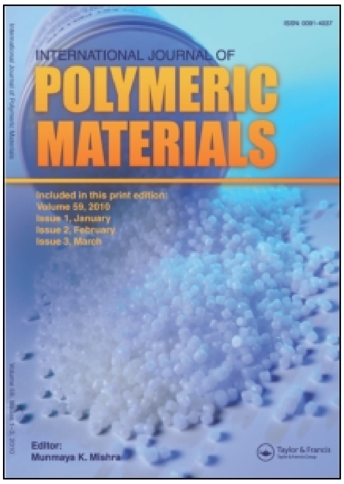

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TWO PACK POLYURETHANE COATINGS FROM ISOPHTHALIC ACID AND BIOMATERIAL BASED POLYESTER POLYOL

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A Polyester polyol was developed from isophthalic acid and starch derived glycol glycosides. Two pack polyurethane system based on this polyester polyol and isocynate adduct was formulated. The performance property reveals that the coatings formed can be successfully used for heavy duty maintenance coating (H.D.M.C) and are considerably influenced by amount of isophthalic acid (IPA) and glycol glycosides.

Keywords: polyurethane, polyester, polyol, glycol glycosides, isophthalic acid, starch

INTRODUCTION

Because of their excellent property profile, polyurethane resins (PU) have special significance as binders for coating formulation. Polyurethane coatings have wide range of applications virtually covering every segment of industrial and non-industrial coatings [1, 2].

Commercial two pack PU coating system comprises an isocyanate adduct and the polyol. Polyols are the polyhydroxy component with polyester, acrylics, polyether and alkyd base. Depending on the nature of base material, inherent properties of the coating matter can be

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tailor-made. With the increase in industrial use of PU coatings, there has been an enormous growth in demand for these groups of raw material (polyols) within the space of just a few years. Polyester polyols have always been viewed as classic co-reactants in two-pack PU coatings. Use of various diols, glycols, adipic, phthalic and maleic acids for the preparation of various polyester polyols for PU coatings is reported [3–5]. We have used isophthalic acid in combination with adipic acid and starch derived glycol glycosides in combination with neopentyl glycol (NPG) for polyester polyol synthesis. Use of biomaterial (starch based) for the manufacturing of polyester polyurethane foams and plastics is reported [6–9].

Use of isophthalic acid increases the hardness properties of the coatings and use of biomaterial may further economize the cost of coatings due to low cost of raw materials [10, 11, 12]. Therefore, in the present work an attempt is made to use biological material for polyol synthesis for the end use in PU coatings. A comparative study of performance properties of the coating materials has been made to find the effect of amount of glycol glycosides in polyol synthesis.

EXPERIMENTAL

Materials

Starch was extracted from potatoes and freed from amylopectins by toluene extraction [13]. Adipic acid and NPG was supplied by Chiti-Chem Pvt, Ltd., Baroda, Gujarat, India. Isophthalic acid and toluene diisocyanate (TDI) was supplied by Marigold Coatings Pvt, Ltd., V.U. Nagar, Gujarat, India. The chemicals and solvents used in this work were of analytical reagent grade.

Glycosylation of Starch

Three hundred ml. of ethylene glycol and 0.5% (by wt of reactants) sulfuric acid were mixed in a three neck flask of 500 ml capacity, equipped with a stirrer, thermowell, nitrogen inlet, and vacuum line. The mixture was heated with constant stirring up to 80°C under nitrogen atmosphere at 125 mm Hg pressure to remove traces of water, and then 10 gms of starch were added and the temperature was raised to 110–120°C. The materials were allowed to react at this temperature and pressure condition for one hour. After this the glycol glycosides formed were transferred to a container and barium hydroxide was added to it to neutralize the leftover sulfuric acid and then pale–yellow–colored viscous glycol glycoside was filtered to remove the barium sulfate formed during neutralization.

The unreacted ethylene glycol was distilled off at 150°C and 125 mm Hg pressure. The yield of the product obtained was 270 gms. Glycol glycosides so prepared, being a mixture of alpha-D-glycol glycosides and Beta-D-glycol glycoside [14], were used as such for the preparation of polyol.

