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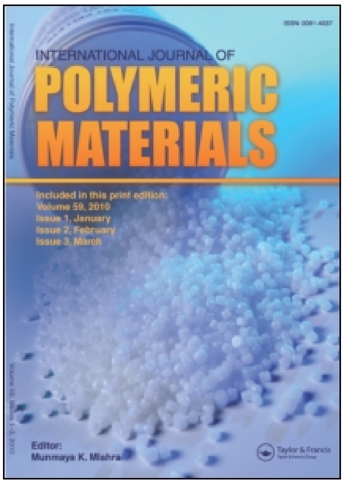

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Two Pack Polyurethane Coatings from PET Waste and Biological Materials

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Feasibility of using starch derived glycol-glycosides for depolyemerising PET waste recycled from post consumer soft drink bottles and the use of the depolymerised oligomers for synthesizing liquid polyester polyol by reacting these oligomers with SOFA for urethane coatings has been studied. The performance properties reveals that the coatings formed can successfully be used for applications in Industrial Maintenance finishes, and are considerably influenced by the amount of PET.

Keywords: Polyurethane; PET waste; Biological materials

INTRODUCTION

Polyurethanes represent a versatile class of polymer used in variety of applications such as adhesives, coatings, rigid foams, flexible foams and cast elastomers. Polyurethanes are rapidly developing products of coating industry having a unique combination of performance and applications properties [1]. PET [Poly(ethylene terephthalate)], is a semi-crystalline thermoplastic polyester widely used in the manufacture of high strength fibres, photographic films and soft drink bottles. Because the management of waste plastics is reaching a crisis worldwide, PET waste has become one of most valuable recycle materials

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today [2]. PET waste can be depolymerised by glycolysis using metal acetate catalyst to obtain oligomaric diols [3, 4]. The glycolysis of PET waste using various glycols like EG, PG, DEG and Diglycerol is reported [5, 6]. We have used glycol glycosides, a products of EG and Starch, for glycolysis of PET waste. Use of glylcolised products for the manufacture of various polyester polyurethane foams and plastics are reported [7 – 10]. Our purpose is to synthesize polyurethane coatings.

India have been lacklustre for a variety of reasons, largely related to the poor availability of raw materials and their high price in the local market. Economic policies also favoured use of natural products [11]. To cut down the cost of polyurethane, the use of biological [12 – 15] and PET waste material [16, 17] for synthesis of polyols are already reported. Here, the feasibility of combining both biological material and PET waste for synthesising polyols and their reactions with aromatic isocyante adduct to form urethane coatings has been discussed. The present work is an attempt to make use of biological and waste material for polyol synthesis for the end use in urethane coatings. This may solve the problems of availability of raw materials and further, economize the cost of coatings due to use of cheaper raw material [18].

In two pack PU coatings, depending on the nature of base materials, inherent properties can be tailor made. Polyester based urethane coatings have better commercial value, therefore in the present study we have used glycolised waste PET oligomeric soysfatty acid (SOFA) based polyester polyol and aromatic isocyanate adduct for preparation of polyurethane. Performance characteristics of the coatings obtained reveal their use as an industrial maintenance coating, having superior mechanical and chemical properties at low price.

EXPERIMENTAL

Materials

Starch was extracted from potatoes and freed from amylopectins by toluene extraction [19]. TDI used for adduct formation and SOFA was supplied by MariGold Coatings Pvt. Ltd., Vithal Udyognagar-388 121, Gujarat. PET was obtained from local recycling company.

The chemicals and solvents used in this work were of analytical reagent grade.

Glycosylation of Starch

Three hundred milliliter of ethylene glycol and 0.5% (by weight of reactants) sulphuric acid were mixed in a three neck flask; equipped with a stirrer, thermowell, nitrogen inlet and vacuum line. The mixture was heated with constant stirring upto 80°C under nitrogen atmosphere and 125 mm Hg pressure to remove traces of moisture and then 10 gm of starch was added and was heated at 110–120°C for one hour. After this, the glycol and glycosides formed were transferred to a container and barium hydroxide was added to it pinch by pinch to neutralize the leftover sulphuric acid and then the pale yellow coloured viscous glycol glycosides was filtered.

The unreacted ethylene glycol was distilled off at 150°C and 125 mm Hg pressure. Glycol glycosides so prepared being a mixture of alpha-D-glycol glycosides and beta-D-glycol glycoside [20] was used as such for glycolysis of PET waste.

Glycolysis of PET Waste

The PET waste was depolymerized by reacting different weight percent *viz.*, 5%, 15%, 25% w of PET with glycol-glycosides using 0.5% w Zinc Acetate catalyst based on wt of PET.

