

Synthesis of Novel Hyperbranched Alkyd Resin from Castor Oil Fatty Amide Polyol and Application in Polyurethane Coating

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Abstract

Abstract A novel hyperbranched alkyd resin has been synthesized using pyrometallic anhydride and castor oil based fatty amide polyol. The chemical properties (acid and hydroxyl values) of the synthesized fatty amide polyol and hyperbranched have been determined. The polyurethanes obtained from hyperbranched alkyd resins were used for coating applications on mild steel and wood. The synthesized hyperbranched alkyd resin was characterized by size exclusion chromatography, NMR, and FTIR. Performance of cured polyurethane coatings in terms of cross cut adhesion, impact resistance, gloss, scratch hardness, and chemical resistance has been studied. The electrochemical properties were studied by potentiostat. The thermal properties of the coatings were determined by thermogravimetric analyzer. Surface morphology of coating films was examined by scanning electron microscopy. Keywords: Hyperbranched alkyd resin, castor oil, fatty amide polyol, polyurethane, coating

Introduction:

Hyperbranched polymers possess unique properties such as highly branched structure, and excellent flow property. Also, the synthesis of HBPs are cost effective than dendrimers synthesis. Therefore many coating industries are turned toward the hyperbranched polymers for coating applications.[1-4] Hyperbranched polymers can possess various kinds of reactive end groups such as hydroxyl, amine, acid, halides etc. therefore they impart the special characteristic properties to substrate.[5] Many polymer researchers have focused on the biobased hyperbranched polymers. There are many natural resources such as vegetable oil, shellac, gum, carbohydrates etc which can be used in coating purpose.[6,7] Among these, vegetable oils are cheap and abundance in nature. Due to this researchers are taking interest in use of various vegetable oils for development of coating materials.[8,9]

Alkyd resins are polyesters modified with unsaturated fatty acids.[10] Alkyd resins are the most widely used polymers for paint and coatings applications.[11,12] They encompass good wetting, mechanical properties and durability.[13] As compared to the linear alkyd resins hyperbranched resin possesses a number of improvements along with same molecular weight, such as lower viscosity, higher gloss, better chemical resistance, and less chemical drying time.[14,15]

Now a day polymer researcher has focused on applications of hyperbranched polymers in coating applications. Bat et al. studied the synthesis of hyperbranched alkyd resins based on a hydroxylated hyperbranched polyester obtained from dipentaerythritol and 2,2-bis(hydroxymethyl) propanoic acid. [16] Karak et al studied highly branched polyester resin prepared from Mesua ferrea L. seed oil.[17] Kuga et al. studied the coating properties of nanocomposite which were prepared from hyperbranched alkyd and magnetite-silica.[18] R. Baloji Naik et al. reported the effect of carbon nanofillers on anticorrosive and physico-mechanical properties and antimicrobial coating application of hyperbranched urethane alkyd.[19,20] Also, R. Baloji Naik et al. prepared moisture-cured hyperbranched urethane alkyd resin for coating applications.[21] Sharif et al. studied the hyperbranched soya alkyd nanocomposites for anticorrosion coating properties.[22] Mansour et al.

synthesized and characterized hyperbranched alkyds for coating applications.[14] Ikladios et al. synthesized alkyd resin from waste PET and hyperbranched polyester for coating applications.[23]

In the present work, we have reported a novel hyperbranched alkyd polymer which was prepared from pyrometallic anhydride and fatty amide of castor oil. The prepared resin was converted into polyurethanes using isophorone diisocyanates and methylene diphenyl diisocyanate. Further coating properties of the samples were studied.

Material

Castor oil was obtained from Merk, India. Sodium methoxide, sodium chloride and diethanol amine were obtained from s.d. fine. Ltd. Pyrometallic anhydride, methylene diphenyl diisocyanate (MDI) and isophorone diisocyanates (IPDI) were obtained from the Sigma Aldrich, India. The solvents diethyl ether, methyl ethyl ketone (MEK) and xylene obtained from Loba Chemicals, India. All the chemicals were used without purification.

Experimental

Synthesis of fatty amide from castor oil

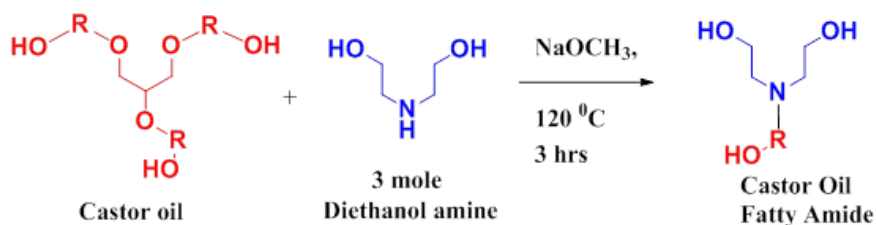
Fatty amide was synthesized by using procedure somewhere used[24]. Castor oil fatty amide was prepared by reaction with diethanolamine (0.32 M) in the presence of sodium methoxide (0.007 M) as a catalyst in a 250 mL three-necked round bottom flask. The flask was placed in an oil bath and fitted with an overhead stirrer, thermometer, dropping funnel, and condenser. The three-necked flask was stirred at 80°C for 20 min in the presence of N₂ atmosphere. Castor oil (0.1 M) was then added drop by drop into the reaction mixture over 60 min with constant stirring and a steady increase in temperature up to 120°C. The reaction mixture was then heated for the next 3 h with continuous stirring at 120°C. Product formation was verified by thin layer chromatography (TLC). Cooled product was dissolved in diethyl ether, washed with 15% aqueous NaCl solution, and dried over anhydrous sodium sulfate. The solvent was evaporated in a rotary vacuum evaporator to obtain fatty amide.