Polyester Polyol Synthesis

To study the effect of amount of glycol glycosides in the polyurethane, the hydroxyl value of all the three polyester polyol formed by reacting glycol glycosides with isophthalic acid was kept identical (180 mg KOH). Fixed amount of isophthalic acid and adipic acid was reacted with variable amount of NPG and glycol glycosides to get the hydroxyl value of all the three polyester polyols to 180 mg KOH. The formation used for polyester polyol preparation is shown in Table 1.

Isophthalic acid is being more stable than phthalic acid, it reacts slowly with glycols. So we have divided the process into two stages:

(i) Dissolution of IPA
(ii) Esterification

The reaction was carried out in N_2 atmosphere in presence of p-toluene sulfonic acid (PTSA) as a catalyst, which reduces the dissolution time of IPA and hence decreases the overall reaction time.

In the first stage of the reaction, a calculated amount of Isophthalic Acid, NPG, Glycol glycosides and adipic acid were taken in a four neck glass reaction kettle fitted with stirrer, thermowell, N_2 purger and Dean & Starke condenser.

P-Toluene sulfonic acid (0.6% by wt of batch) was added as a catalyst. The temperature was raised slowly with constant stirring at 120°C. As dissolution of IPA proceeds with time, temperature was increased up to 150–160°C at this temperature IPA dissolves completely within 3 to 4 hours.

TABLE 1 Formulations of Polyester Polyol Synthesis

Sr. no	Name of chemical	Weight in gms. Set 1	Weight in gms. Set 2	Weight in gms. Set 3
1.	Isophthalic acid	27.47	27.47	27.83
2.	Adipic acid	24.16	24.16	24.50
3.	Neopentyl glycol	44.62	35.22	25.50
4.	Glycol glycosides	43.00	13.13	22.18

In the second stage this melt was cooled down to 120°C and xylene was added to remove water formed during the reaction. Temperature was raised again to 160°C and water of reaction was removed by Dean & Starke condensor in the form of xylene water azeotrope. After complete removal of water and xylene, the temperature was raised to 180°C–90°C and was maintained for an hour. Total reaction taken 6–8 hours. The product obtained was of brownish color and was used as a polyol as such for polyurethane resin preparation without further purification.

Polyurethane Formation

A two-pack polyurethane coating system based on polyester polyol (base component) and isocyanate adduct (hardener component) was formulated. A polyester polyol synthesized by the above process was used as a base component and aromatic di-isocyanate adduct (Prepolymer) was prepared by the reaction of 2,4-TDI, TMP and isooctanol as per the process reported in author's earlier publication [15] was used as a hardner component for PU resin synthesis.

Two components were mixed at the time of application on mild steel (M.S.) panels and were allowed to cure for 72 hours before testing their performance properties.

RESULTS AND DISCUSSION

Glycosylation of starch, esterification and PU formation was confirmed by IR spectroscopy and performance properties of the coatings were evaluated as per the Indian Standards [16].

IR Spectroscopy

Figure 1 shows the IR spectra of glycol glycosides. It shows ether linkages at 1094 and 1052 cm^{-1}, which are the key bands which confirms the formation of glycol glycosides. OH bending vibrations at 3369 cm^{-1}confirm the presence of hydroxyl functionality. Figure 2 shows the IR spectra of polyester polyol formed; peaks at 3348 and 1750 cm^{-1} are due to OH bending and CO stretching of ester group, which confirms esterification and hydroxyl functionality of a polyol. Figure 3 shows the IR spectra of polyurethane. The peak at 3388 cm^{-1} is due to NH deformation present in urethane group, peaks at 1608 and 1541 cm^{-1} are due to urethane linkage, that is NHCOO group.

