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Starch based PMDI (Polymeric methyl diphenyl diisocyanate) Adhesives for Plywood

Ganesh Gopal T.M.[1], S.K. Nath[2] , Sujatha D[3], Rangaraju T.S.[4]
[1,2,3,4]*(Indian Plywood Industries Research and Training Institute, Bangalore)*

Abstract: *PMDI (polymeric methyl diphenyl diisocyanate) resin cannot be used for plywood manufacturing through conventional method due to its high reactivity towards active hydroxyl containing compounds. The PMDI adhesives are mixed with starch to control the reactivity and to make its easy application for plywood. The urethane formation between starch and PMDI was confirmed using FTIR. The adhesive was used to make plywood. But the bond strength was not satisfactory. The bond strength was improved by the addition of tannin and hexamine solution. But the bonding was not enough to get satisfactory results as per IS 848-2006. This starch-PMDI adhesive after mixing with tannin and hexamine were admixed with PCF (Phenol Cardanol Formaldehyde) resin and used for manufacturing plywood. The resulting boards were of 'Excellent' grade as per IS 848-2006 for BWP grade.*

Keywords: *PMDI, Plywood, Adhesives, Starch, Tannin*

I. Introduction

In wood panel production the mostly used resins are formaldehyde based resins like phenol, urea and melamine formaldehyde resins which involve the formation of methylol group by the reaction with formaldehyde and condensation of these methylolated monomers to form cross-linked polymer. But in PMDI resins, the resulting product is the urethane group formed by the reaction of NCO group with active hydrogen containing compound (Fig 1).

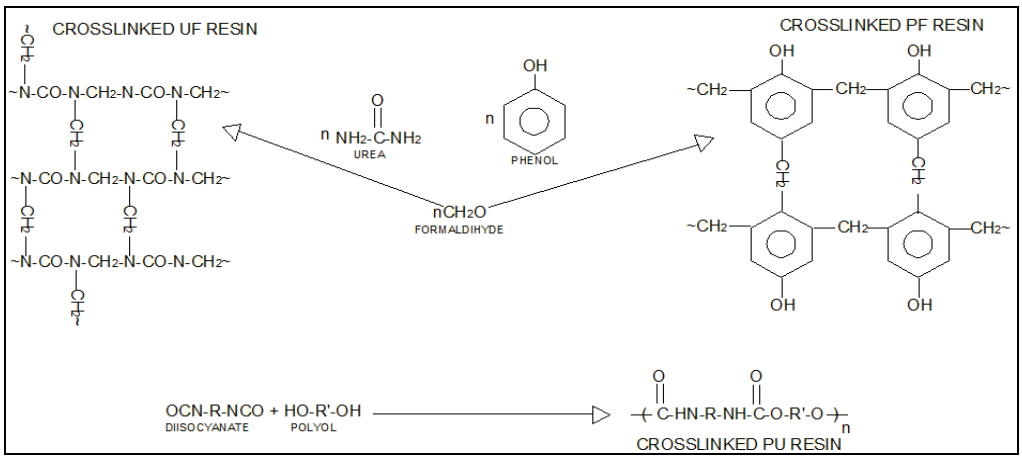

Figure 1 Reactions of Diisocyanate and formaldehyde based resins

The PMDI resins are already proved for manufacturing wood panel products like Particle board, Medium Density Fibreboard etc[1-4]. But its use as an adhesive for plywood manufacturing is limited due to several reasons. They include (1)The equipments used for spreading on to the veneers are very difficult to clean with water, if PMDI resins are used (2) The NCO group in PMDI may react with the hydroxyl group present in wood and the curing starts before the assembly of veneers for hot pressing. (3)The PMDI resin may also stick with the caul plates placed above the boards while pressing which creates further difficulties in taking out the plywood (4) The adhesives used in plywood are mostly aqueous based. But the PMDI cannot be mixed with water due to its high reactivity with water.

The high reactivity of Polymeric methyl diphenyl diisocyanate (PMDI) with water is a drawback for its use as an adhesive for plywood using conventional methods. The reaction of isocyanate with water at room temperature can be made slow, if it is emulsified in a starch solution. The mobility of water molecules was expected to be reduced when they were bound to numerous hydroxyl groups present in starch [5]. The thermal behavior and mechanical properties of starch based polyurethane is improved by the modification with tannin.

