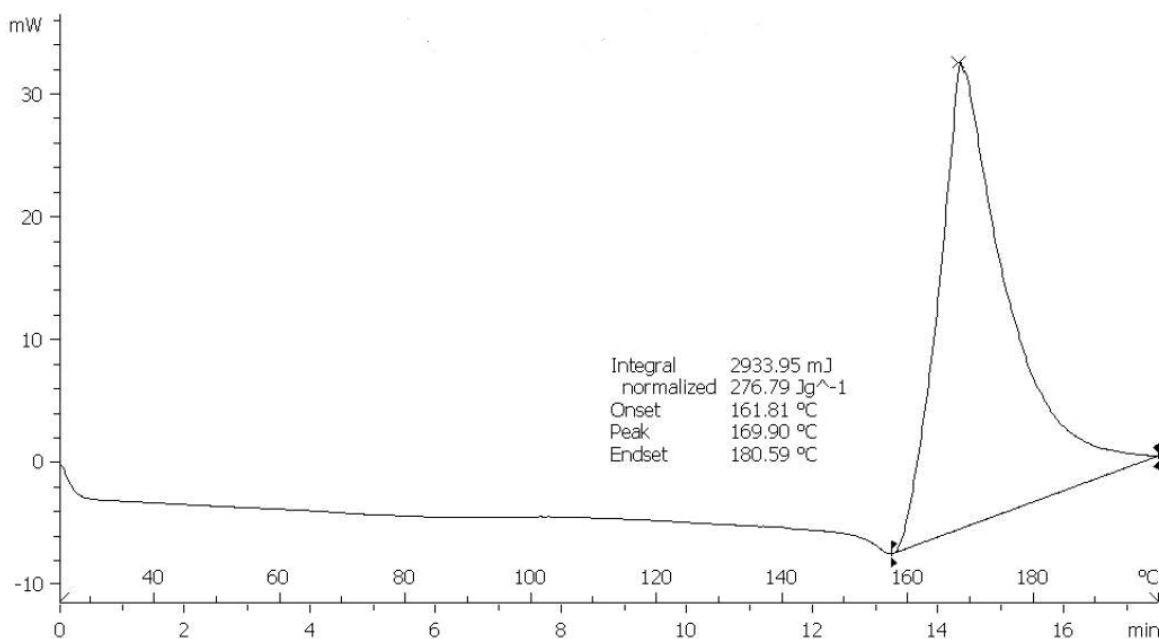
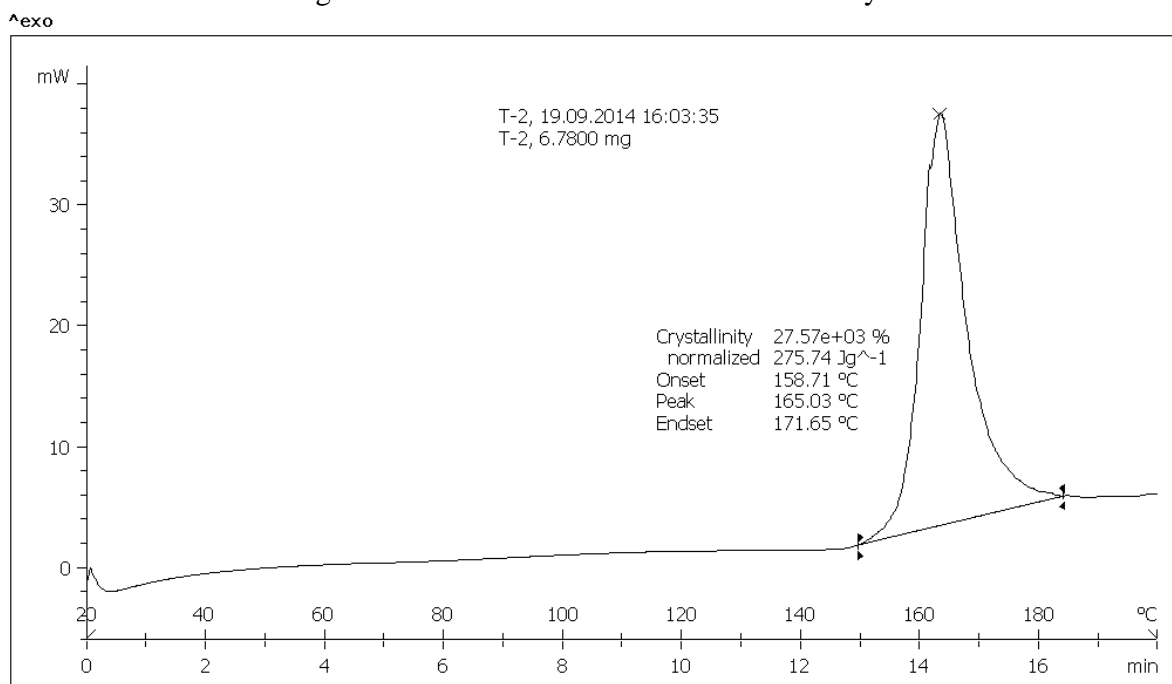


