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Synthesis of Flame Retardant Polyurethane Coating Using Bis(2hydroxyethyl) terephthalate Derived from Chemical Scavenging of Waste Clothes

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ABSTRACT

In continuous to our previous work, we were synthesized flame retardant polyols using the bis(2-hydroxyethyl) terephthalate derived from chemical scavenging of post-consumed clothes. Phosphorous containing polyols and diisocynates were mixed in appropriate molar ratio in reference to prepare flame retardant PU coatings. Various mechanical, chemical and flame resistance properties of prepared PU coatings were investigated. The formulated PU coatings showed higher flame retardency over the PU coatings synthesized from petro-based raw materials. A mechanical and chemical property also shows as high as that of PU coatings from petro-based raw materials. In order to evaluate flame retardant properties of the PU coatings limiting oxygen index analysis and UL-94 test methods were performed. Utilizing recycled product as replacement to petro-based raw materials in PU coatings, hence waste management indeed.

Keywords: Waste polyester clothes, Bis(2-hydroxyethyl) terephthalate (BHET), Flame retardant polyol, Polyurethane, Flame Retardant Coating.

INTRODUCTION

From the perception for preservation of petrochemicals and environmental conservation, utilizing recycled waste and natural based renewable ones are considerable issue for researchers to overcome [1]. Polyurethanes are one of the most useful commercial classes of polymers which are widely used in both industry and in everyday life. As an important engineering material, polyurethane (PU) exhibits many attractive properties, such as excellent abrasion resistance, low temperature flexibility, excellent chemical, mechanical and physical properties because of its special soft and hard segment structure [2-3]. Polyurethanes have found extensive use in numerous commercial applications such as coatings, foams, adhesives, sealants, synthetic leathers, membranes, elastomers as well as in many biomedical applications due to the wide range of possible compositions [4]. It is well known that polyester poyols and diisocynates are used as a soft segments and hard segments respectively to prepare PU coatings [5-7]. Since polyurethanes are in general flammable materials, many efforts have been directed to improve their flame retardency. However, the additive flame retardants are usually easy to separate out from PUs, especially for micromolecular liquid flame retardants, which decreases the permanent flame retardency [8]. Therefore, a great effort has been made in exploiting flame-retarded polyol. One of the problems facing polyurethanes nowadays is their dependence on petroleum derivative products. Thus, developing a novel polyurethanes coatings system with flame retardant property from recycled product as a replacement to petroleum derivative products were thought of. Inclusion of Phosphorus containing compounds yields an environmental friendly flame retardant polymeric system due to advantages such as low toxicity, no release of poison gas and halogen acids during combustion, and producing low smoke during burning [9-12]. Considering the above, current work aims at an effective utilization of bis(2-hydroxyethyl) terephthalate (BHET) for flame retardant polyurethane coatings preparation. Phosphorous containing polyester polyols were synthesized in two step processes by reacting glycolyzed BHET and phosphorous oxychloride, followed by reaction with phthalic anhydride and diols. To prepare flame retardant polyurethane coatings various diisocynates were allowed to react with synthesized polyols on the surface of substrate. Various physical, mechanical, flame-retardant, and chemical resistance properties were investigated.

MATERIALS AND METHODS

Post consumed polyester clothes were collected from the local area. Mild steel coating test panels were used as substrate in the coating application. All chemicals and solvents were obtained from commercial suppliers and were used without further purification. Toluene diisocynate (TDI) and Hexamethylene diisocynate (HMDI), containing 13.3 (\pm 0.4) % free-NCO, was kindly supplied by Gads fine chem. Itd, Ahmadabad, Gujarat, India.

2.1. Bis(2-hydroxyethyl) terephthalate (BHET)

After giving primary treatment, post consumed polyester clothes were subjected to glycolysis according to the preeminent processes conditions of our earlier reported method [13]. The glycolysis was carried out at 180 °C temperature under reflux for 8 h to get higher conversion of pure BHET through repeated crystallization, by using 1% (W/W) zinc acetate as catalyst and 5:1 (w/w%) ethylene glycol: PET ratio.



Tris[bis(2-hydroxyethyl)terephthalate]monophosphate

Figure 1: Reaction mechanism of the monomer (TBM)

2.2. Synthesis of monomer

Monomer tris [bis(2-hydroxyethyl)terephthalate] Monophosphate (TBM) for the synthesis of flame retardant polyols was prepared by reacting glycolyzed BHET and phosphorous oxychloride. The ration BHET: POCl₃ 3:1 (Mol/Mol) was subjected to the reaction vessel together with solvent N, N-Dimethyl formamide and catalyst Tri ethyl amine (0.20 Mol) at reflux temperature. Progress in reaction was supervise by using thin layer chromatography, after 8 h

the reaction was stopped and the resultant mass was washed with ether followed by dissolution in acetone, neutralization and precipitation in cold water. The reaction mechanism of the monomer (TBM) is shown in Figure-1.