Some studies proved that addition of tannin had great effect on the density of cross-linking and morphology of starch polyurethane [6].

Hexamethylene tetramine is a widely used catalyst for tannin based adhesives. Studies showed that in the presence of highly reactive phenols like tannin, with negative charge under alkaline conditions, the curing chemistry of tannin and hexamine is proceeded through the formation of reactive imines and slight amount of imino methylene bases which confirmed that the curing is not through decomposition of formaldehyde and hence do not emit formaldehyde [7].

The addition of Mimosa and Quebracho tannin based adhesives to the corn starch mixed with sodium hydroxide, along with hexamethylene tetramine reduced the viscosity of adhesives and improved the shear strength[8].

In this study, the Polymeric diphenyl methane diisocyanate (PMDI) mixed in starch soluble was studied for using as a suitable plywood adhesive. The bonding of adhesives were also studied by the addition of tannin, hexamine and also by the addition of a two stage phenol cardanol formaldehyde (PCF) resin[9].

II. Materials And Methods

The PMDI resin used was Desmodur 44V20L supplied by M/s Bayer Material science. The potato starch, Sodium hydroxide and hexamine of LR grade were purchased from Merck Millipore. The Tannin used was condensed tannin extracted from *Mimosa Sp.*

2.1FTIR (Fourier Transform Infrared Spectroscopy) of starch-PMDI resin

The FTIR of starch-PMDI resin was studied in the range of 400-4000cm^{-1} using Thermo nicolet avatar 370 from STIC, Kerala. The PMDI mixed in starch was allowed to cure in an electric oven at 102±2^oC for 2 hour and the powdered mixture was characterized using FTIR analysis. The starch solution without the addition of PMDI was also studied.

2.2Preparation of adhesives

2.2.1Adhesive I

In a 500 ml beaker with 50 ml of water, 30 g of starch was slowly added while stirring. After stirring for at least 5 minutes, 40 g of PMDI was slowly added, and stirred well.

2.2.2Adhesive II

The above mixture (Adhesive I) was prepared again and 6g tannin dissolved in 10ml of water was added in to the solution and stirred.

2.2.3Adhesive III

In a 50ml of water, 40g of Starch was slowly added while stirring. The solution was allowed to stir for 5 minutes. The pH of the solution was adjusted to 7.5-8.0 using 30% sodium hydroxide (NaOH). In to this solution 10g tannin and 5g hexamine dissolved in 10 ml of water was added while stirring. 30 g of Desmodur®44V20L was slowly added and stirred well to get a homogeneous solution

2.2.4Adhesive IV

In a 50 ml of water, 20 g of starch was added and stirred well. The pH of the solution was adjusted to 7.5-8.0 using 30% NaOH. About 10 ml of Tannin dissolved in water in the ratio 1:2 was added to the solution. A two stage Phenol Cardanol Formaldehyde resin [9] of 50g prepared in the ratio 1:1.6 was added to the solution while stirring. In to this solution 40g of Desmodur®44V20L was slowly added and stirred well for at least 5 minutes. To this adhesive, 2g hexamine dissolved in 5ml of water was added and stirred just before plywood manufacturing.

2.3Plywood manufacturing

All the adhesives prepared were used to manufacture three ply plywood with silver oak veneers having moisture content 6-8% with an average thickness of 1.5 mm and pressed in a hot press using a press temperature of 150^oC for 7 minutes and subjected to test as per IS 848-2006 [12] to study the bond strength. Three replicate boards were made for each adhesive. The board made with adhesives were denoted as SMDI, STT, STH and STC for adhesive I, II III and IV respectively.