Figure 5 DSC of Blocked PMDI without catalyst



Lab: METTLER

STAR[®] SW 9.30

Figure 6 DSC of Blocked PMDI with 0.5% Triethylamine

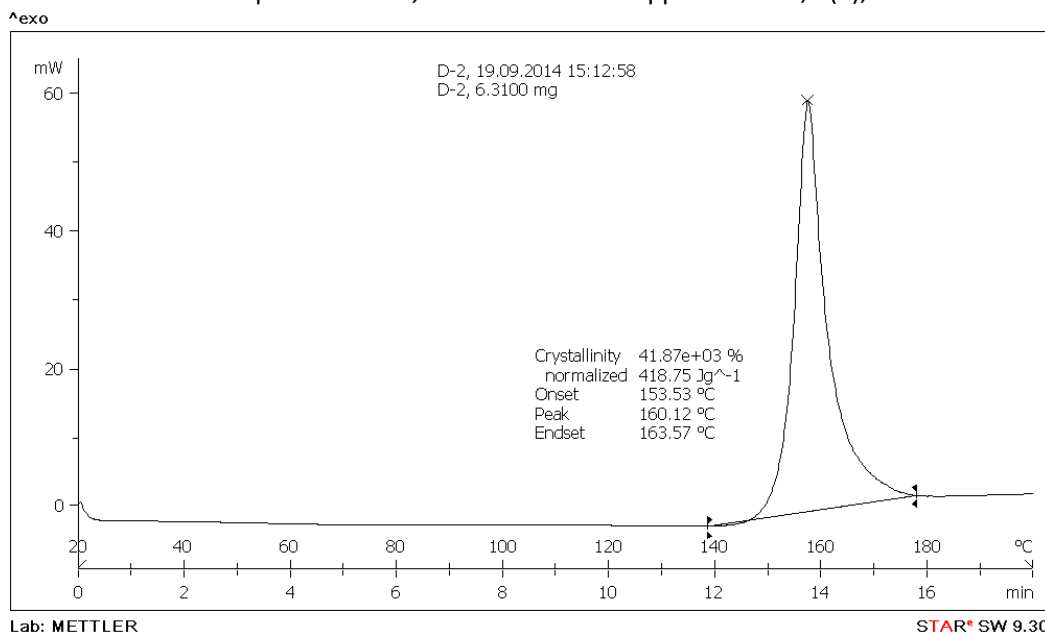


Figure 7 DSC of blocked pmmdi with 0.5% addition of dbtl

Fourier Transform Infrared Spectroscopy

The FT-IR spectra of PMDI-PCF resin as showed in Figure 8-9, showed an absorption peak between 3520 to 3320cm^{-1} which shows the formation of N-H stretch in urethane group. The addition of DBTL increased the intensity of this peak as shown in Figure 9. Also an absorption peak is formed in the DBTL catalyzed resin in

the region 1678cm^{-1} which shows the -C=O in urea. The addition of DBTL to the PMDI-PCF hybrid resin improved formation of urea and urethane linkages. These urethane linkages are expected to be formed by the reaction of NCO group in PMDI with methylol (CH_2OH) group present in the PCF resin.