Synthesis of hyperbranched alkyd resin

The calculated amount of pyrometallic anhydride (1.18 g, 0.1M) and fatty amide (14 g, 0.45 M) were charged in three necked round bottom flask fitted with mechanical stirrer, dean-stark apparatus and nitrogen gas inlet in xylene as an azotropic solvent. The reaction as carried at temperature 160 °C to 180 °C until the acid value reached below ten.

Preparation of polyurethane coatings from alkyd resin

Polyurethane coatings were prepared by using hyperbranched alkyd resin and cross linker diisocyanates (IPDI and MDI) in xylene/MEK (3:1 v/v) solvents. The ratio of OH: NCO was kept 1:1.2 for all PU coatings. The prepared coating material was applied on mild steel panel and wood plates. After curing the plates were kept in vacuum oven at 45°C for 40 min to evaporate the solvent. The PU-coating prepared by IPDI and MDI were represented as PMFAI and PMFAM respectively.



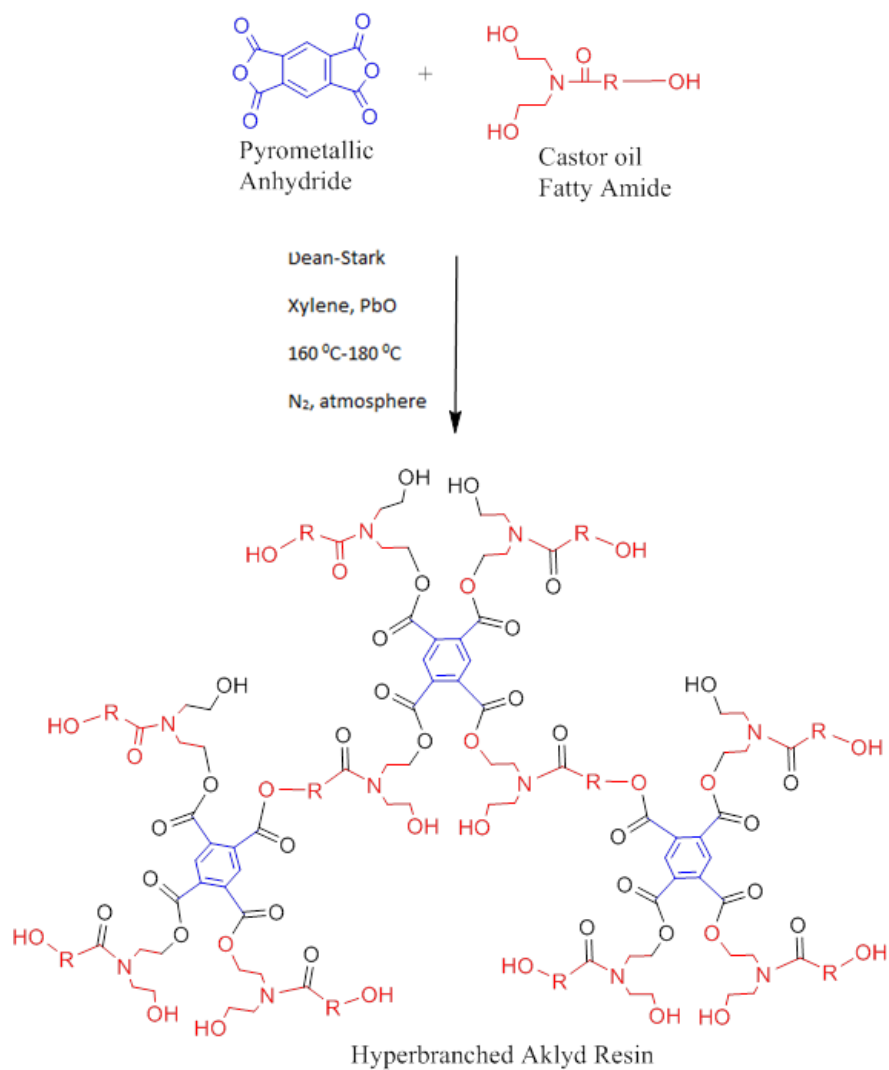