III. Results And Discussions

3.1FTIR of starch-PMDI adhesive

The FTIR of starch alone and starch-PMDI were analyzed (Fig 2 and Fig 3). The starch with the addition of PMDI and without PMDI formed a peak around 3700-3200cm^{-1} and the formation of new peak in

starch-PMDI (Fig 3) other than the hydroxyl peak in starch (Fig 2) is expected to be due to formation of NH stretch in urethane group and 1775 cm^{-1} represents the C=O linkages in urethane group. This confirms the urethane formation in starch-PMDI

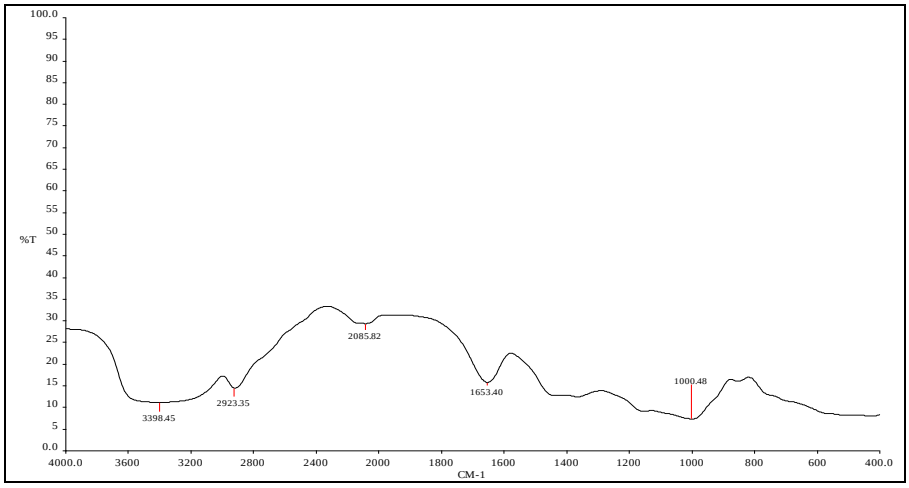

Figure 2 FTIR of starch

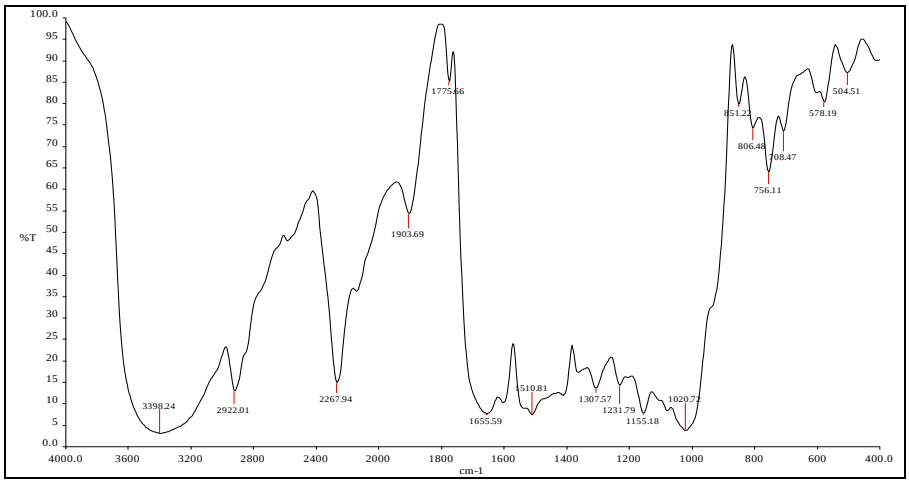

Figure 3 FTIR of Starch-PMDI

3.2 Properties of adhesive

The viscosity and pH of the adhesives are shown in TABLE 1. The addition of tannin reduced the viscosity of starch-PMDI adhesive.

TABLE 1 Properties of Starch-PMDI adhesives

Properties	Adhesive I	Adhesive II	Adhesive III	Adhesive IV
pH	7	6	8	8
Viscosity (cp) at 27^{o}C	90	50	80	80

3.3 Bond strength of plywood

The bond strength of plywood was checked by knife test as per IS 848-2006 [12] after required cyclic boil dry test. The boards SMDI, STT and STH failed to achieve water proof grade. The bond strength of these boards without subjecting to cyclic boil water test was studied. The board denoted as 'STT' in which tannin was added, showed more wood failure than board 'SMDI' without the addition of tannin and also the board 'STH' showed better bond strength than both 'SMD' and 'STT' which could be due to the catalysis of hexamine (Plate 1).