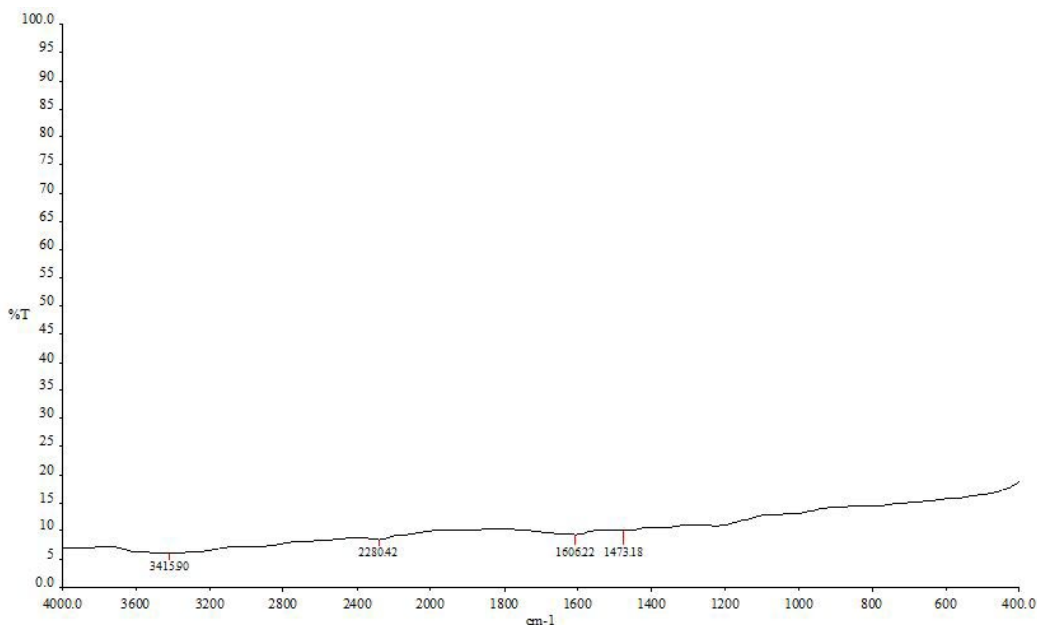


Figure 8 PMDI-pcf hybrid resin

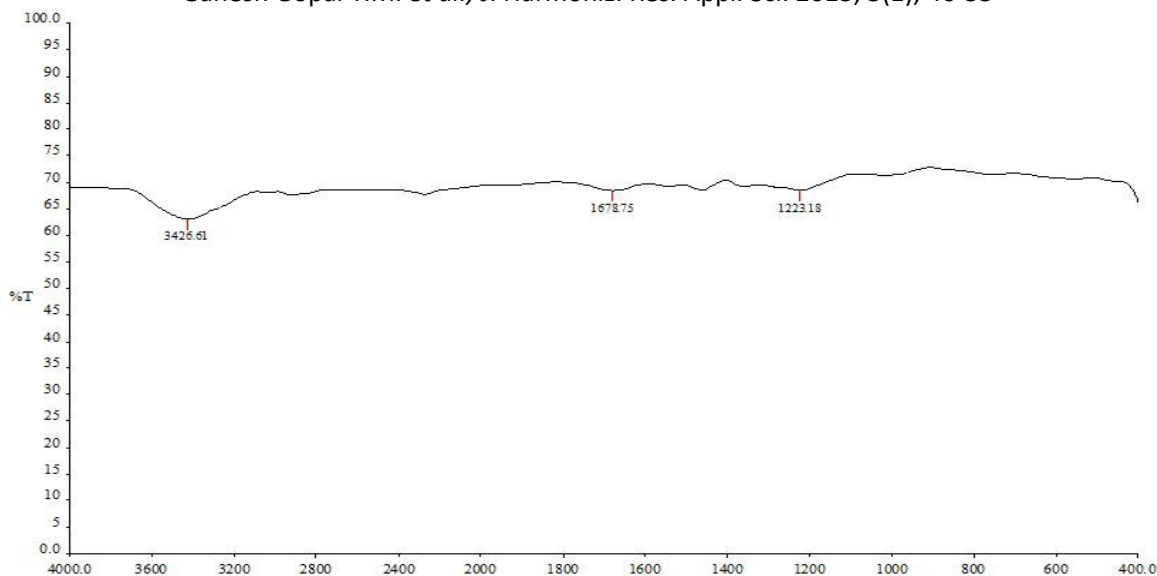


Figure 9 pmdi-cpf resin with 0.25 % dbtl

Thermo gravimetric analysis

The blocked resin without any catalyst started extensive thermal decomposition after 200°C as showed in Figure 10. The primary weight loss was observed at 248.98°C. The dibutyltindilaurate (DBTL) catalyzed blocked resin loosed its thermal stability before 200°C and showed primary weight loss at 198°C (Figure 11). The tertiary amine catalyzed blocked resin started thermal degradation at 212°C (Figure 12). The tertiary amine (TEA)