PET waste, glycol-glycosides together with catalyst was charged to a four-necked resin reaction kettle, fitted with stirer, reflux condensor, Nitrogen inlet and thermometer. The temperature was brought upto 150°C in one hr. PET flakes dissolves in an hour at this temperature. The temperature is further raised upto 190°C and was maintained until completion of the reaction. The brown coloured product obtained was analysed for hydroxyl number [21] and was used for esterification with SOFA without any further purification.

Polyester Polyol Preparation

To study the effect of amount of PET in the polyurethane, hydroxyl value of all the three polyester polyol formed by reacting depolymerised oligomers containing different amount (5, 15, 25% w) of PET with SOFA was kept identical (250 mg KOH/gm sample). Fixed amount of depolymerised oligomers was reacted with required amount of SOFA to get the hydroxyl value of all the three polyester polyol to 250 mg KOH.

SOFA, depolymerised PET oligomers and xylene were changed into a four necked reacion kettle fitted with a stirrer, thermometer pocket, nitrogen purger and dean and starke condensor for removing xylene water azeotrope. The SOFA acts as a catalyst as well as a reactant. The reaction temperature was raised upto 150°C. At this temperature water of reaction was removed by xylene water azeotrope with the help of dean and starke condenser. After complete removal of water and xylene, the temperature was raised upto 180°C and was kept there for about an hour. The product obtained was reddish-brown in colour and was used as a polyol(base component) as such without further purification for polyurethane resin synthesis.

PU Formation

A two pack polyurethane coating system formulated from a Polyol obtained from the esterification of depolymerised PET oligomers and SOFA as a base component and aromatic di-isocyanate adduct obtained by the reaction of 2,4-TDI, TMP and Isooctanol as a hardner component. Adduct was prepared as per the process reported in our earlier publication [22]. Two components were mixed at the time of application and the mixture was applied to a mild steel panels which were allowed to cure completely (72 hr) before testing their performance properties.

RESULTS AND DISCUSSION

This includes a discussion on the results obtained on depolymerizing PET by starch derived glycol-glycosides and on the results of performance properties of PU coating from this depolymerised PET derived polyol.

Glycolysis

PET waste could be depolymerised by glycolising it with glycol glycosides. The data of hydroxyl value of glycolysed PET are given in Table I.

The results indicate that the hydroxyl value of oligomers decreases with increase in amount of PET. It is consistent with the earlier reported observation [23]. The hydroxyl value was measured without removing excess of glycol-glycosides as it is not required looking to the end use as a coating material. Further, the glycolysis of PET using glycol-glycoside was confirmed by Infrared spectroscopy. Figure 2 shows the comparative IR spectras of glycolised PET with different %wt of PET. Figure shows a stretching —C=O— vibrations at $1742\,\mathrm{cm}^{-1}$ which is the key band confirming the ester linkage formed due to glycolysis of PET. Comparison with the IR spectra of glydol-glycosides shown in Figure 1. We can conclude that a band at $1742\,\mathrm{cm}^{-1}$ was different in both spectras. Also, on looking at the sharpness of peak at $1742\,\mathrm{cm}^{-1}$of the IR spectras of different amount of PET it was found that sharpness of peak increase with increase in amount of PET which also confirms the glycolysis reaction. The formation of polyol was confirmed by IR spectra. Figure 4 shows the IR spectra of polyol. The peak at $3400\,\mathrm{cm}^{-1}$ and $1700\,\mathrm{cm}^{-1}$ confirms the polyol formation from depolymerised PET oligomers and SOFA. The H.V. of the three polyol containing different amount of PET (5, 15, 25% w) was kept same – 250.

The formation of polyurethane was also confirmed by IR spectroscopy. Figure 3 shows the IR spectra of polyurethane. The peaks at 1729 and $1610\,\mathrm{cm}^{-1}$ are due to urethane linkages, peak at $3348\,\mathrm{cm}^{-1}$ is due to NH deformation.

