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Polyurethane coatings based on biomass resources

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ABSTRACT

Polyurethane resins are largely used in high performance Surface Coatings, Paints and Inks. Fast reduction of petroleum stockpile and increase in their cost, puts limit to their use in future for invention of petroleum based resins. As a result, the need for consumption of biomass resources as a replacement to petrochemicals products is vital. In the present work, the utilization of biomass resources is done in the preparation of polyurethane coatings. Lignocellulosic waste comprising of Mast Seed and Water Hyacinth waste were liquefied using PEG (200,400 and 600) in presence of acid Catalyst. The various low molecular weight liquefied waste biopolyols obtained were evaluated for their characterization like hydroxyl value, viscosity and FTIR. The series of Polyester biopolyols were prepared from these different low molecular weight liquefied waste biopolyols by reacting them with Adipic acid and propylene glycol, and were characterized for their Physico-chemical properties. Polyurethane coating systems were formulated by reacting Polyester biopolyols and aromatic diisocyanate adduct. Coated films of PU are found to have best Physico-chemical and performance properties.

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KEYWORDS

Biomass resources;
Cellulosic polyols;
Biopolyols;
Polyurethanes.

INTRODUCTION

Fossil fuel reserves could sustain our current energy needs well into the future: but at what cost? The search for renewable forms of energy that emit less greenhouse gases relative to fossil fuels is likely to be a major challenge for the next generation of scientist and engineers. The alternate energy production from low carbon sources such as photovoltaic solar, wind, geothermal, biomass and hydroelectric will require parallel development of various renewable energy sources.

Lignocellulosic biomass represents a renewable,

abundant and cheap source of raw materials for the chemical industry to develop biofuel, chemicals and biomaterials. The lignocellulosic whole materials have generally several benefits such as the decreased wear of machinery used, low cost, biodegradability and absence of toxic byproducts. A major limitation to the use of lignocellulosic material as a chemical feedstock is structural and chemical variety of its components. Liquefaction of lignocellulosic biomass to obtain liquefied products under mild conditions using polyhydric alcohol as solvent has been studied intensively by several authors^[1,2]. Liquefying materials such as such as

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polyhydric alcohols,^[3] phenol^[4] ethylene carbonate^[5] dioxane^[6] ethanol^[7], acetone^[8], supercritical phenol^[9] and supercritical alcohols^[10] are reported in the literature. Liquefaction produces multifunctional liquid polyols rich in hydroxyl groups which can be used as starting materials in polymer products for several coating, foam and adhesive segments. Recently, scientific interest in applying liquefaction using polyhydric alcohols to other bioresources has grown. Following this trend, several Lignocellulosic residues (based on Mast Seed and Water Hynth) have been successfully modified using polyethylene glycol (200,400 and 600) and Polyester biopolyols were prepared by using above biomass polyols with adipic acid and propylene glycol. High performance Polyurethane coating systems were developed by reacting Polyester biopolyols with aromatic diisocyanates. The encouraging results obtained by these authors justify the interest in exploring the preparation of low-cost polyols from lignocellulosic agro-industrial residues.

EXPERIMENTAL

Materials & methods

Lignocellulosic wastes, Mast Seed and Water Hynth were procured locally and treated in our laboratory. Polyethylene Glycol (PEG-200,400 & 600), Propylene glycol, Adipic acid, DBTDL were procured from Chitichem Corporation, Baroda. Aromatic Isocyanates adduct were received from Marigold Paints Pvt Ltd, Vithal Udyog Nagar, Gujarat, India.

TABLE 1 : Physical Properties of Glycols

Sr. No.	Glycols	Mol. Wt. (M _w)	Density g/cm ³
1	PEG-200	190-210	1.124 @ 20 °C
2	PEG-400	380-420	1.128 @ 20 °C
3	PEG-600	570-630	1.12 @ 20 °C
4	Propylene Glycol	76	1.036

Synthesis

Preparation of low molecular weight liquefied waste biopolyols.

The Lignocellulosic wastes (Mast seed and Water

Hynth) were dried to < 1% Moisture content using an oven drier at 100°C (± 5°C) for 24 hrs. Then it is milled to uniform size and was mixed with PEG in the ratio of (1:3). Sulfuric acid was added as a catalyst of 2% by weight of charge. The charge is heated at 150-180°C for 2-3hrs. there after the dissolute (Liquid Waste) and residues were separated by a nylon filter cloth. Finally liquefied waste was collected, characterized and used for synthesis of Polyester biopolyol.

Synthesis of polyester biopolyols.

A series of hydroxyl-terminated polyester biopolyols were synthesized from above prepared low molecular weight liquefied waste biopolyols (MPG-2, MPG-4, MPG-6 and WPG-2) along with Adipic acid and propylene glycol (as per TABLE 2) in the three-neck flask equipped with thermometer, inert gas spurge, dean and stark and condenser. All the materials were charged along with xylene and were heated at 220°C and maintain at that temp. Acid value was measured at half an hour interval throughout the reaction. When acid value reach below 15, heating was stopped and xylene was distilled off using vacuum distillation.

Characterization of polyester biopolyols.

The Polyester biopolyols (MPG-2PE, MPG-4PE, MPG-6PE and WPG-2PE) prepared as above are free flowing liquids, as similar to the conventional polyols (NPE). Various characteristics of these Polyester biopolyols were determined as per the standard methods. Thus the properties like Non Volatile Contents (%), Color and Clarity, Viscosity [Brookfield viscometer, RV-II (cPs)], Density (wt /ltr.) and Hydroxyl value were determined. These Polyester biopolyols were also characterized by instrumental methods like IR-Spectroscopy and Gel Permeation Chromatography (GPC).