catalyzed blocked resin showed comparatively better thermal stability than that of DBTL catalyzed resin. But the blocked resin without catalyst is more thermally stable than catalyzed blocked resin. PCF/blocked PMDI hybrid resin, are more thermally stable than blocked resin alone which showed a major weight loss at 346.24°C (Figure 13) and the DBTL catalyzed PCF/blocked PMDI hybrid resin showed weight loss at 351.52°C (Figure 14).

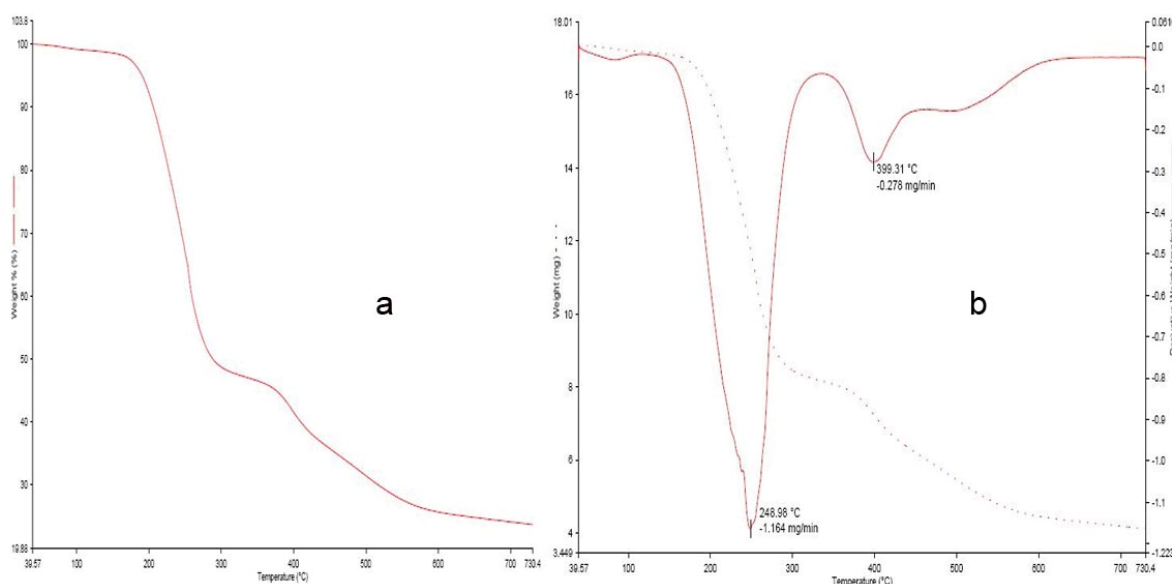


Figure10: a) TGA of blocked PMDI resin; b) Derivative weight loss of blocked PMDI resin