2.3. Formulation of flame retardant polyols

Polyols were synthesized in two steps [14]. The reaction set up comprised 1L four necked round bottom flask equipped with Dean and Stark apparatus, water condenser, mechanical stirrer, nitrogen inlet and thermometer. In the first step tris[bis(2-hydroxyethyl) terephthalate] Monophosphate (1 Mol) and phthalic anhydride (3 Mol) were reacted at 190 °C. Xylene was used as a reaction medium. Acid value was determined at specific time intervals and when the value reached 30 the reaction was stopped.

In second step, resulted polyester (1 Mol) was allowed to react with ethylene glycol (3 Mol) and catalyst para toluene sulfonic acid (0.002% by weight) in the presence of xylene solvent, at above mentioned reaction condition. Progress in the conversion to flame retardant polyol was monitored by determining the acid number. The reaction was continued until the polyol had the value in range of 10 to 12 mg KOH/gm. Water being the by product at both the reaction step, the pure product (FRP-1) was obtained by vacuum distillation. The other two flame retardant polyol FRP-2 and FRP-3 were synthesized using the above method, where polyethylene glycol and 1,3- propane diol were used instead of ethylene glycol. The reaction mechanism is shown in Figure-2.

2.4. Preparation of polyurethane coatings

Polyurethane coating systems were formulated from a synthesized polyols as a base component and Toluene diisocynate (TDI) or Hexamethylene diisocynate (HMDI) adducts as a hardener components.



Figure 2: Reaction mechanism of Flame retardant polyol

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Both the components were mixed in a stoichiometric amount at the time of application in a minimum amount of methyl ethyl keton solvent and catalyst. Resulted mixtures were applied on mild steel panel with the help of film applicator. The panels were kept at room temperature for 6 h and post curing were carried out in an oven at 110 °C for 1 h. The panels were stored in vacuum desiccators and used for the characterization of different properties.

2.5. Casting of polyurethane films

Two steel plates, free from surface imperfections such as rolling marks, scores, scales etc. having the dimensions 0.1 \times 17 \times 17 cm, for Plate A and 0.2 \times 17 \times 17 cm, for Plate B were taken. Plate B was cut from inside leaving 2.5 cm edges all around. A silicon coated paper was placed on the flattened steel plate-B onto which plate-A was placed. The edges were sealed with wax and the assembly was placed on a triangular leveling plate and leveled by moving the rotating screw of the leveling plate. Required amount of polyurethane was mixed with MEK solvent (2%) and poured on the prepared site of the sheet. The assembly was kept for 4 h in open environment at room temperature for moisture curing. The assembly was then kept inside a preheated oven at 50 °C for 24 h for complete setting. After cooling, the films were removed from the mold and used for the measurement of flame-retardant properties.

RESULTS AND DISCUSSION

3.1 Characterizations of BHET:

Gel permeation chromatography of the glycolyzed product was performed to study the average molecular weight and polydispersity of the synthesised BHET monomer using Perkin Elmer turbo matrix-40. THF was used as mobile phase at a flow rate of 1 ml/min. The chromatogram in Figure-3 portrays a single narrow peak at retention time 7.46 min and molecular weight of 254.5 g mol⁻¹ which confirms the molecular weight of BHET monomer. The Mw/Mn ratio of the glycolyzed product obtained was 1.02 which strongly designates mono dispersion of BHET monomer.

MASS spectrum of glycolyzed product in Figure-4 enumerates a molecular ion peak at 254.5 which conforms the molecular weight and presence of BHET monomer.

3.2 Characterizations of monomer (TBM)

Fourier Transform Infrared Spectroscopy was done to identify the functional groups and chemical bond of the synthesized monomer (TBM) using Perkin Elmer FT-IR Spectrum 100 (USA). In Figure-5 the absorption of 3427.9 cm⁻¹ indicated the presence of hydroxyl (–OH) alcoholic group. A band at 2961.5 cm⁻¹ indicates C–H stretching, a narrow sharp band of C=O was observed at 1726.4 cm⁻¹. The bands at 1278.3 cm⁻¹ and 1018 cm⁻¹ are due to P=O and P–O–C stretching frequencies respectively, which demonstrates the successful reaction of BHET with POCl₃.