The IR spectras were scanned by FTIR Spectrometer, Spectrum GX, Perkin Elmer, series-200.

The GPC chromatograms were scanned by HPLC machine (GPC mode), Perkin Elmer, Series-200. Tetrahydrofuran was used as a mobile phase, flow rate was 1ml/min and run time was 15 minutes.

COATING COMPOSITIONS

Two component polyurethane coating compositions formulated from different Polyester biopolyols are

TABLE 2 : Preparation of Polyester biopolyols

Ingredients	Muster seeds			Water Hynth	Pure Polyester Resin
	MPG-2PE	MPG-4PE	MPG-6PE	WPG-2PE	NPE
Adipic acid	38.77	35.82	27.71	37.90	45.20
Propylene glycol	57.93	49.04	41.41	56.63	67.53
MPG-2	22.86	0	0	0	0
MPG-4	0	36.24	0	0	0
MPG-6	0	0	47.41	0	0
WPG-2	0	0	0	24.82	0
Neopentyl Glycol	0	0	0	0	13.41
Total	119.56	121.1	116.53	119.35	126.14
Water of Reaction	9.5	8	7	9.5	11
Net Weight	110.06	113.1	109.53	109.85	115.14
Xylene for Reflux	11	11	11	11	11
DBTDL	0.08	0.08	0.08	0.08	0.09

MPG-2PE = Mast Seed reacted with PEG-200 polyester; MPG-4PE = Mast Seed reacted with PEG-400 polyester; MPG-6PE = Mast Seed reacted with PEG-600 polyester; WPG-2PE = Water Hynth reacted with PEG-200 polyester; NPE-PE = Neopentyl glycol based polyester.

shown in TABLE 3. All the coating compositions were formulated by mixing weighed quantities of polyols and aromatic isocyanate adduct. Isocyanate content of the adduct is 13%.

TABLE 3 : Composition of Polyurethane Coatings

Sr. No.	Code of PU	OH : NCO	% Wt. Composition	
			Polyol	Isocyanate
1	MPG-2PEAr110	1:1.0	52.02	47.97
2	MPG-2PEAr115	1:1.1	49.64	50.35
3	MPG-2PEAr120	1:1.2	47.47	52.52
4	MPG-4PEAr110	1:1.0	55.70	44.29
5	MPG-4PEAr115	1:1.1	53.34	46.65
6	MPG-4PEAr120	1:1.2	51.17	48.82
7	MPG-6PEAr110	1:1.0	60.37	39.62
8	MPG-6PEAr115	1:1.1	58.07	41.92
9	MPG-6PEAr120	1:1.2	55.93	44.06
10	WPG-2PEAr110	1:1.0	52.16	47.83
11	WPG-2PEAr115	1:1.1	49.77	50.22
12	WPG-2PEAr120	1:1.2	47.60	52.39
13	NPE-PEAr110	1:1.0	49.80	50.19
14	NPE-PEAr115	1:1.1	47.42	52.57
15	NPE-PEAr120	1:1.2	45.26	54.73

APPLICATION AND TESTING OF FILM PROPERTIES

The Polyester biopolyols (MPG-2PE, MPG-4PE, MPG-6PE and WPG-2PE) and Aromatic diisocyanate adducts were thoroughly mixed just before the application to form films onto the well prepared surface steel panels and compared the cured films performance properties with Pure Polyester Resin Polyol (NPE) and Aromatic diisocyanate adducts. Films were applied with varying wet film thickness, such that the dried films of all the compositions had a thickness of 20-35 microns. The films were allowed to cure at ambient conditions for at least 7 days before tests for mechanical and chemical properties were carried out.

FILM CHARACTERIZATION

The coated panels were examined for various mechanical properties like Adhesion, Flexibility, Impact resistance and Scratch hardness as per ASTM D-3359-97 a, ASTM D-0522-93 and ASTM 2197 respec-

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tively. The impact resistance of dried films was checked by Tubular impact tester. The film was also evaluated for the chemical corrosion and solvent resistance as per methods of the characterization described in literature^[11]. The performance of Coatings formulated from biopolyols was compared with conventional polyester polyols. Film thickness was measured by using micro test Magnetic coating thickness gauze. Each panel had an average of three measurements to determine the thickness of panels.