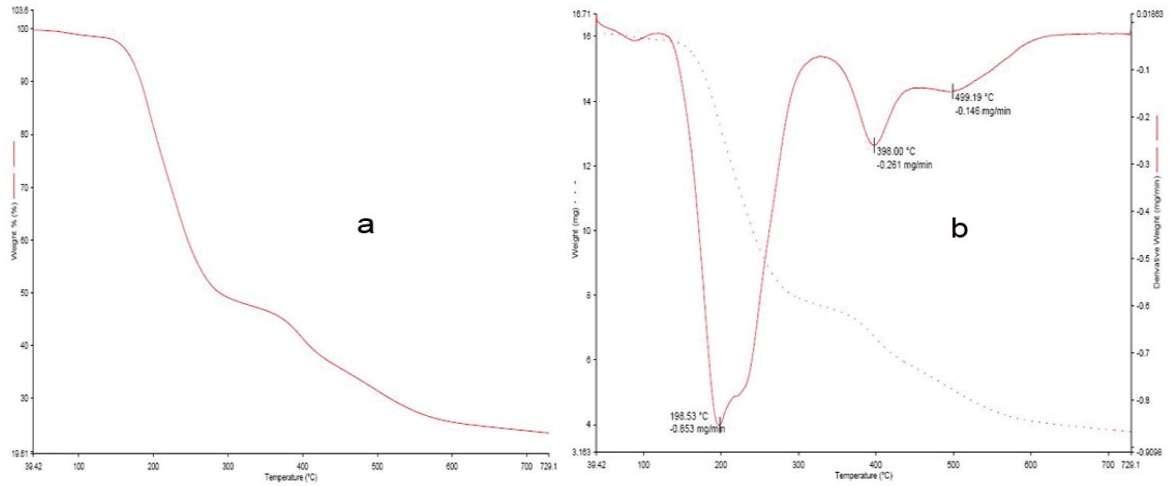


Figure 11: a) TGA of DBTL catalyzed blocked PMDI resin; b) Derivative weight loss of DBTL catalyzed blocked PMDI resin

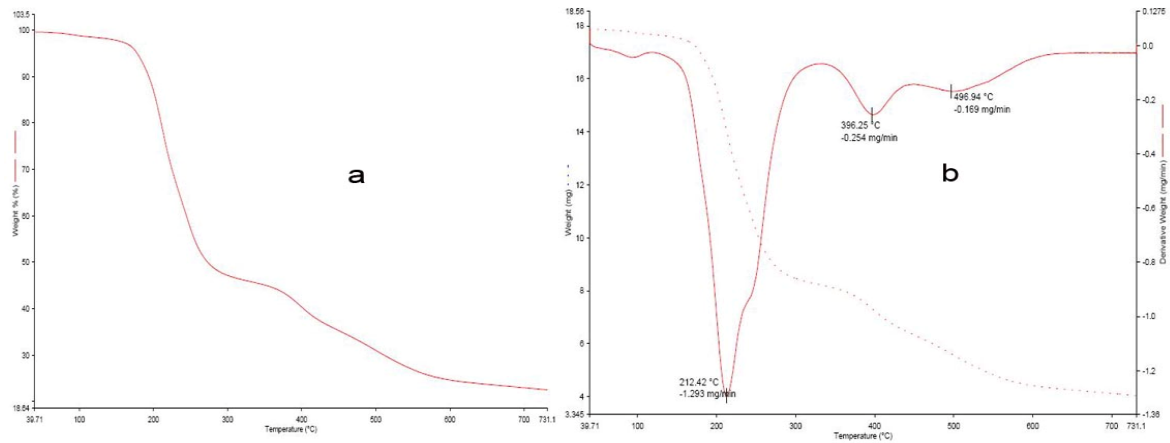


Figure 12: a) TGA of TEA catalyzed blocked PMDI resin; b) Derivative weight loss of TEA catalyzed blocked PMDI resin

