A greener and sustainable approach for converting polyurethane foam rejects into superior polyurethane coatings

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A R T I C L E   I N F O

A B S T R A C T

Recycling is a crucial area of research in Green Polymer Chemistry. Various developments in recycling are driven by Environmental concerns, interest in sustainability and desire to decrease the dependence on non-renewable petroleum based materials. Polyurethane foams [PUF] are widely used due to their light weight and superior heat insulation as well as good mechanical properties. As per survey carried Polyurethane Foam Association, 12 metric tonnes of polyurethane foam are discharged during manufacturing and/or processing and hence recycling of PUF is necessary for better economics and ecological reasons. In present study, rejects of PUF is subjected to reaction with a diethylene amine in presence of sodium hydroxide [NaOH] as catalyst, as a result depolymerised product containing hydroxyl and amine groups is obtained. Conventional and Microwave reaction for depolymerizing polyurethane foam have been carried, and best results are obtained by Microwave reaction. Further depolymerised product with hydroxyl and amine functionalities are reacted with bis (2-hydroxyethyl terephthalate) [BHET] obtained by recycling polyethylene terephthalate [PET] and sebacic acid, with stannous oxalate [FASCAT 2100 series] as catalyst to obtain Polyester amides. These Polyester amides having hydroxyl and amino groups in excess are cured with isocyanates - Hexamethylene diisocyanate biuret [HDI biuret] and Isophorone diisocyanate [IPDI] for coating applications. The coated films are characterized using physical, mechanical and chemical tests, which shows comparable physical, mechanical properties but alkali resistance is poor.

Capsule Summary: Polyester amide coatings can be synthesized by depolymerizing polyurethane foam and obtained aminolysed product are reacted with bis (2-hydroxyethylterephthalate) [BHET] obtained by recycling of PET bottle. Comparison between conventional and microwave methods for depolymerizing of polyurethane foam is also studied in the current work.

Abbreviations: EDA—Ethylene Diamine, KOH—Potassium Hydroxide, MEK—Methyl Ethyl Ketone , NaOH—Sodium Hydroxide, HDI—Hexamethylene Diisocyanate , ATR—Attenuated Total Reflectance, IPDI—Isophorone Diisocyanate, PEA —Polyester amide, BHET—Bis(2- hydroxyethyl terephthalate), DFT—Dry Film Thickness, PU—Polyurethane, DMF—Dimethyl Formamide
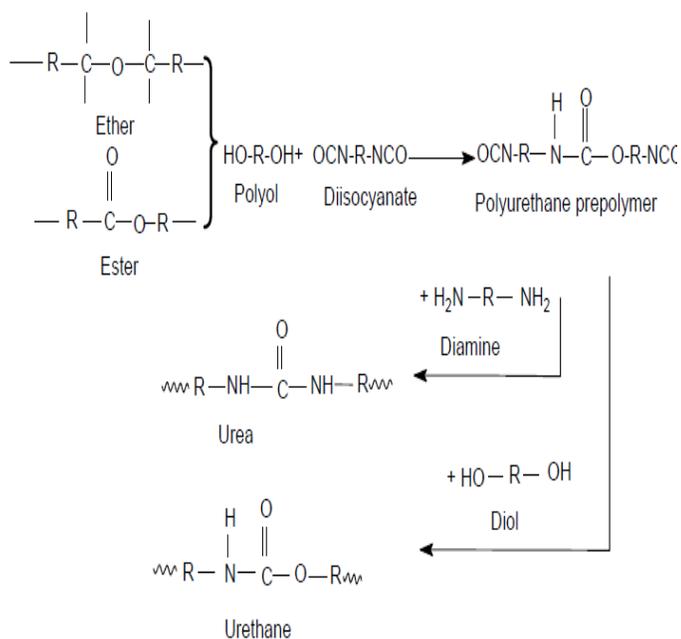
INTRODUCTION