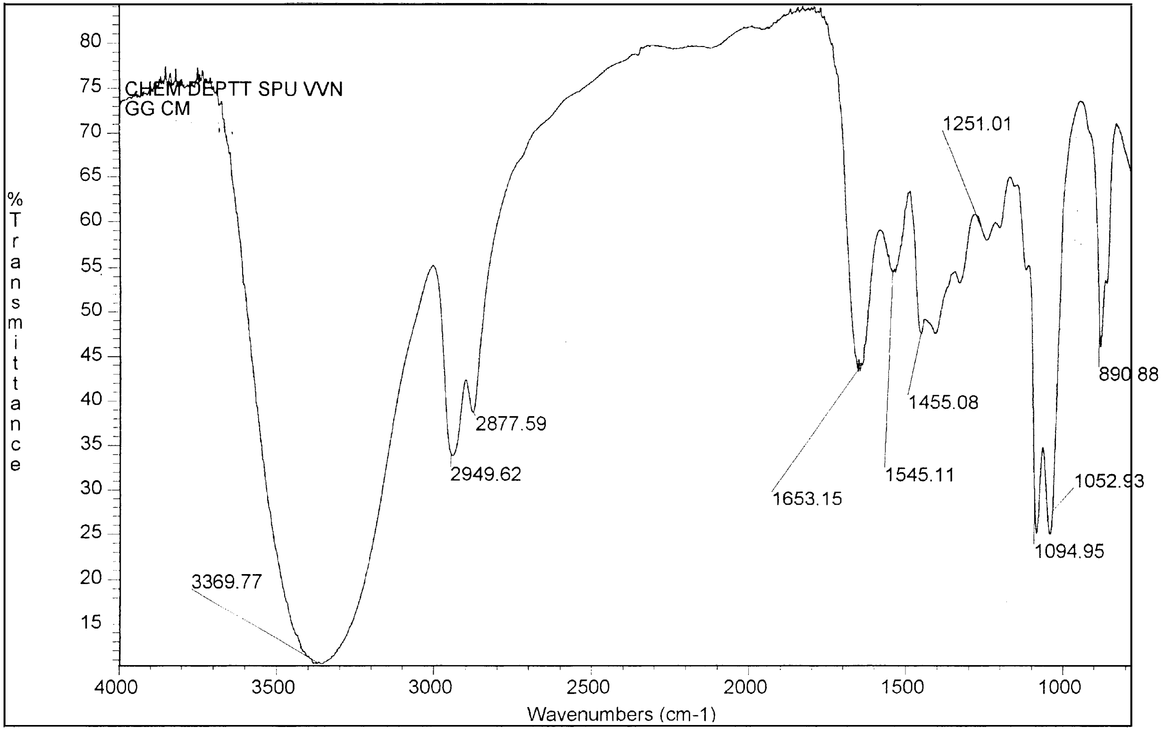

FIGURE 1 IR spectra of glycolglycosides.