TABLE I Hydroxyl value of depolymerised PET oligomers

Sr. No.	*Glycolysied PET code*	*Percentage PET %*	*Hydroxyl value without removal of glycol-glycosides mg KOH/gm sample*
1	GPET-5	5	1100
2	GPET-15	15	1010
3	GPET-15	25	925

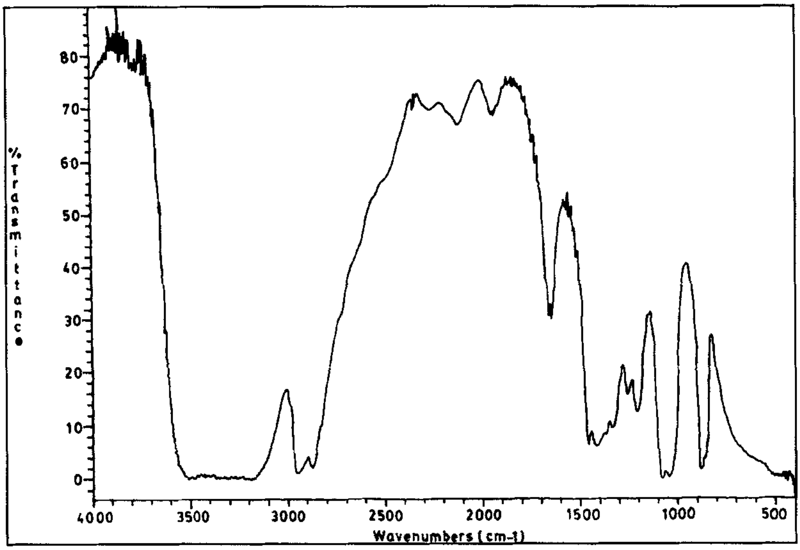

FIGURE 1 IR spectrum of glycol-glycosides.

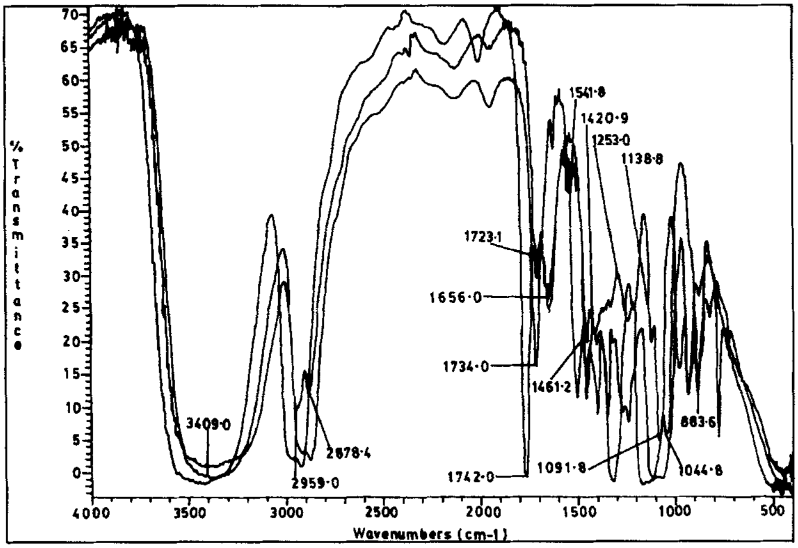

FIGURE 2 Comparative IR spectrum of depolymerised PET.

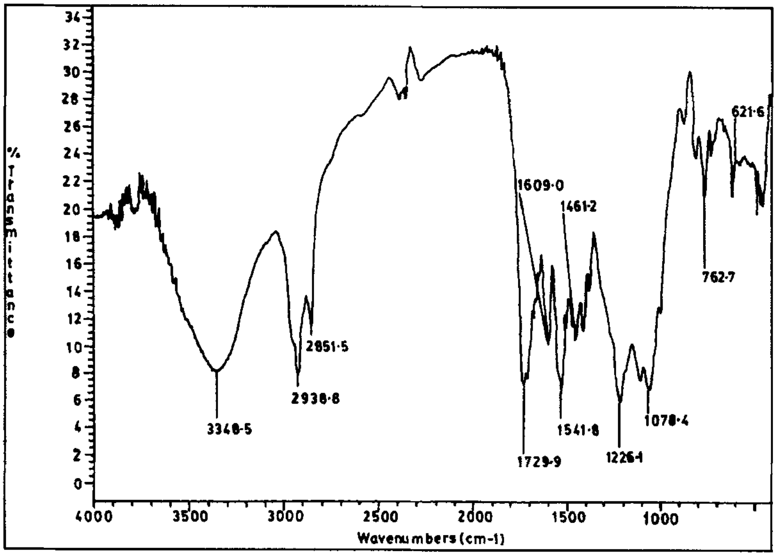

FIGURE 3 IR spectrum of polyurethane.