Figure 2 Synthesis of hyperbranched alkylid resin

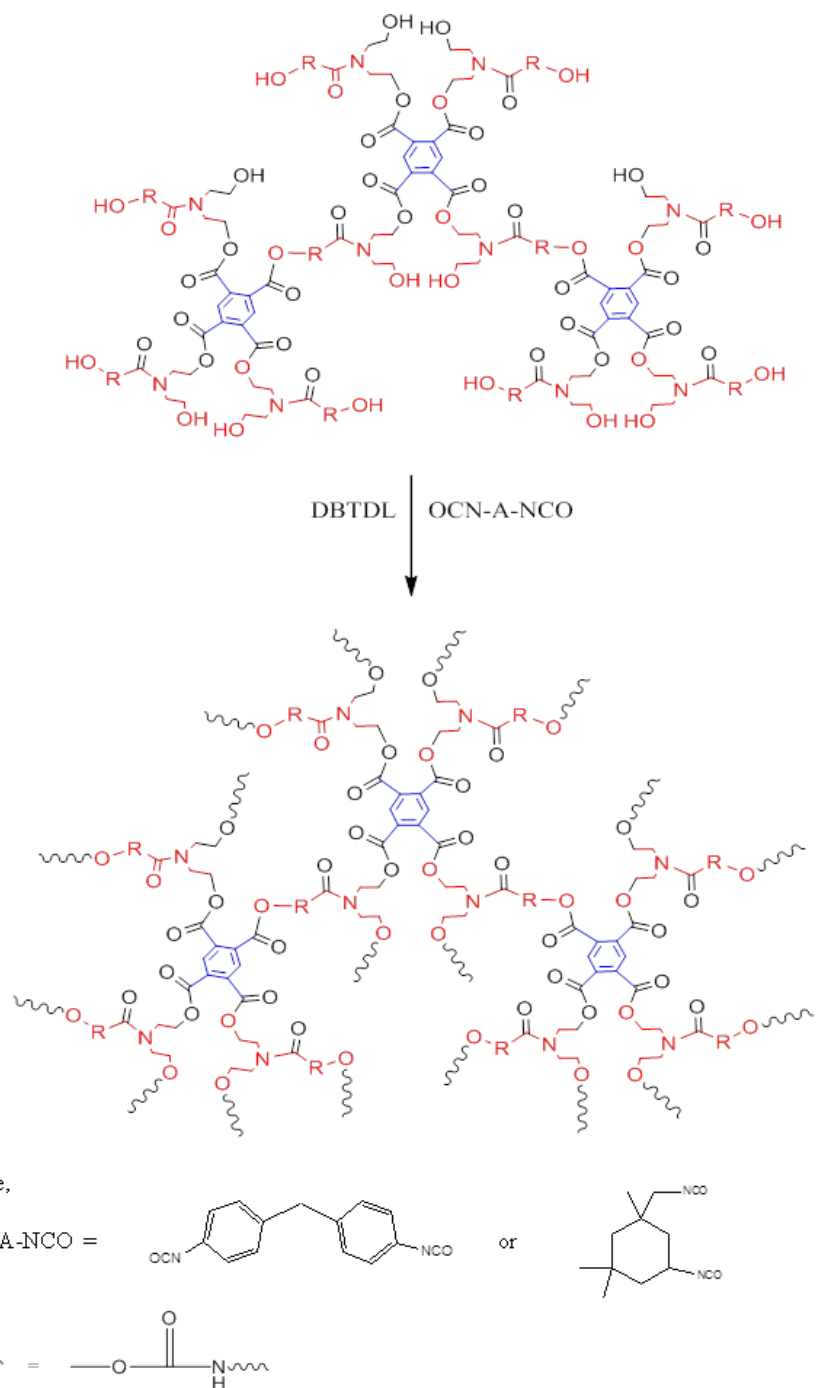


Figure 3 Synthesis of polyurethanes from hyperbranched alkyd resin

Characterization:

End group analysis

The end group analysis of the hyperbranched resin such as acid value (ASTM D 1980) [25] and hydroxyl value (ASTM D2849)[26] determined for polyurethane preparation.

Size exclusion chromatography

The molecular weight of PMFA was determined by size exclusion chromatography (SEC) technique (Waters Corporation, USA). The instrument was calibrated by styrene. The sample was run with solvent tetrahydrofuran (THF) with 50 μ l injection volume for 15 min.

Spectroscopic study

The functional groups of synthesized hyperbranched resin were recorded by FTIR (Nico-let 360) using KBr pellet at wavelengths ranging from 4000 to 400 cm^{-1} . The structure of hyperbranched resin was recorded by NMR (Bruker 400 MHz NMR spectrometer) in d_6 -DMSO solvent and trimethyl silane (TMS) as standard.