RESULT AND DISCUSSION

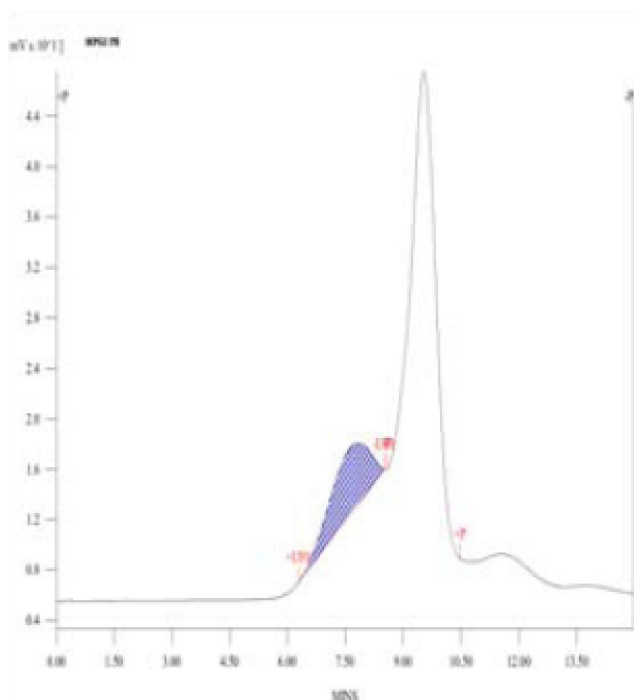
Physical properties

The viscosity of all Polyester biopolyols compositions (MPG-2PE, MPG-4PE, MPG-6PE and WPG-2PE) and pure polyester resin (NPE) is found to be higher. This can be assigned to higher molecular weight^[12] of the biopolymer present in the above sets. This is also supported by GPC-chromatogram in which as we go from lower molecular weight polyol (PEG-200) to higher (PEG-600), the Mw increases from 2369 to 3922 (as shown in GPC chromatograms GPC-1, GPC-2 and GPC-3). This is due to increased interaction between low molecular weight liquefied waste biopolyols and Propylene Glycol and Adipic acid. The results are shown in TABLE 4 below:

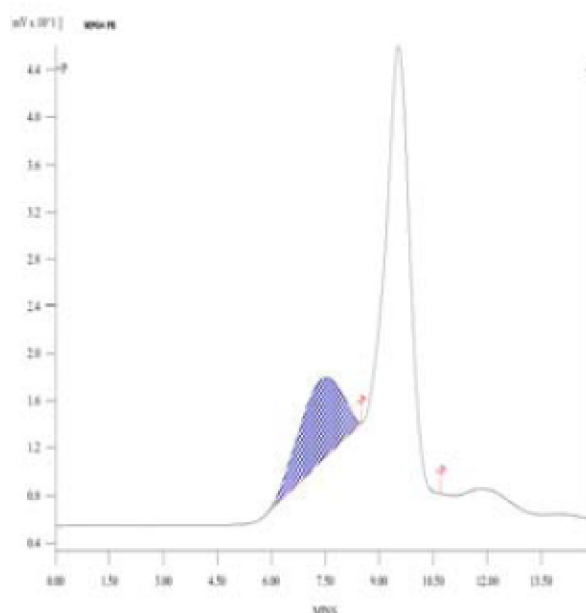
GPC CHROMATOGRAMS

Mechanical properties

Among all compositions of Polyurethane Coatings, Resin Based on Pure Polyester NPE-PEAr110, NPE-PEAr115 and NPE-PEAr120 shows the highest scratch hardness (2.5 kg). While Resins based on biopolyols systems confirm 1.49 to 2.3 kg scratch hardness which



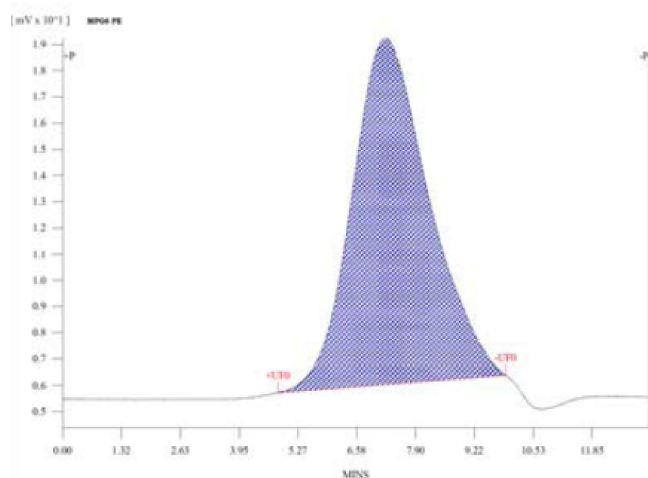
GPC 1: (MPG2 PE)



GPC 2: (MPG4 PE)

TABLE 4 : Characterization of Polyester biopolyols

Code	Viscosity (cPs @ °C)	Color	Wt./ltr.	% NVM	Hydroxyl Value		Molecular Weight Practical (GPC)
					Theoretical	Practical	
MPG-2PE	40.90	11	1.248	99.54	158	160.11	2369
MPG-4PE	44.30	11	1.259	99.68	134	138.08	3513
MPG-6PE	60.10	11	1.285	99.92	113	113.98	3922
WPG-2PE	40.20	11	1.247	99.24	155	159.26	3525
NPE	55.25	8	1.225	99.91	175	170.05	



GPC 3 : (MPG6 PE)

is comparable with NPE-PEAr110, NPE-PEAr115 and NPE-PEAr120 which is due to the addition of Cellu-

lose Glycoglycoside based biopolyols and this can be attributed to increase in cross-linked density due to higher functionality.

The toughness and adhesion properties are mainly governed by more polar urethane and ester groups, which provide sufficient adhesion and toughness to the coatings^[13], the same is also being improved by addition of Biopolyols moiety.