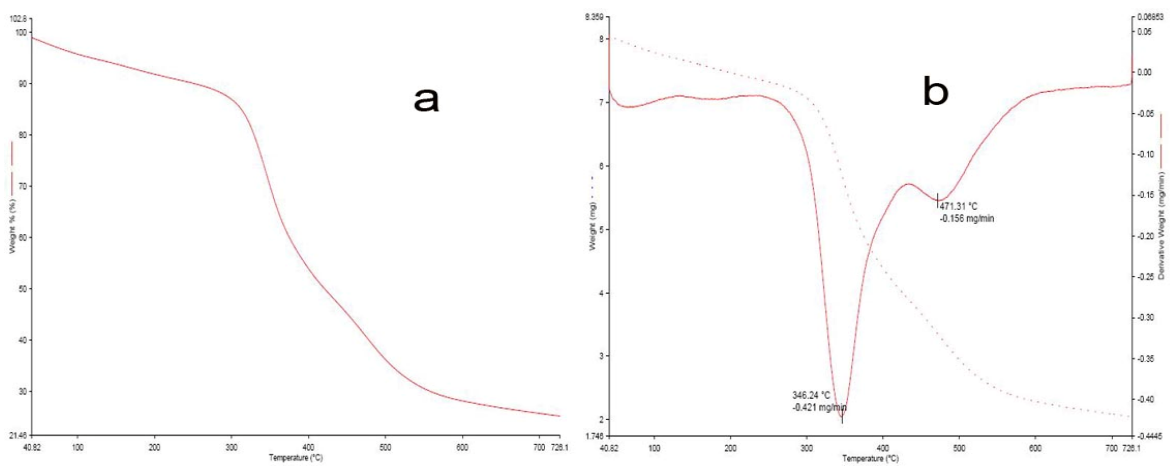


Figure 13: a) TGA of PCF/blocked PMDI hybrid resin; b) Derivative weight loss of PCF/blocked PMDI hybrid resin

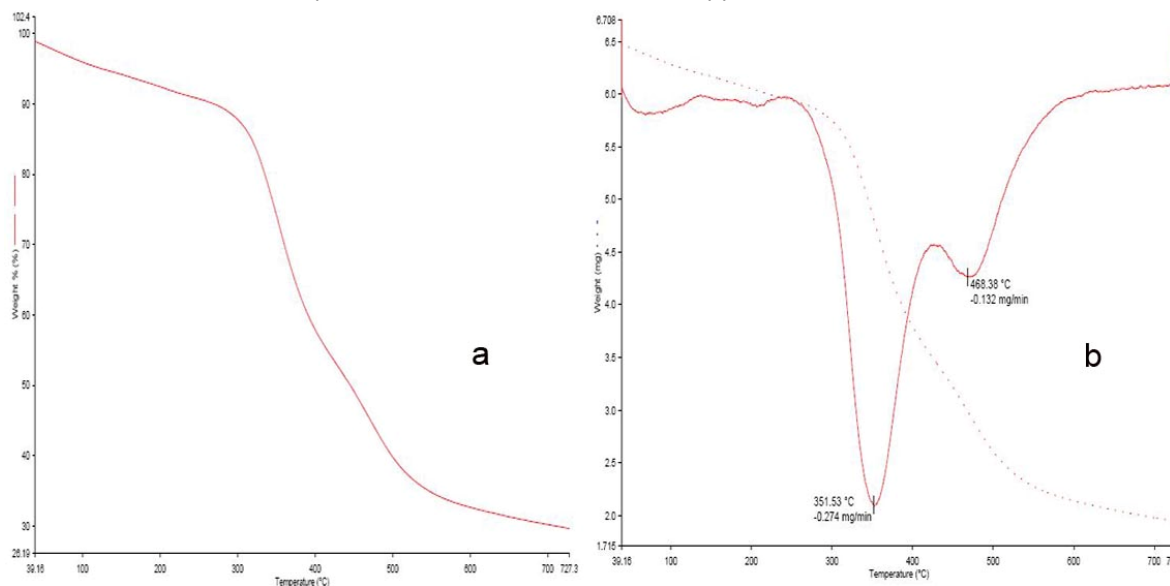


Figure 14: a) TGA of DBTL catalyzed PCF/blocked PMDI resin; b) Derivative weight loss of DBTL catalyzed PCF/blocked PMDI resin