Coating properties

Crosshatch adhesion test

According to the ASTM D 3359, crosshatch adhesion test[27] was performed for the coatings. The crosshatch cutter, which has 11 blades, was used for to make a lattice pattern of hundred squares on the mild steel surface. Cellotape was applied over the lattice. The tape was pulled off rapidly after one minute at an angle of 180°. Visual verification at that time was used to calculate the percentage of squares removed from crosscut panels with respect to the total initial number present.

Impact resistance

The impact resistance was determined by tubular impact tester (SHEENREF804) according to ASTM D 2794. [28] The tubular impact tester is loaded with an intender, weight of 1.35 lbs which was dropped from the certain height starting from 5 inch and ending at 100 inch until the film under goes deformations like peeling, cracking, and film detachment. Impact resistance was calculated by multiplication of weight of intender and height.

Scratch resistance test

The scratch resistance test was performed by scratch resistance test tool (Elcometer 3000) according to ASTM D 7027. In this method include various types of loads which are ranges from 0 to 5 kg.

Pencil hardness test

Pencil hardness was determined by the ASTM D 3363. In this test pencil hardness tester (Elcometer 501) was used with various grades of pencils. The hardness of pencil ranges from soft to hard (6B to 6H). Pencils of various grades of hardness were moved over the coated surface at an angle of 45° to the horizontal with a force so that did not rupture or scratch the coating.

Stain test

Stain test of coatings was performed according to ASTM D 3023. The coatings were applied onto wood substrate (3 × 3 inch). Different stain was applied on coatings and covered with filter paper for 24 h, they were washed with water and then ethanol.

Thermal analysis

The thermal study was carried by thermogravimetric analysis (Shimadzu TGA-50) in a nitrogen atmosphere at rate of heating 10⁰C min⁻¹.

Immersion test

The immersion test was determined on coated mild steel plates according to ASTM D 6943. The coated mild steel plates had been allowed to dry for 3 days. The plates were immersed in 2N NaOH, 2N H₂SO₄, xylene, and water. Any changes in appearance were observed visually after each 24 h up to 168 h.

Electrochemical Property

The electrochemical study of the coatings was carried on a potentiostat (Autolab, PGSTAT101, Metrohm India Ltd). The potentiostat was with three electrodes such as platinum mess as a counter electrode, Ag/AgCl in KCl solution as a reference electrode and coated metal as a working electrode. The exposed surface area of working electrode (bare and coated substrate) was 1 cm². The electrochemical properties like corrosion current, corrosion potential and corrosion rate was determined in 3.5 % NaCl as electrolyte using the scanning rate 0.5 mV/s.

Surface morphology of coatings

The surface morphology of PMFAI and PMFAM coating films was studied by field emission scanning electron microscopy (FESEM) (Hitachi, S-4800 II).

Results and Discussion

End group analysis

Acid and hydroxyl value of the synthesized hyperbranched polymer found to be 9.1 and 147.31 mg of KOH per gram of sample respectively.

Size exclusion chromatography

The molecular weight of the synthesized hyperbranched PMFA was determined from the chromatogram shown in Figure 4. According to SEC graph weight average molecular weight (M_w) and number average molecular weight (M_n) of hyperbranched PMFA was 5322 and 5106 dalton, respectively. The distribution of the polymer is measured by the polydispersity index, which is 1.04, it indicates the narrow distribution of polymeric molecular weight.

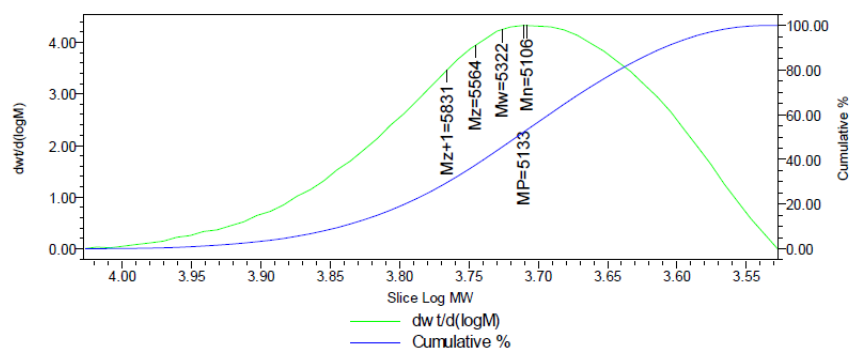


Figure 4 Size exclusion chromatography

FTIR and NMR study

FTIR spectra of the hyperbranched PMFA shows the peaks at 3412.08 cm⁻¹ corresponds to -OH stretching, 2929.87 corresponds to -C-H stretching cm⁻¹, 2864.29 cm⁻¹ corresponds to -N-H stretching , 1728.22 cm⁻¹ corresponds to carbonyl group stretching, 1643.35 cm⁻¹ corresponds to amide group stretching, 1446.61 cm⁻¹ corresponds to N-H bond stretching, 1253.73 cm⁻¹ corresponds to C-N bond stretching.