The remarkable flexibility (conical mandrel test) is conferred due to the chains of Cellulose based biopolyols and adipic acid moiety and also assisted by the presence of more polar urethane and aliphatic ester groups that yield a well adhered coating system. Results are displayed in TABLE 5

Solvent resistance

Solvent resistance is the inbuilt property of ther-

TABLE 5 : Mechanical Properties of Polyurethane Coatings Based On Polyester biopolyols

Sr. No.	PU Code	DFT Micron	Impact Resistance (Lb/Inch)	Flexibility 1/8" Mandrel	Scratch Hardness (gms)	Cross-hatch Adhesion (%)	Pencil Hardness
1	MPG-2PEAr110	26	F (at 24")	P	1490	65	4H
2	MPG-2PEAr115	28	F (at 24")	P	1500	65	4H
3	MPG-2PEAr120	30	P (at 24")	F	1400	70	4H
4	MPG-4PEAr110	27	P (at 24")	P	1850	50	5H
5	MPG-4PEAr115	29	P (at 24")	F	1890	50	5H
6	MPG-4PEAr120	31	P (at 24")	F	1900	65	6H
7	MPG-6PEAr110	28	P (at 24")	P	1900	65	6H
8	MPG-6PEAr115	29	P (at 24")	F	1900	65	6H
9	MPG-6PEAr120	28	P (at 24")	F	2100	60	6H
10	WPG-2PEAr110	25	P (at 24")	P	2000	100	6H
11	WPG-2PEAr115	25	P (at 24")	P	2300	100	6H
12	WPG-2PEAr120	26	P (at 24")	F	2200	100	6H
13	NPE-PEAr110	26	P (at 24")	P	2500	100	6H
14	NPE-PEAr115	27	P (at 24")	P	2500	100	6H
15	NPE-PEAr120	30	P (at 24")	F	2500	100	6H

P: Pass, F: Fail.

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mosetting coatings, the degree of cure and the number of cross-linked density (XLD) affects^[15] the solvent resistance. Results of MEK double rub test (> 200) indicate that in general polyurethane films based on all biopolyols have good resistance to polar solvents and that may be due to higher concentration of softer segments (Adipic Acid) in the film matrix & the sets having higher concentration of hard segments (Cellulose) & higher XLD shows good MEK resistance.

Chemical & corrosion resistance

The –NH groups of urethane linkages form hydrogen bond with carbonyl groups of the biopolymer itself. The lone pair of electrons of nitrogen atoms of –NH groups interact with vacant d-orbital of mild steel substrate, which further facilitates adhesion between the resin and the mild steel substrate resulting in a well adhered coating system which, on interaction with various solvents and chemicals does not allow the corrosive ions to penetrate easily through the coating network and gives Chemical and corrosion resistant film. The results of chemical & corrosion resistance reveals that experimental sets having high urethane linkages show good performance which is shown in TABLE 6.

Characterization by IR spectroscopy

The IR analysis of the low molecular weight lique-

fied waste biopolyols, Polyester biopolyols and Polyurethane cured film were done on Fourier transform infrared