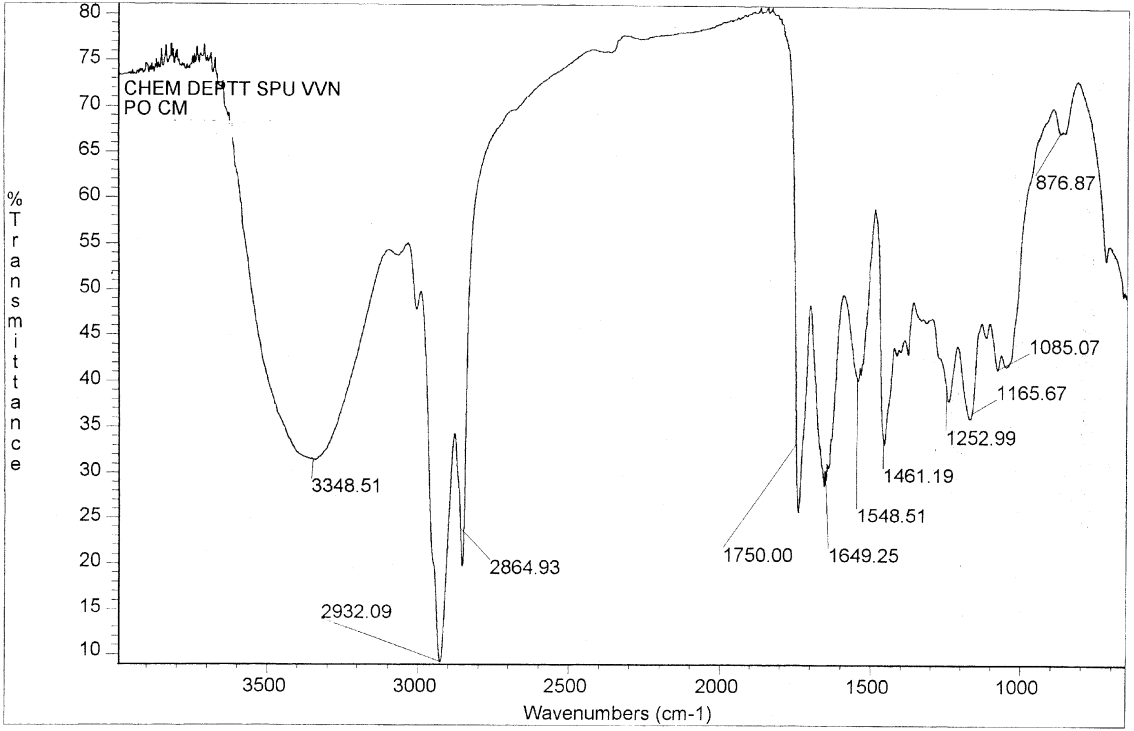

FIGURE 2 IR spectra of polyester polyol.

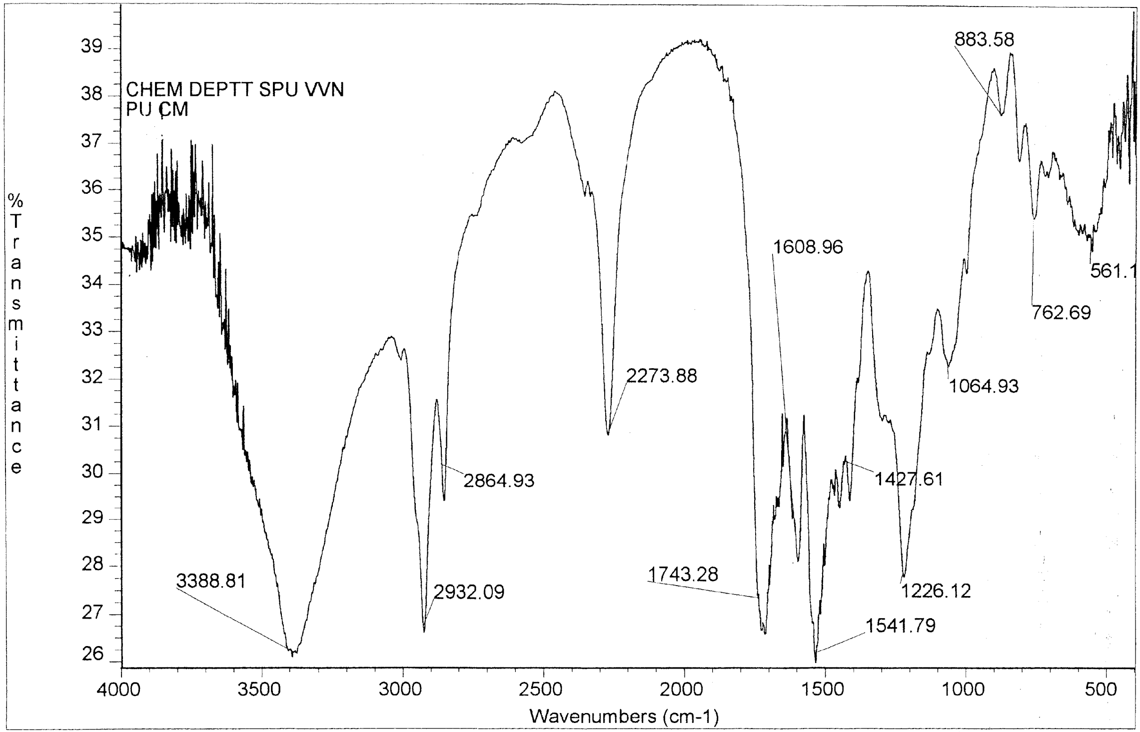

FIGURE 3 IR spectra of PU.

Performance Properties

Performance properties of the material decide the specific application of the material, so they are very important. PU coated panels were evaluated for drying time, scratch, pencil and impact hardness, flexibility, and for chemical and solvent resistance. These properties reveal that the resin formed can be used successfully for H.D.M.C.

Drying Time

The drying time (surface dry and tack free) was found to decrease with increase in the content of glycol glycosides, as it will increase the molecular weight of the polyol and polymer, which brings down the drying time. Table 2 shows the drying time for different amounts of glycol glycosides in polyol.

Gel Time

Gel time is very important for a coating system from the application point of view. It indicates the maximum length of time, the system remains fluid. Gel time varies from 2.5 to 4 hours with variations in amount of glycol glycosides and NCO : OH ratio.