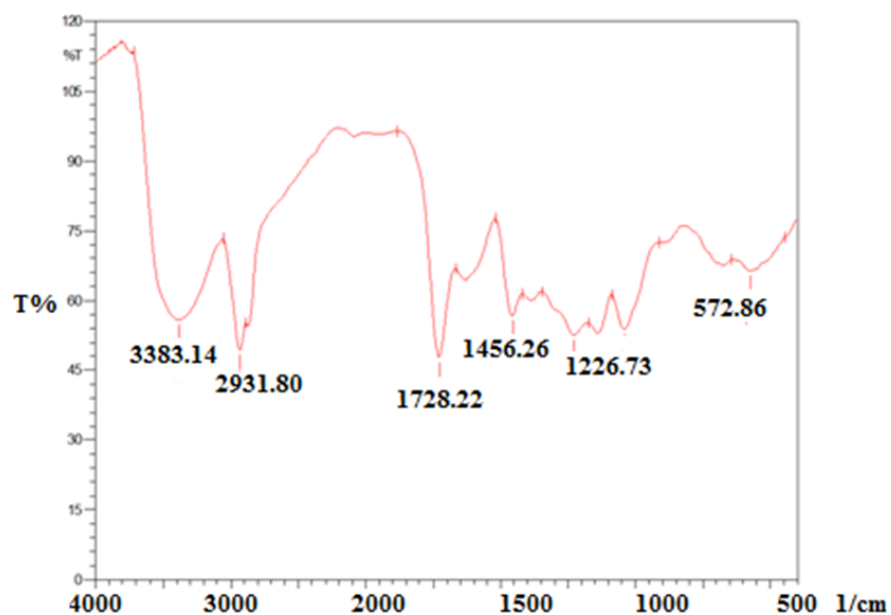
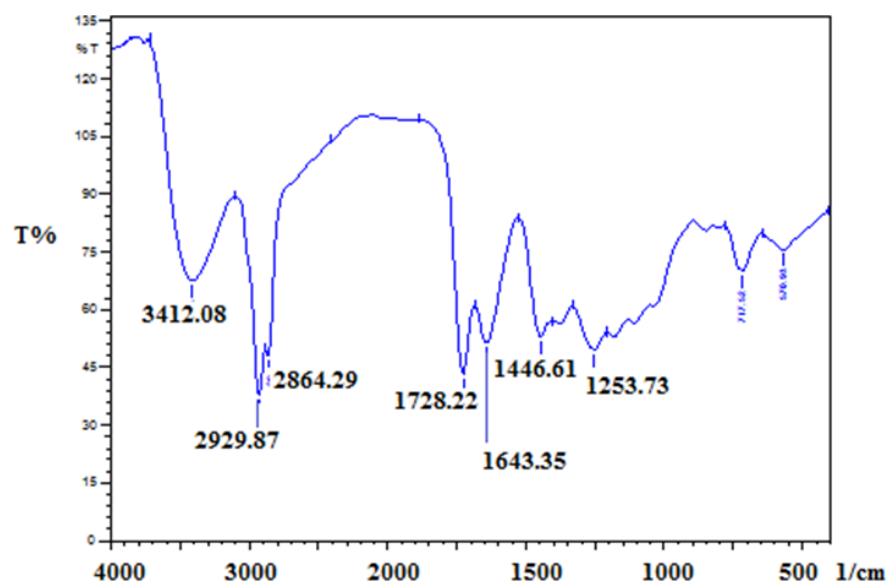