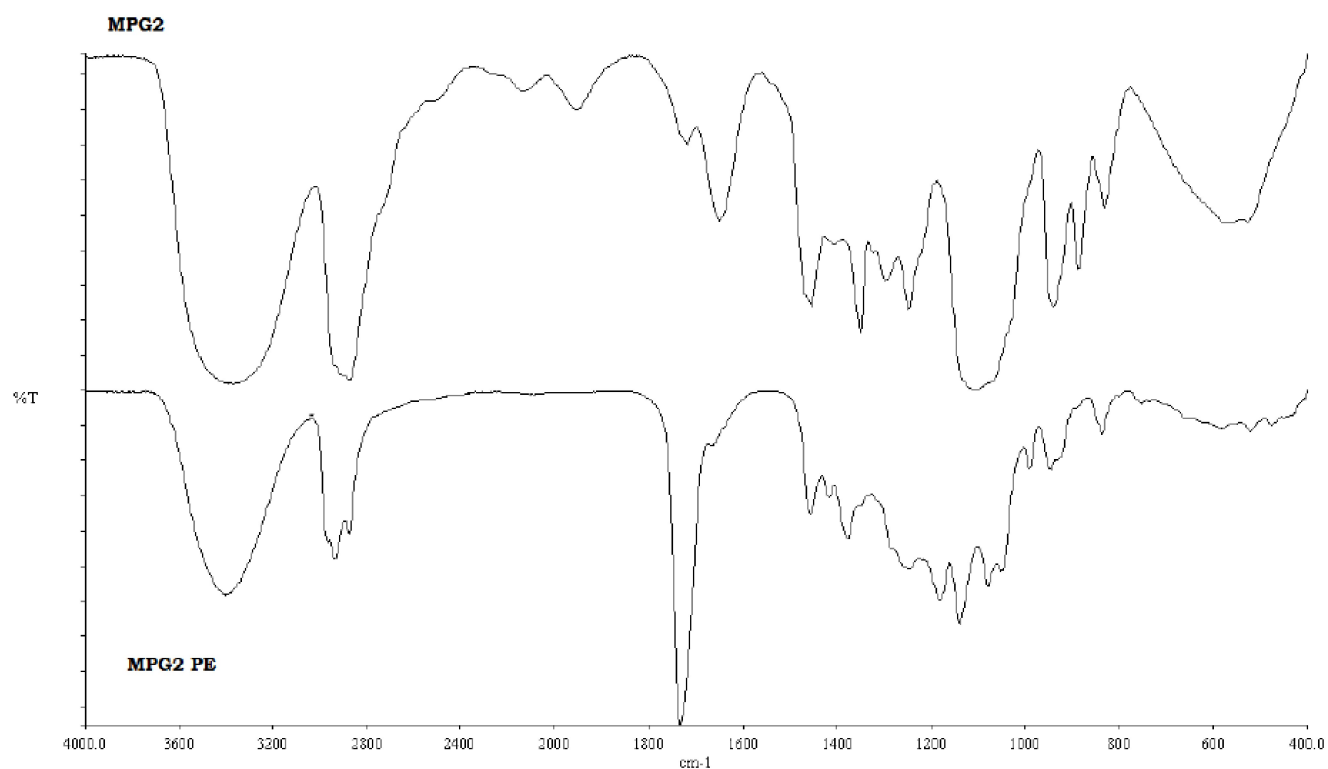
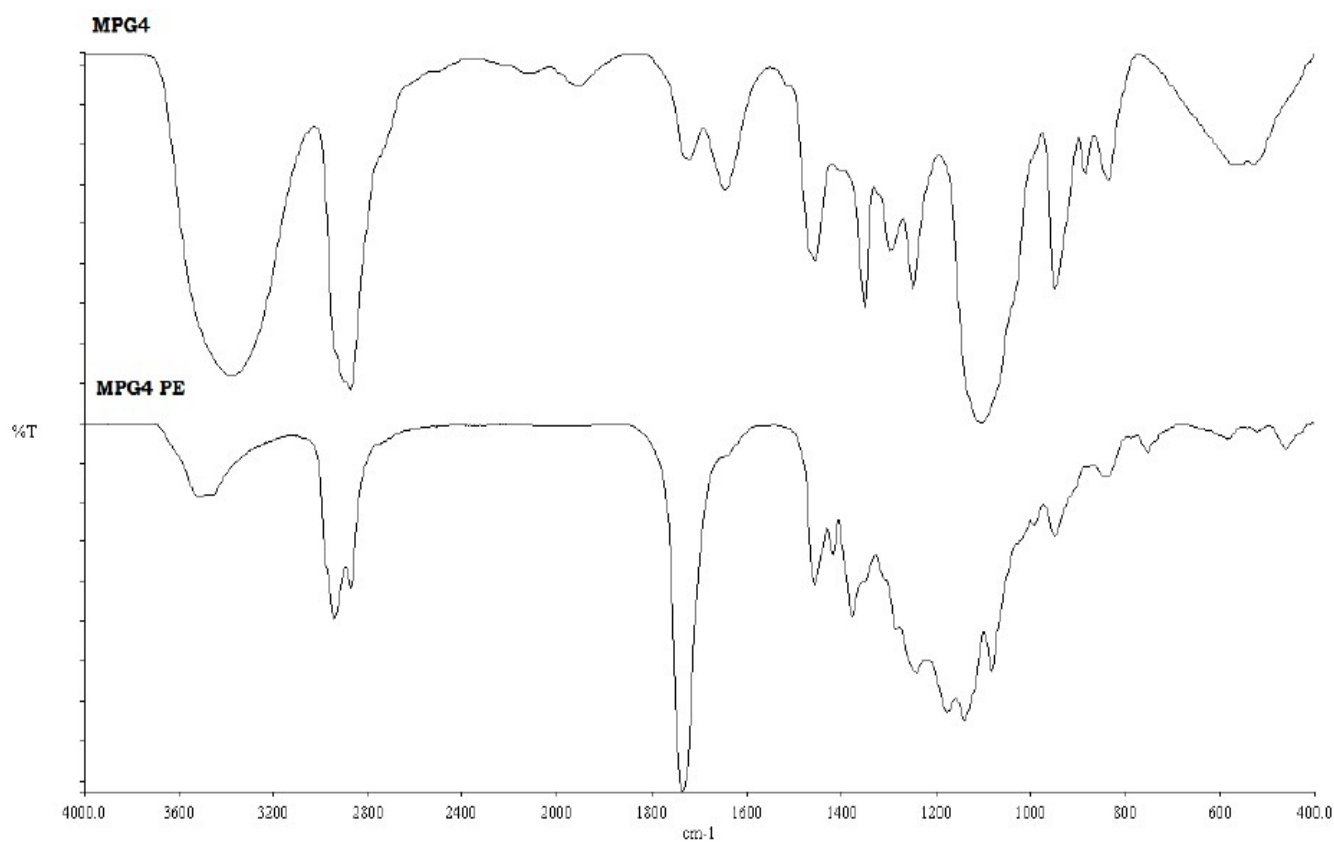
(FTIR) spectrometer using the KBr technique. Figure IR-A,B and C shows the overlay of IR spectras of low molecular weight liquefied waste and its corresponding polyester biopolyol which give you an idea about ether linkages at 1104 cm⁻¹ and confirms the liquefaction of cellulosic waste. While OH bending vibrations at 3391 cm⁻¹ further confirm the presence of hydroxyl functionality in the liquefied waste biopolyols. Absorption peaks at 3403 cm⁻¹ and 1733 cm⁻¹ are due to OH bending and CO stretching of ester group, which confirms presence of ester linkage and free hydroxyl functionality for cross linking with Polyisocyanate curing agent in a Polyester biopolyols.