Bonding strength of plywood

The bond strength of the plywood is checked by knife test after required cyclic boil dry test as per IS 848:2006 for boiled water proof (BWP) grade¹⁰. The samples are subjected to six cycles of boil-dry test and the knife test was performed to assess the bond quality of the panels. The test result is given in Table 3. Board ‘CD’ in which

dibutyltindilaurate is added showed better glue strength compared to Board ‘CT’ in which triethylamine is used as a catalyst. Both CD and CT showed good bonding strength than PCF resin bonded plywood. The Blocked PMDI-PCF spread easily on plywood and when coated in the presence of catalysts improved the bond strength of plywood.

Table 3: Cyclic Test Result as Per IS: 848-2006 (BWP Grade)

Board Type	Wood failure (%)
CD	80-90%
CT	70%
CMD	60%

Conclusion

The phenol blocked PMDI resin used in this study is efficiently catalyzed by the addition of triethylamine and dibutyltin dilaurate. Dibutyltin dilaurate catalyzed blocked PMDI resin cured at lower temperature compared to that made using triethylamine. The FTIR studies showed that the DBTL catalyzed the formation of urea and urethane linkages in the hybrid PCF/blocked PMDI resin and the plywood bonded with DBTL catalyzed PCF/Blocked PMDI resin showed good bonding strength. The uncatalyzed blocked resin showed more thermal resistance than catalyzed resin. The DBTL catalyzed blocked resin are less stable than triethylamine catalyzed blocked resin. The TGA analysis also

showed that the PCF/blocked PMDI hybrid resin is thermally more stable than blocked resin alone. The adhesive developed was suitable to manufacture BWP grade plywood which confirmed the IS 848:2006- Specification for synthetic resin adhesive for plywood.

Acknowledgements

The authors are thankful to M/s Bayer Material science, IISC Bangalore and SAIF, CUSAT, Kerala for their timely support.

References

1. A. Pizzi, Advanced Wood Adhesives technology, Marcel Dekker Inc, Newyork, 1994, 132-135
2. A.Despres, A.Pizzi, L. Delmotte, ‘13 CNMR investigation of the reaction in water of UF

- resins with blocked emulsifiable isocyanates', J. Applied Polymer Science., 2006, 99:589-596.
3. Sobhan Niyogi, Sanjay Sarkar, and Basudham Adhikari, 'Catalytic activity of DBTDL in polyurethane formation', Indian Journal of Chemical technology, 2002, 19:333.
 4. Britain J.W., Gemeinhardt P.G., 'Catalysis of the isocyanate-hydroxyl reaction, J Appl Polymer Science.,1960, 4 (11), 207-211.
 5. Smith H A 'Catalysis of the formation of urethanes', J Appl Polymer Science, 1963, 7(1), 85-95
 6. Dow polyurethanes- Amine catalysts role in foam formulations.
http://dowac.custhelp.com/app/answers/detail/a_id/13327/~/dow-polyurethanes---aminecatalysts-role-in-foam-formulations
(accessed on 12 December 2014)
 7. IPIRTI research report, RR.82, 'Partial replacement of phenol with cardanol for the preparation of highly water soluble phenolic resin suitable to bond BWR and BWP grade plywood'.
 8. Product information sheet (issued on 1998), Desmodur 44 V20L, Polyurethane Business group, Order no:PU51204 E, edition no: 3 page:1-3.
 9. Ganesh Gopal T.M, S.K. Nath and Sujatha D., 'Blocking of PMDI resin and mixed phenol blocked PMDI/phenol cardanol formaldehyde hybrid resin for plywood', International Journal of Applied Science, 2014, 1(3), 117-128, www.ijas.org.uk
 10. Anon; Specification for synthetic resin adhesives for plywood (Phenol and amino plastics) Bureau of Indian Standards, IS: 848, New Delhi, 2006.