Figure 5 FTIR of fatty amide



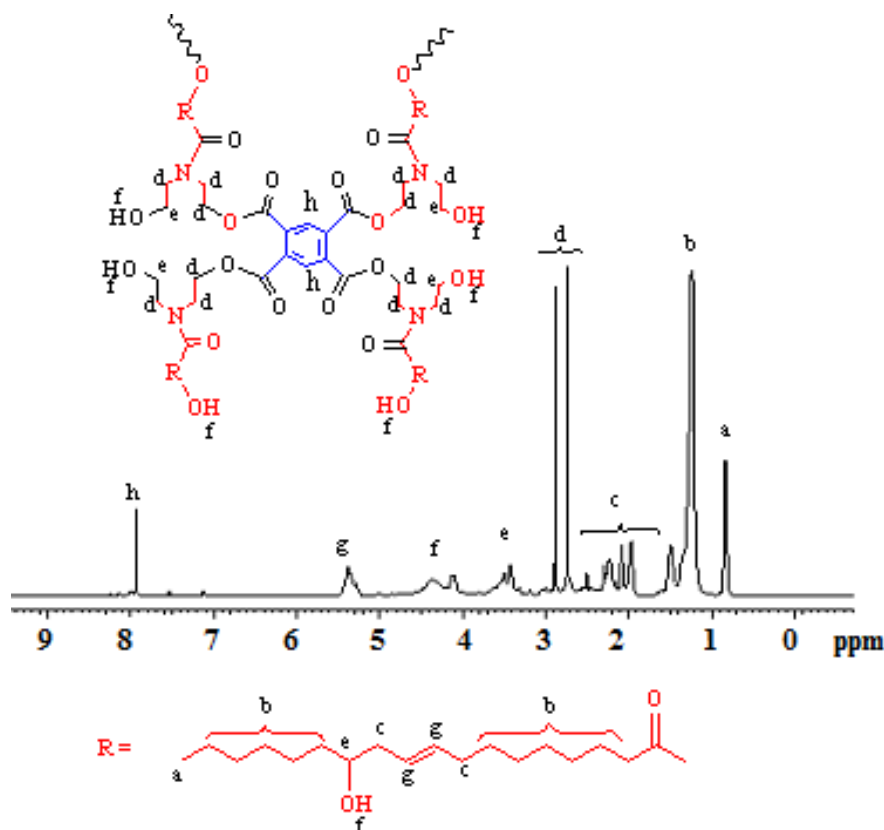


Figure 7 ^1H NMR spectra of hyperbranched alkyd resin

NMR spectra are useful for the structural determination of hyperbranched PMFA. The peak obtained at 0.9 ppm related to terminal $-\text{CH}_3$, 1.2 ppm corresponds to $-\text{CH}_2$ chain in castor oil. The multiplet at 2.0 ppm to 2.4 ppm associated to $-\text{CH}_2$ group attached to $\text{C}=\text{C}$ and $\text{C}=\text{O}$ moieties. The peak at 2.8 ppm correlated to $-\text{CH}_2$ group attached to nitrogen and peak at 3.0 ppm corresponds to $-\text{CH}_2$ group attached to oxygen in fatty amide. The peak obtained at 3.5 ppm related to $-\text{CH}$ attached to hydroxyl group. The peak obtained at 4.3 ppm to 4.5 ppm due to the $-\text{OH}$ group. The peaks obtained at 5.4 ppm and 7.8 ppm corresponds to alkenes and aromatic protons in hyperbranched polymers respectively.

Coating properties

The coating properties of the polymer samples were performed on mild steel panels. The gloss of PMFAI coating is higher than the PMFAM because PMFAI containing large number of CH_2 group which reflect the light while in PMFAM contain aromatic ring which are responsible for light absorption. The mechanical properties like cross cut adhesion, impact strength, pencil hardness, and scratch resistance were found excellent in PMFAM. This may due to higher cross linking in coating. Along with this, PMFAM have aromatic rings which interact with iron of mild steel. All coatings illustrated the good flexibility due to the presence long chains.

Table 1 Coating performance of coated mild steel panels

PU-Resin	PU-Resin	PU-Resin
Coating properties	PMFAI	PMFAM
Gloss at 60°	120.6	76.4
Cross cut Adhesion (%)	0	100

PU-Resin	PU-Resin	PU-Resin
Impact strength (Ib.in)	74.3	94.5
Pencil hardness	2H	6H
Scratch resistance in Kg	0.5	1.5
Flexibility	pass	pass

Stain test

Stain tests of hyperbranched coatings onto wood substrate was carried out according to ASTM D 3023 with mustard oil, permanent ink, ball-point ink, washable ink, wax, hair oil, sauce, shoe polish, and tincture of iodine. The coating showed excellent stain resistance due to the presence of long alkyl chain of fatty amide and also due to the highly cross linked network.

Table 2 Stain test of coatings on wood

Coating Sample	Mustard oil	Permanent Ink	Ball-point Ink	Washable Ink	Wax	Hair oil	Sauce	Shoe polish	Ti
PMFAM	5	4	4	5	5	5	4	2	1
PMFAI	5	5	5	5	5	5	5	4	4
Stain	Stain	Stain	Stain	Stain	Stain	Stain	Stain	Stain	Stain
resistance	resistance	resistance	resistance	resistance	resistance	resistance	resistance	resistance	resistance
of coatings is	of coatings is	of coatings is	of coatings is	of coatings is	of coatings is	of coatings is	of coatings is	of coatings is	of coatings is
rated	rated	rated	rated	rated	rated	rated	rated	rated	rated
from	from	from	from	from	from	from	from	from	from
1-5, 1	1-5, 1	1-5, 1	1-5, 1	1-5, 1	1-5, 1	1-5, 1	1-5, 1	1-5, 1	1-5, 1
= poor	= poor	= poor	= poor	= poor	= poor	= poor	= poor	= poor	= poor
and 5	and 5	and 5	and 5	and 5	and 5	and 5	and 5	and 5	and 5
=	=	=	=	=	=	=	=	=	=
excellent	excellent	excellent	excellent	excellent	excellent	excellent	excellent	excellent	excellent

Immersion tests

In immersion test was carried in 2N HCl, 2N NaOH, 3.5% NaCl, water, and xylene for 7 days (168 h) tolerance. All coatings have ester and urethane moiety. These moieties are very reactive towards the acid as well as alkali. The reaction results in breaking of ester and urethane bonds present in coatings films. Due to this there are some defects on coatings in terms of loss in gloss, cracks on, film etc. The observations are given following Table 3. PMFAI coating shows excellent anticorrosion property as compared to PMFAM. This is attributable to the presence of aliphatic as well as oil chain, and higher crosslink in coating.