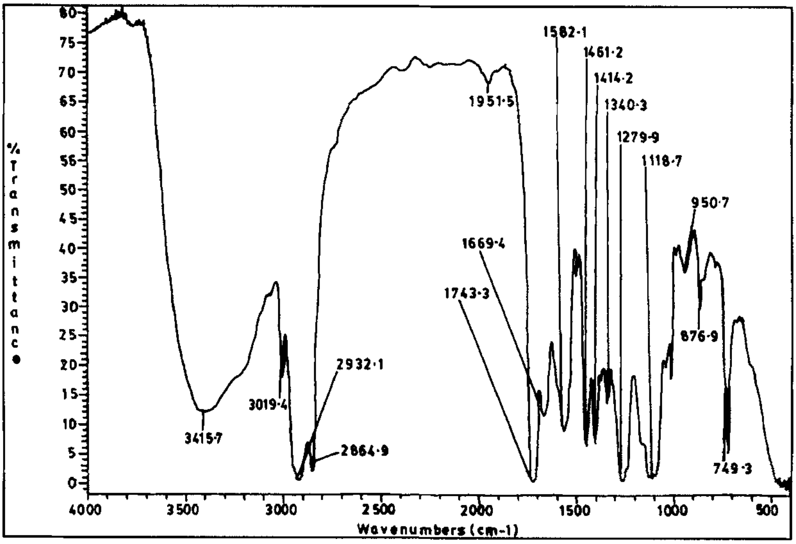

FIGURE 4 IR spectrum of PET SOFA polyol.

Performance Properties

Polyurethane coated panels were evaluated for drying time, scratch and impact hardness, flexibility and for chemical and solvent resistance. The hydroxyl value of all the three polyols were kept equal *i.e.*, 250 so the yield of all the three polyol remains the same. So the effect of amount of PET on the performance properties can be studied.

Drying Time

The drying time (tack-free) was found to decrease with increase in amount of PET, as with increase in amount of PET the mol.wt of polyol also increases which will decrease the drying time. PU takes 4.5 to 3.5 hr for drying when amount of PET varies from 5–25% w. The data are reported in Table II.

Scratch Hardness

It is an important property of coatings and indicates the resistance to abrasion. It was found to increase with increase in amount of PET. It was found to be varying from 2.5 kg to 3.7 kg with PET varying from 5–25% w. The data are reported in Table II.

Impact Hardness

It evaluates the ability of a coating to withstand impact without cracking when the deformation is sudden. Table II indicates that the impact hardness (both reverse and forward) increases with increase in amount of PET.

TABLE II Performance properties of polyurethane coatings

Sr. No.	*PU code*	*Percent PET*	*Impact hardness (psi)*	*Scratch hardness(kg)*	*Flexibility (mandrel)*	*Drying time hr*
1	PUPET-5	5	250(f), 100(r)	2.5	Fair	3.5
2	PUPET-15	15	275(f), 200(r)	3.3	Good	4.0
3	PUPET-25	25	300(f), 250(r)	3.7	Excellent	4.5

Flexibility

It was found that the flexibility was improved with increasing amount of PET because with increasing amount of PET a thermoplastic character is added to the polyol which improves the flexibility. The data are reported in Table II.

Percentage Adhesion

It is the degree of attachment between a coating film and the underlying material which may be another film of paint or any other material or substrate. It was measured in terms of force required to remove the coating from the substrate under controlled conditions. The percent adhesion for the coatings was determined by the cross hatch test. Table II indicates that percent adhesion was found to be 100% for all the urethane and is independent of increasing amount of PET in the polyols.

Chemical and Solvent Resistance

The panels were coated as per IS specifications and then dipped in 5 per cent NaCl, 2 per cent alkali, 2 per cent acid, water and xylene for 24 hrs and panels were checked for softness, gloss loss, adhesion loss, lifting, blistering and rupture for every 2 hrs. The chemical and solvent resistance was found to increase with increase in amount of PET, it was observed that alkali resistance is somewhat poor which might be due to presence of PET and SOFA in the system. The data are reported in Table III.

TABLE III Chemical and solvent resistance

Sr. No.	*PU code*	*Percent PET*	*2% NaCl*	*2% NaOH*	*2% HCl*	*Water*	*Xylene*
1	PUPET-5	5	3	5	7	1	2
2	PUPET-15	15	1	5	5	1	1
3	PUPET-25	25	1	3	5	1	1

1 = No effect, 2 = Softens, 3 = Loss in gloss, 4 = Loss in adhesion, 5 = Lifting, 6 = Blistering, 7 = Rupture.

CONCLUSION

Waste PET can be successfully depolymerised by glycolysis with starch derived glycol-glycosides and polyol prepared from esterification of depolymerised PET oligomers with SOFA can be used as a base component for formulating two component polyurethane coating system. Use of waste and biological materials for synthesising urethane coatings may reduce the problems of availability of raw materials and high cost of products without compromising on quality of the coatings formed. Also it may prove as an aid for using recycled plastics for an important applications like coatings and thus helping the waste management of plastics.

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