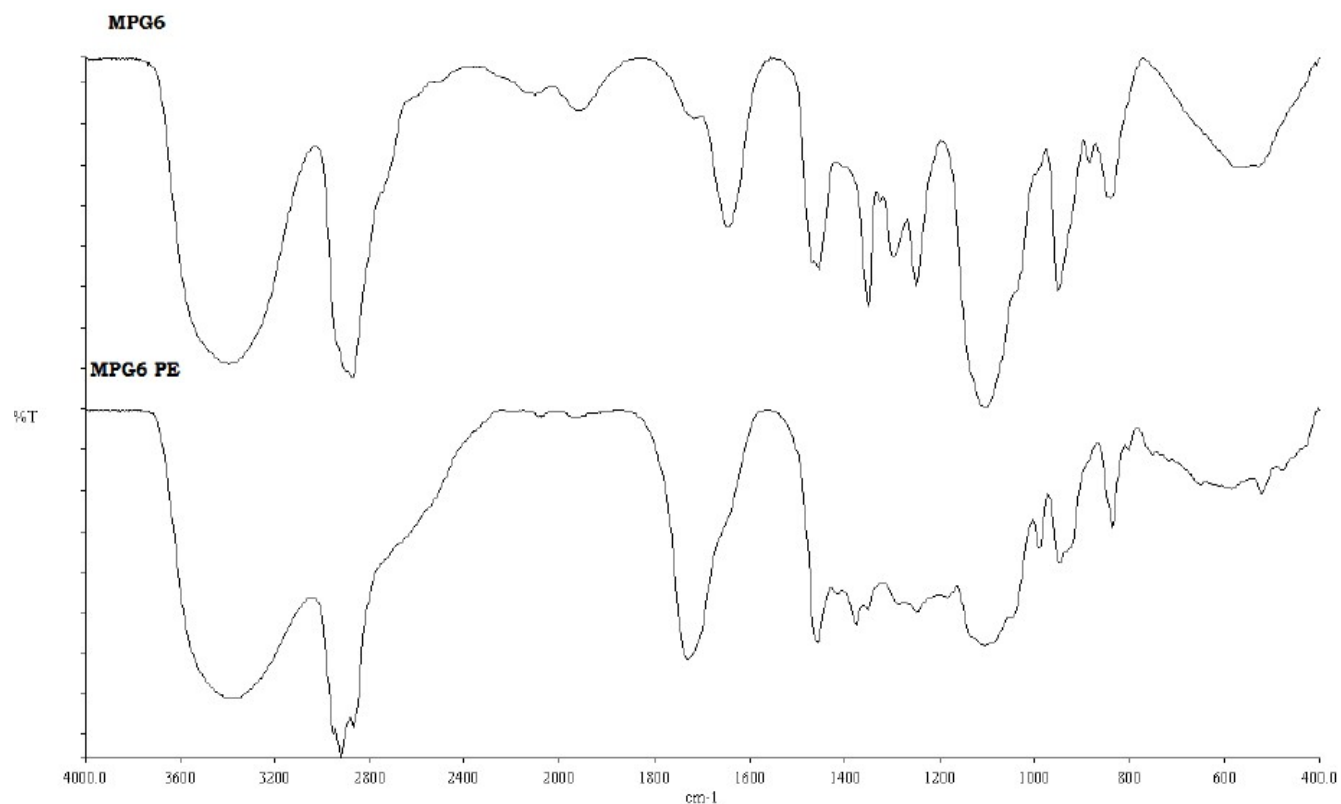
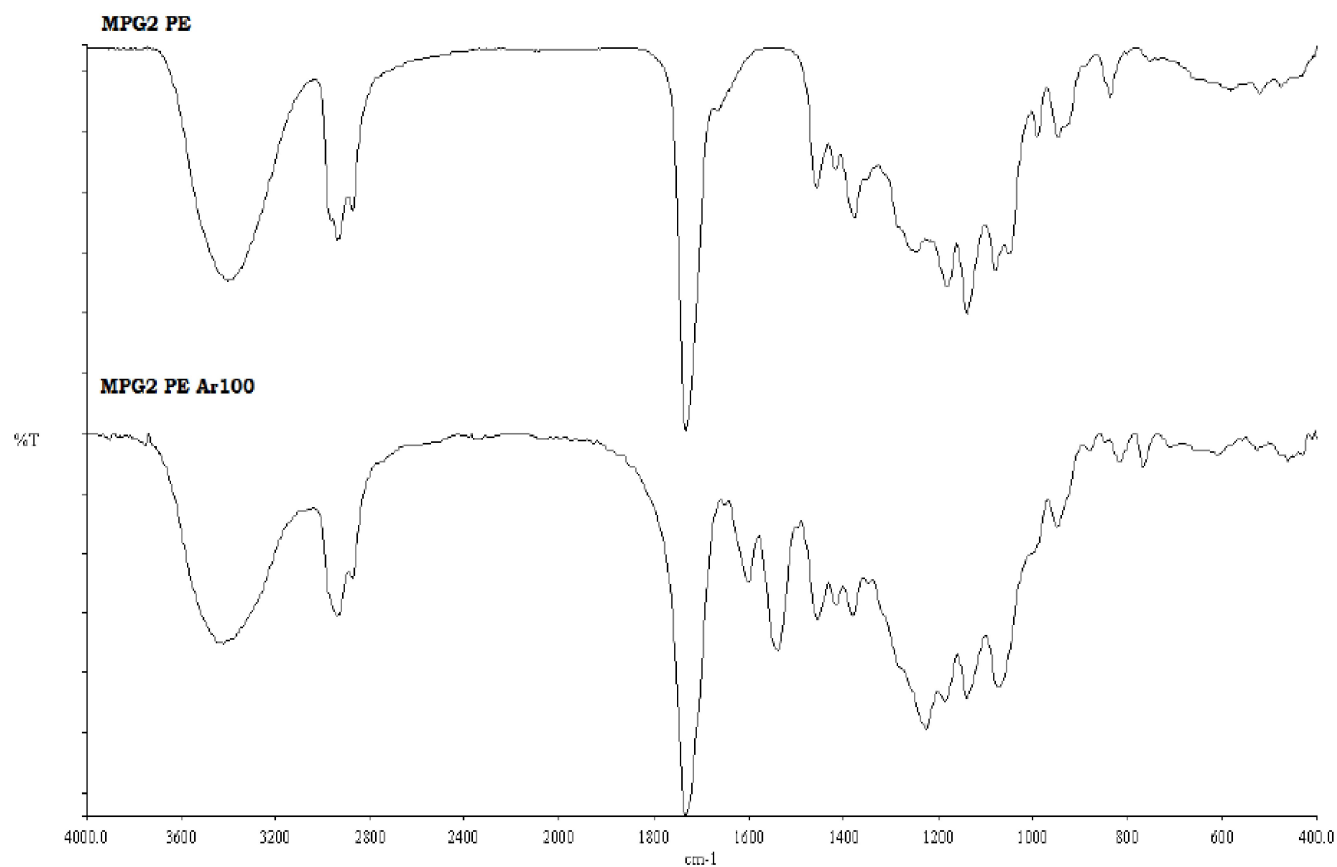
Figures IR-D,E and F shows the overlays of polyester biopolys and corresponding polyurethanes. It is evident from these spectras that urethane formation has taken place from the reaction between polyester biopolyol and aromatic isocyanate hardener. Bands at 3358 cm⁻¹, 1603 cm⁻¹ and 1537 cm⁻¹ (which correspond to N–H, CO–NH, NH₂) shows urethane linkages and methyl groups at 2960 cm⁻¹ which proves the chemical curing reaction in the IR spectrum of Polyurethane cured film.