Hardness

Hardness is the resistance of a material to indentation or scratching. The three most widely used tests for testing the hardness of the coatings are (i) scratch, (ii) impact, (iii) pencil. Table 3 shows the impact and pencil hardness.

TABLE 2 Drying Time and Gel Time

PU Code	NCO : OH	Surface dry in hrs	Tack free time in hrs	Get time in hrs
Set 1	1.1	4	4.25	4.5
	1.3	3	4	4.5
	1.5	2.25	3.5	4
Set 2	1.1	3	4	4
	1.3	2.5	3.5	4
	1.5	2	3	4
Set 3	1.1	1.25	2.25	2.5
	1.3	0.75	2	2.25
	1.5	0.5	1.5	2

TABLE 3 Impact and Pencil Hardness

		Impact hardness lb. inch		
PU Code	NCO : OH	Direct	Reverse	Pencil hardness
Set 1	1.1	58	55	4H Pass
	1.3	28	20	5H Pass
	1.5	26	16	5H Pass
Set 2	1.1	60	60	4H Pass
	1.3	32	26	5H Pass
	1.5	28	22	5H Pass
Set 3	1.1	60	60	5H Pass
	1.3	60	60	6H Pass
	1.5	60	60	6H Pass

Note 60 lb.inch is maximum scale of the tubular impact tester.

Scratch Hardness

Excellent scratch hardness is obtained in all the formulations, without any type of dependence on amount of glycol glycosides used. This is clearly due to use of IPA in polyester polyol synthesis. All the coated panels passed 5 kg scratch hardness.

Pencil Hardness

It was observed that pencil hardness increases with increase in NCO : OH ratio and was independent of amount of glycol glycosides used. So it is also only due to IPA used and NCO : OH ratio. It was found that as NCO : OH ratio increases from 1.1 to 1.5, pencil hardness increases from 4H to 6H due to increase in NCO groups.

Impact Hardness

Impact hardness was carried out on a Tubular Impact tester with indenter weight of 1.8 kg. It was found that impact hardness increases with increase in amount of glycol glycosides and with decrease in NCO :OH ratio, as film becomes brittle due to increase in NCO content.

% Adhesion

Adhesion is very important for the coating material as all other properties can be measured only when coating adheres properly on a particular substrate like wood, metal, plaster, or plastic, etc. It was

TABLE 4 Chemical and Solvent Resistance

PU Code	NCO : OH	2% NaCl	2% NaOH	2% HCl	Water	Xylene
Set 1	1.1	1	5	4	1	2
	1.3	1	3	2	1	1
	1.5	1	3	1	1	1
Set 2	1.1	1	3	1	1	1
	1.3	1	1	1	1	1
	1.5	1	1	1	1	1
Set 3	1.1	1	1	1	1	1
	1.3	1	1	1	1	1
	1.5	1	1	1	1	1

1 = No effect, 2 = loss in gloss, 3 = soften, 4 = loss of adhesion, 5 = blistering, 6 = lifting, 7 = rupture.

determined by cross hatch test and was found that all the three formulations gave 100% adhesion.

Flexibility

Flexibility is a measure of sufficient elasticity of the coating material so that it can withstand weather and service conditions. It was found that all the panels pass both 1/4″ and 1/8″ mandrel flexibility test, which is due to the use of polyester polyol in polyurethane synthesis.

Chemical Resistance and Solvent Resistance

The panels were dipped in 5% NaCl solution, 2% alkali solution, 2% acid solution, water and xylene for 24 hours and were checked for softness, gloss loss, adhesion loss, lifting blistering and rupture for every 2 hours. It was found that with the increase in the amount of glycol glycosides chemical and solvent resistance increases. Also the alkali resistance results were good in this case, although polyester polyol was used, which generally gives poor alkali resistance, but due to better stability of IPA, alkali resistance was found excellent. Table 4 shows these data.

CONCLUSION

A polyester polyol from glycol glycosides and IPA can be successfully synthesized and urethane resins can be successfully synthesized from them. Use of starch for synthesizing urethane coatings may reduce the cost without compromising the quality. The performance properties of the coating materials vary with the amount of glycol glycosides used in the polyester polyol synthesis and were found suitable for the application of coating material in H.D.M.C.

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