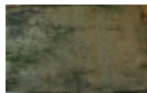

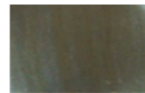


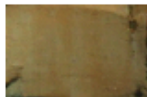
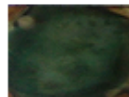

Sample	2N HCl 7 days	2N NaOH 7 days	3.5 % NaCl 7 days	Water 7 days	Xylene 7 days
PMFAM					
PMFAI					

Figure 8 Images of immersion test

Table 3 Immersion test of coatings

Sample	2N HCl
PMFAM	a
PMFAI	a
a = loss in gloss, b = film swells, c = slightly cracks, d = film partially removed, and e = unaffected	

Electrochemical Study

Electrochemical property of the coating materials was studied by the electrochemical polarization technique. This technique is three electrode system, in which coated mild steel used as a working electrode, Ag/AgCl as used a reference electrode and platinum wire as used a counter electrode. Electrochemical test carried in potential range of -1V to +1 V with rate of 0.01 V/s, in 3.5% NaCl electrolyte solution. The corrosion potential and corrosion rate of blank panel was obtained at -819.4 V and 34.9×10^{-2} mm/year respectively, PMFAI coating showed the corrosion potential and corrosion rate at -412.7 V and 3.1×10^{-3} respectively, while PMFAM coating showed the corrosion potential and corrosion rate at -396.6 V and 1.1×10^{-3} correspondingly. PU coating PMFAM showed the better corrosion rate as compared to PMFAI. These results are endorsed to the presence of high degree of branching, higher extent of polymerization, and better cross-linking density in HBPs.

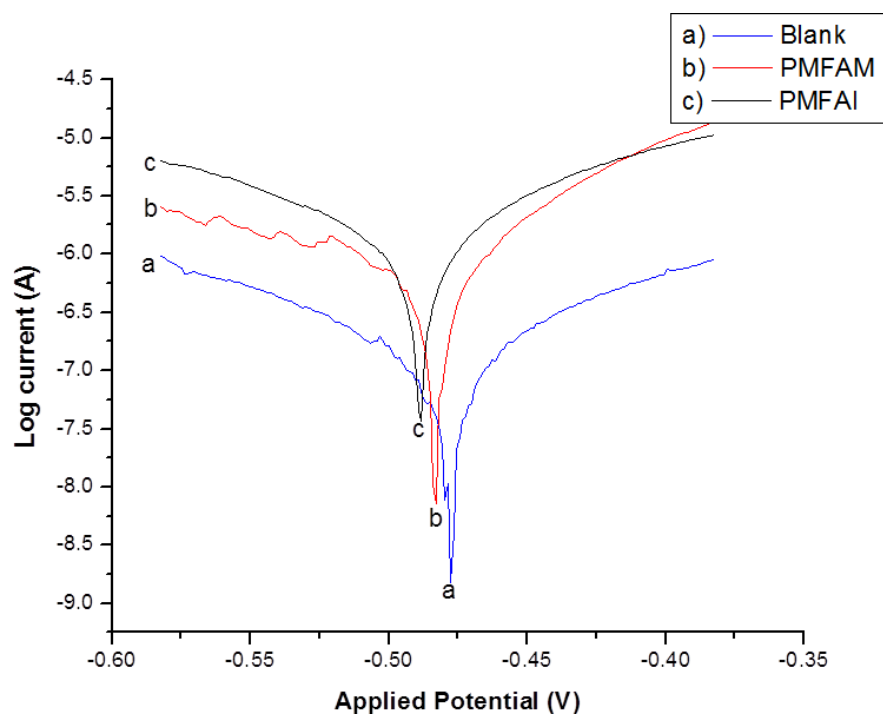


Figure 9 Tafel plot of coatings

Table 4 Electrochemical properties of coatings

Sample code	Electro chemical Parameters	Electro chemical Parameters	Electro chemical Parameters
	E_{corr}(V)	I_{corr} (A/cm²)	Corrosion rate (mm/year)
Blank	-819.4	30.0	34.9×10^{-2}
PMFAI	-412.7	270.7	3.1×10^{-3}
PMFAM	- 396.6	100.8	1.1×10^{-3}