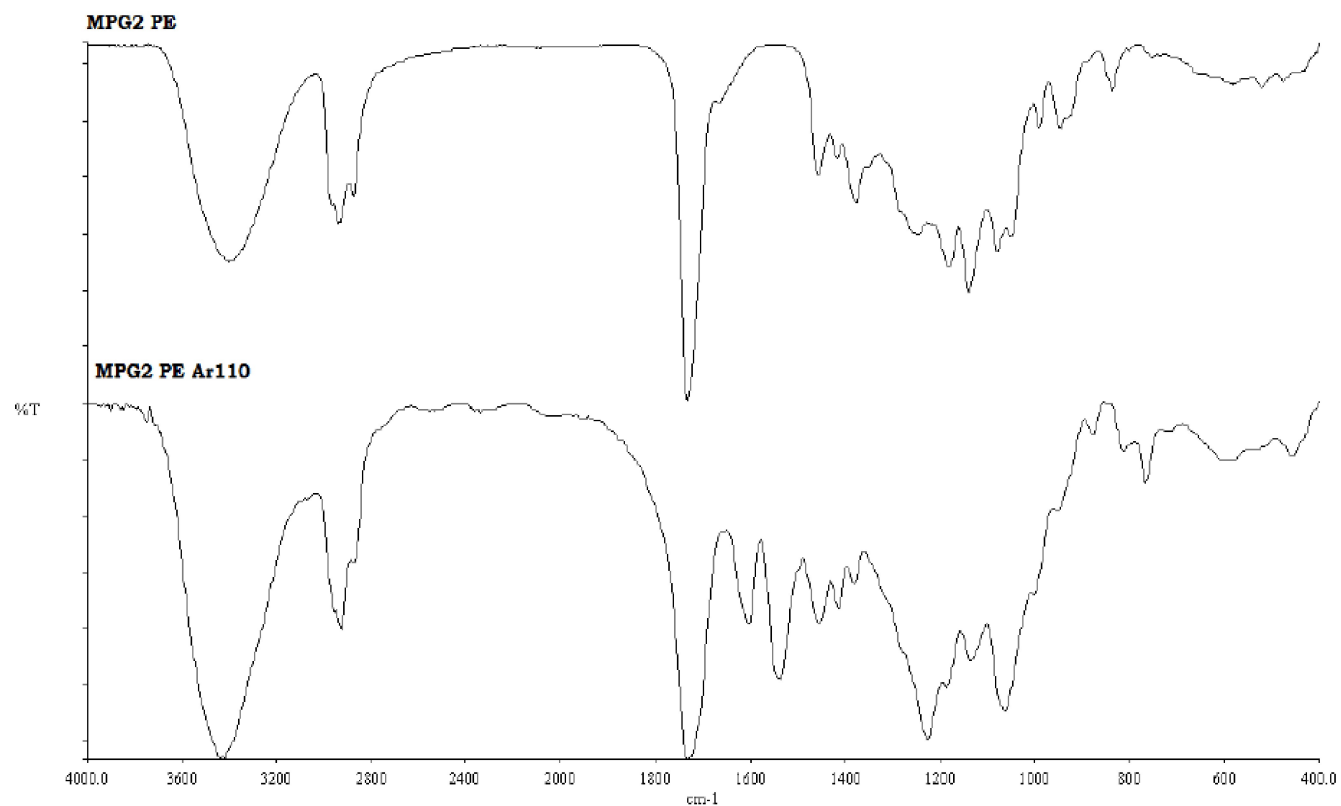
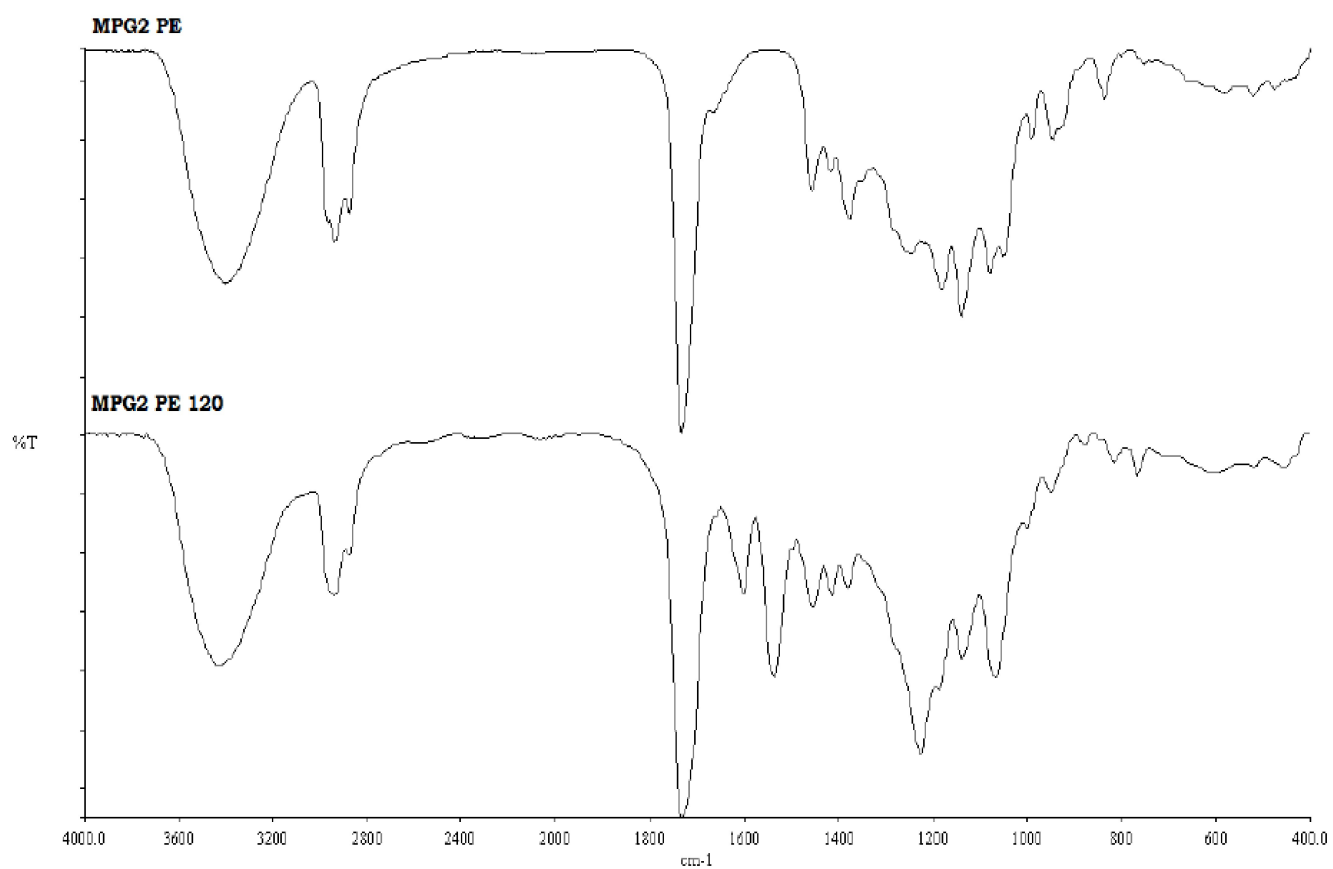
TABLE 6 : Chemical Properties of Polyurethane Coatings Based On Polyester biopolyols