Figure 3: Gel permeation chromatogram of the glycolyzed product



Figure 4: MASS spectrum of glycolyzed product

¹H NMR and ³¹P NMR of the synthesized monomer (TBM) were performed using a Brucker Avance II 400 MHz in DMSO solvent in order to characterize the chemical structure. Figure-6 shows the ¹H NMR spectrum of the monomer with peaks at $\delta = 8.09-8.14$ ppm respect to aromatic protons of the benzene ring, 4.73 ppm for the protons of hydroxyl group (–OH), 4.59- 4.63 ppm indicate the protons of the methylene group near –COO– group, and 3.99- 4.02 ppm for the protons of the methylene group adjacent to the outermost hydroxyl group (CH₂-OH). The structure of the monomer was also confirmed from the ³¹P NMR spectrum as shown in Figure-7, where a sharp signal was observed at -11.0 ppm.

The experimental values obtained in the elemental analysis are C (53.67%), H (4.88%), and O (37.68%). These values are in accordance with the theoretical values of C (53.60%), H (4.86%), and O (37.68%), which provides strong evidence for the structure conformation of the monomer (TBM).

3.3 Characterizations of flame retardants polyols:

The acid value and hydroxyl value of poyols were determined as per Indian Standard. Intrinsic viscosities of these polyols were measured by Ubbelohde suspended level viscometer in toluene. The values are between 0.62 and 0.71 dl/g.

Average molecular weights were determined by the gel permeation chromatographic (GPC) technique using Perkin Elmer turbo matrix-40. THF was used as mobile phase at a flow rate of 1 ml/min. Figure-8, Figure.9 and Figure.10 shows the chromatogram of the average molecular weight and polydispersity of the synthesized polyols. All these results of flame retardant polyols are depicted in Table 1.

3.2 Setting Characteristics of coatings:

Physical parameters of the formulated coatings like pot life and various drying properties such as surface drying, tack- free drying, and hard drying were resolute in the laboratory and are depicted in Table 2.



Figure 5: FT-IR Spectrum of the monomer (TBM)



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Figure 7: ³¹P NMR of the synthesized monomer (TBM)



Figure 8: GPC Chromatogram of FRP-1



Figure 9: GPC Chromatogram of FRP-2



Figure 10: GPC Chromatogram of FRP-3

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Polyols	Reaction Conditions		Intrinsic Viscosity g/dl = g	Number average molecular weight Mn	Weight average molecular weight Mw	Mw/Mn	Acid Value	Hydroxyl Value
	(°C)	(h)	g/ui – g	IVIII	141 W			
FRP-1	190	8	0.62	1091	1290	1.19	09	134.4
FRP-2	190	8	0.71	1490	1917	1.28	10	122.2
FRP-3	190	8	0.70	1493	2059	1.37	05	120.6

Table 1: Reaction conditions and properties of polyester polyols

Results shows that TDI based formulated systems have fastest drying and shorter pot life compare to HMDI based formulated systems. This may be due to the higher reactivity of –NCO group with –OH group of polyols. The results of pot life and drying properties of TDI based formulated systems have higher and HMDI based formulated systems have comparable properties to the results of formulated systems by Patel et al.,2014 [15]. They formulated coatings, from bisphenol-A bis(hydroxy phenyl phosphonate) based polyol, in which starting material is based on petroleum feedstock.

3.3 Performance characteristics of coatings

Various mechanical properties like hardness, impact resistance, flexibility, and adhesion properties were determined by ASTM standard methods. scratch hardness is the most important test used for coatings. Crosshatch scratch hardness tester was used to determine the hardness of coatings (ASTM D 5178). Result depicted in Table 3, shows that FRP-3 based coatings have the highest scratch hardness, which may be due to the rigid nature of the 1,3 propane diol moiety in the polymer structure. FRP-2 based coatings have the lowest scratch hardness due to the presence of long, flexible moiety that makes films less rigid compare to others.

Polyols	Isocyanates used for coating	Pot life at room temperature Min.	Drying properties			
			Surface drying	Tack-free drying	Hard drying	
			Min.	Min.	Min.	
FRP-1	TDI	155	30	165	275	
	HMDI	190	45	175	290	
FRP-2	TDI	190	50	180	275	
	HMDI	240	65	195	300	
	TDI	145	35	145	250	
FRP-3	HMDI	180	60	165	290	

ASTM D 3363 method used to determine the Pencil hardness properties of the formulated coatings. Overall result shows that TDI based formulated coatings have superiors scratch and pencil hardness compare to HMDI based formulated coatings. These results were in agreement with the previous work by Patel et al. 2012 [14] on polyester polyol, based on tris (bisphenol-A) Monophosphate as a starting monomer.