Thermal study

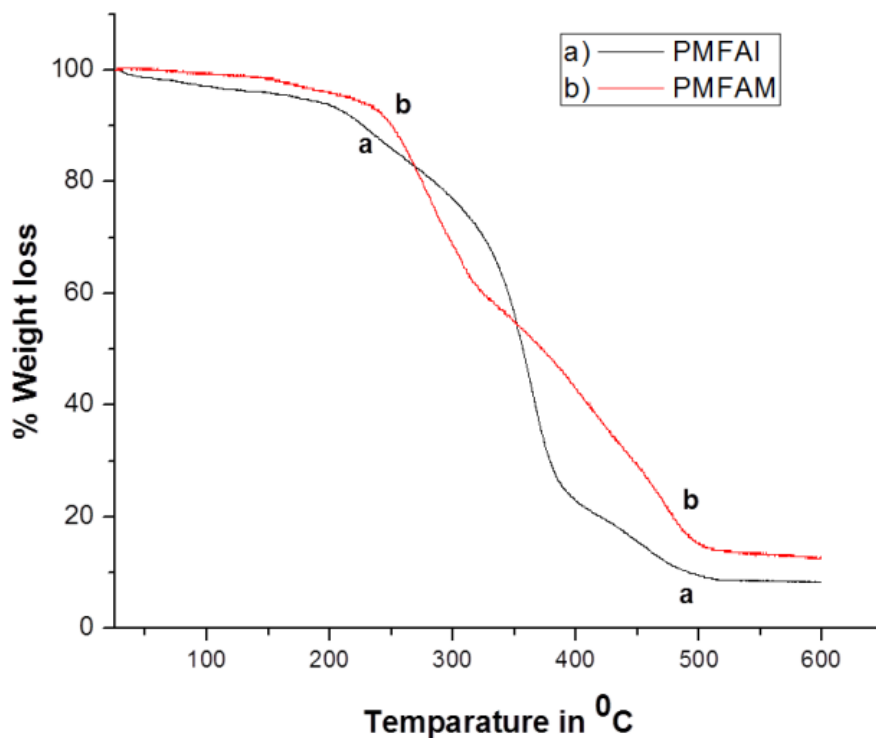


Figure 10 Thermogravimetric analysis of coating films

Thermogravimetric analyzer (Shimadzu TGA-50) was used to record the thermal behavior of prepared PMFAI, and PMFAM coatings. The range of temperature was between 25 to 600 °C with heating rate of 10 °C/min in N₂ as an inert atmosphere. The TGA graph indicates the thermal stability of both PMFAI, and PMFAM coatings. The 10 % and 50 % weight loss in PMFAI at temperature 224.2 °C and 356.5°C respectively. While in, PMFAM, 10 % and 50 % weight loss obtained at temperature 248.9 °C and 370.2°C. This is due to PMFAI has aliphatic ring and PMFAM has aromatic ring in back bone chain. Aromatic rings are more thermally stable because they have *pi* bond interaction with other ring due to this it requires more temperature for segmental motion in polymer. Therefore, PMFAM shows higher thermal stability. Also, the presence of hyperbranched structure crosslink density is more which affects on the thermal stability.

Table 5 Thermal Properties of coatings

Thermal decomposition of coatings	Thermal decomposition of coatings	Thermal decomposition of coatings
Weight % thermal decomposition of polymer at different temp.	T ₁₀ °C	T ₅₀ °C
PMFAI	224.2	356.5
PMFAM	248.9	370.2

Surface morphology of coatings

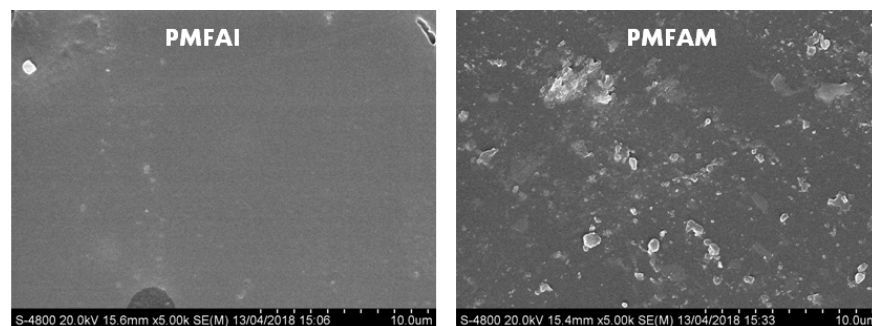


Figure 11 SEM images of coating films

Above image shows the morphology of the coating films. Image of PMFAI film showed the homogeneous and smooth surface due to the proper distribution of hard and flexible segments. Image of PMFAM showed the rough and inhomogeneous surface. Due to the high reactivity of MDI hard and flexible segments were not distributed properly.

Conclusion

Novel hyperbranched polyol from castor oil fatty amide and pyrometallic anhydride was synthesized successfully. Molecular weight distribution of the hyperbranched polyol was determined by the size exclusion chromatography. With help of FTIR, NMR and size exclusion chromatography structure of polyol is confirmed. Polyurethanes PMFAI and PMFAM were prepared and coated on mild steel and wood panel. PMFAM revealed the better coating properties as compared to PMFAI. Electrochemical properties of PMFAM exhibit better corrosion resistance than PMFAI. Thermal stability of PMFAM was more as compared to PMFAI. Stain test performed on wood coated panel, all coating shown excellent stain resistance property.

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