Sr. No.	PU Code	H ₂ SO ₄ (30%) 7-Days	KOH (20%) 7-Days	NaCl (5%) 7-Days	MEK Double Rub.
1	MPG-2PEAr110	5	5	4	>200
2	MPG-2PEAr115	5	5	5	>200
3	MPG-2PEAr120	5	5	5	>200
4	MPG-4PEAr110	4	4	3	>200
5	MPG-4PEAr115	4	4	4	>200
6	MPG-4PEAr120	5	5	5	>200
7	MPG-6PEAr110	5	5	4	>200
8	MPG-6PEAr115	5	5	5	>200
9	MPG-6PEAr120	5	5	5	>200
10	WPG-2PEAr110	5	5	5	>200
11	WPG-2PEAr115	5	5	5	>200
12	WPG-2PEAr120	5	5	5	>200
13	NPE-PEAr110	5	5	4	>200
14	NPE-PEAr115	5	5	5	>200
15	NPE-PEAr120	5	5	5	>200

1 - Complete lifting of film; 2 - Film softens - Rust spot observed; 3 - Severe blistering; 4 - Very slight blistering; 5 - Not affected.

FTIR Spectras**IR-A : (MPG2 TO MPG2 PE)****IR-B : (MPG4 TO MPG4 PE)**

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**IR-E : (MPG2 PE TO MPG2 PEAr110)****IR-F : (MPG2 PE TO MPG2 PEAr120)**

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CONCLUSION

In the present work, Polyester biopolyols with different Lignocellulosic waste comprising of Mast Seed and Water Hyacinth waste were prepared, having different hydroxyl value and compared with conventional Pure Polyester resin system. Their structure and molecular weight were confirmed by FTIR and GPC. The investigation of the Polyurethane coating system reveal the various physical as well as film performance properties in the above product which proves to be very interesting. The improvement in terms of mechanical and chemical properties are always expected from such Polyester biopolyols resins which are required for High performance industrial coating applications.

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