Crosshatch method by means of ASTM D 3359 standard and Mandrel bend test method by means of ASTM D 522 standard were used to determine the strength of adhesion to the coated substrate and flexibility of coatings, respectively. The results in Table 3, shows that in all systems the test panels have 100% adhesion and also pass mandrel flexibility.

An impact resistance of coated panels was determined by a tabular impact tester according to ASTM D 2794 method. An indenter 500 gm was dropped on coated panels from certain height until the film cracked. Results show that due to the presence of flexible moiety, FRP-2 based systems have higher impact resistance than the others.

Table 3: Performance properties of polyurethane coatings

Polyols	Isocyanates used for coating	Scratch hardness gm.	Pencil hardness ^a	Flexibility 1=4" mandrel	Adhesion (cross- hatch) [*]	Impact resistance
FRP-1	TDI	1800	1H	Р	Р	200
	HMDI	1700	Н	Р	Р	250
FRP-2	TDI	1750	1H	Р	Р	300
	HMDI	1650	Н	Р	Р	400
FRP-3	TDI	1900	2H	Р	Р	250
	HMDI	1750	Н	Р	Р	300

^a6H>5H>4H>3H>2H>1H>H>1HB>2HB>3HB>4HB>5HB>6HB; * P = Pass

3.4 Chemical resistance characteristics of coatings

These properties of coatings were determined by the immersion test method. In these method panels were immersed in different solution of chemical, like 5% Sodium chloride, 5% hydrochloric acid and 5% sodium hydroxide in closed glass chamber. After seven days panels were removed from the solutions and stored in vacuum desiccators. Visual observation of these panels were carried out in terms of change in colour, softening and blistering of films, and partial or complete removal of coating from test panels. The observation of immersion test shows that all the panels were unaffected by sodium chloride solution. Neither blistering nor removal of coatings from panels was observed. Coating based on polyethylene glycol was weakly affected by acid and alkali solution. Slight softening is observed in few samples. Results shows that formulated coatings have superior chemical resistant properties than the formulated two-pack coatings systems by Patel et al. 2006 [16].

3.5 Flame retardant characterization of films

Flame retardant properties of casting films were measured by limiting oxygen index (LOI) and vertical test methods (UL-94) according to ASTM D 2863 standard and ASTM D 3801 standard tests, respectively. LOI is the measurement of the minimum concentration of oxygen, in terms of volume percentage, in a mixture of oxygen and nitrogen that will just support flaming combustion of material in specific conditions. In the UL-94 test method, samples achieve V_0 rating when itself extinguishes within 10 s and there is no sign of dripping of the burning part. If the sample continuously burn or drips, a V_1 or V_2 rating is assigned. All these results are depicted in Table 4. Analysis results of the limiting oxygen index, revels that TDI-based polyurethane films have the highest LOI value (32-35%) in the series. These may be due the presence of aromatic nature. While HMDI-based polyurethane films more easily deteriorate in the presence of flame and achieve the lowest value of LOI (28-29%). These may be due to presence of aliphatic nature of the HMDI. These data are also supported by UL-94 test, which shows that TDI-based polyurethane films achieve a V_0 rating, while HMDI-based polyurethane films achieve V_1 rating. In all these systems phosphorus compound capture oxygen and hydrogen from the surface of film during a fire and converted into phosphoric acids. The resulted layer of acids on the film can block heat and oxygen contact to retard fire until it completely extinguishes. LOI value of TDI-based polyurethane films have higher and HMDI-based polyurethane films have comparable value than the value demonstrated in the earlier published work (Park et.al., 2006 [17], Yuan et.al., 2008 [18]).

Table 4: Flame-retardant behaviour of polyurethane film

Polyols	Isocyanates used for coating	LOI%	UL-94
FRP-1	TDI	34	V_0
	HMDI	28	V_1
FRP-2	TDI	35	V_0
	HMDI	29	V1
FRP-3	TDI	32	V_0
	HMDI	29	V1

CONCLUSION

The driving force behind the attempts is the urge for the conservation of costly and scarce energy and feedstock as well as growing consciousness of environment. The obtained BHET monomer based on post consumed cloths was further utilized as precursor in synthesis of flame retardant polyol. Flame retardant polyurethane coating was successfully prepared by reacting polyols with different disocyanates. A good balance between mechanical, chemical and flame retardant properties is observed in the polyurethane coating systems. As these attempts used waste and non halogenated compound as sources of starting materials, it proved to be beneficial from economic as well as environmental point of view. Thus it provides a better solution to the solid waste problem and also contributes to the conservation of raw chemicals and energy.

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