Plate1 Dry Bond strength of SMDI, STT and STH without cyclic test

The board 'STC' which was manufactured using Adhesive IV achieved boiled water proof grade (BWP) with 'excellent' standard as per IS 848-2006 [12]. This may be due to the reaction of methylol groups with isocyanate to form a fine cross linked structure (Plate 2).

Plate 2 Wet bond strength of adhesive IV coated plywood as per IS 848-2006 for BWP grade

3.4 Expected Reaction Mechanisms

From FTIR studies, the formation of urethane from Starch-PMDI is proved. The hydroxyl group present in starch thus formed urethane bond with NCO group in PMDI resin. The reaction of condensed tannin with hexamine proceeds through the formation of benzylamine linkages [7]. As per studies these benzylamine linkages formed are highly stable and are not rearranged to methylene bridges after curing [10]. The NCO group in PMDI resin can also react with hydroxyl group present in tannin to form urethane linkages. The hydroxyl groups in flavanoid B ring in tannin is expected to be more reactive with NCO groups of PMDI to form urethane linkages [11]. The reaction of NCO group with the methylol group present in PCF resin also form urethane linkages. The curing of the phenol cardanol formaldehyde through methylene linkages are also involved. All these reactions result in to a cured structure (Fig 4).

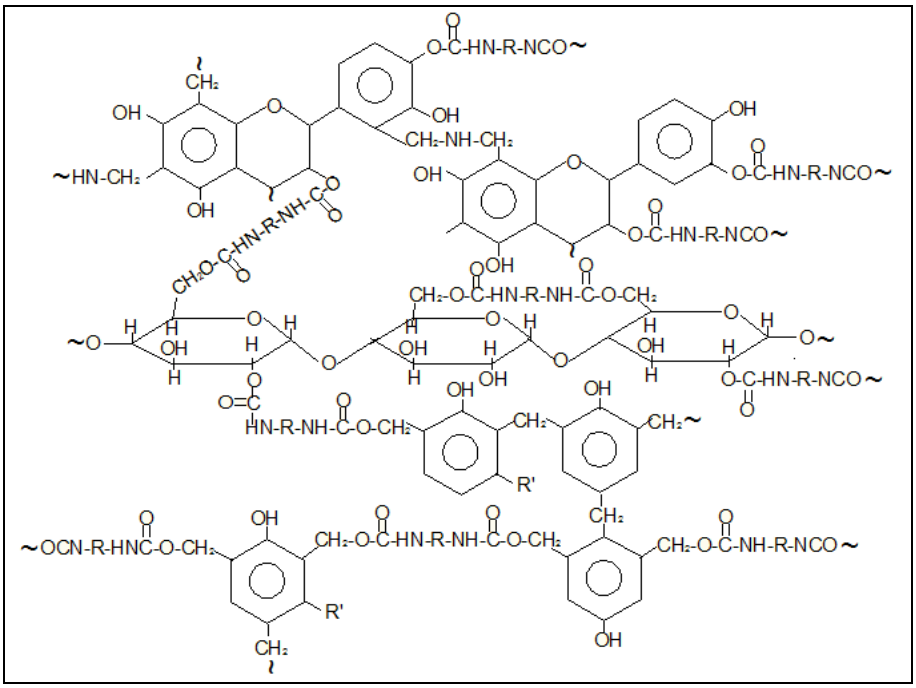

Figure 4 Expected curing reactions for Adhesive IV

IV. Conclusion

The reaction of PMDI with water, when emulsified in starch solution was slow. But the bonding achieved was not enough to attain water resistant grade. When tannin and hexamine was added in to starch-PMDI solution the bond strength was improved, but delaminated when tested as per IS 848-2006 [8]. The FTIR of starch PMDI confirmed the urethane formation.

The bond strength of PMDI resin emulsified in starch when admixed with Phenol cardanol formaldehyde resulted in exterior BWP grade plywood. The viscosity of the adhesive solution was also not increased quickly which helped its easy application for plywood.

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