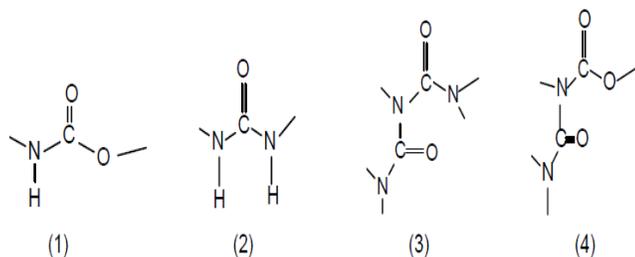**Fig. 1:** Chemical reactions involved in Polyurethane synthesis

Fig. 2: Chemical structures of different isocyanates linkages (1. Urethane 2.Urea 3. Biuret 4. Allophanate)
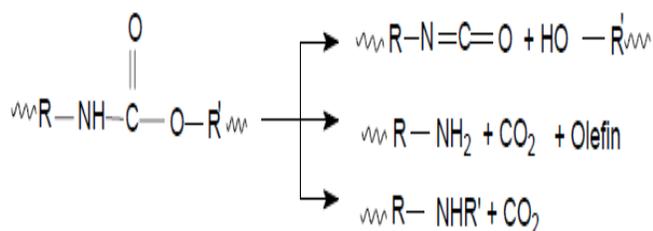

Fig. 3: Thermal degradation of Urethane linkage

Polyurethanes are one of the most versatile polymers. They are synthesized by a polyaddition process of polyisocyanate and polyalcohol as depicted in figure1. Even though they are named after the characteristic urethane group, other moieties like ether

or ester groups and links like urea, biurets or isocyanates can be seen in figure 2.

In a wide variety of applications in consumer and industrial goods, the broad range of properties that can be tailored according to the need of the user, ensure a sustainable utilization. It is important to mention here that there is no universally accepted definition of sustainability, but in its most widely acceptable meanings, it is a "Sustainable development that meets the needs of present without compromising the ability of future generations to meet their own needs. It demands the reconciliation of environmental, social and economic demands (Avar et al., 2012).

Some of the most attractive properties of polyurethanes are their high strength, satisfactory abrasion resistance and inertness against oxygen and ozone. Most of the polyurethanes produced are used in formulations of rigid/flexible foam and elastomers with a wide variety of applications as adhesives, coatings, and insulating agents etc. Foams are obtained by blowing air through the polymer or by adding water which reacts with residual isocyanate groups. The degree of rigidity of the resulting polymer can be controlled as per the end use by changing the groups, for example; additional hydroxyl groups can lead to a crosslinked polymer matrix of higher rigidity. Polyurethane foams are extensively used in the automotive industry due to their superior contribution in comfort with minimal addition in weight of the vehicle. With regard to chemical recycling of polyurethanes two aspects must be highlighted 1. Polyurethane are used to manufacture durable goods, which means that it takes several years for these items to be disposed of into the solid waste stream, 2. Moreover polyurethanes contain around 4 wt% of Nitrogen, which may hinder their recycling by oxidative treatments such as incineration or gasification due to the potential release of significant amounts of NO_x, in the gaseous effluents (Avar et al., 2012). Application of heat causes both physical and chemical changes in the polymer resulting in undesirable changes in its properties (Beyler et al., 2002). Heat can cause degradation of polyurethanes. The onset of allophanate dissociation is around 100°C to 120°C. The dissociation temperature of biuret is around 115°C to 125°C. The reactions are dissociations and somewhat reversible which revert to the urethane or urea from what they were formed. Urethane linkage may undergo three separate types of thermal degradation, the formation of the precursor isocyanate and the precursor alcohol, cleavage of the oxygen of the alpha methyl group and association of one hydrogen on second methyl group lead to the carbamic acid and olefin with subsequent carbamic acid decomposition to give a primary amine and CO_2, the formation of a secondary amine and CO_2 (Naturalium, 2004).

The most important chemolysis methods so far developed to depolymerise polyurethane are glycolysis and hydrolysis while aminolysis is comparatively less investigated as aminolysis lead to multiple side reactions and hence we have proposed aminolysis using microwave waves, which will avoid side reactions. Separation of amines from depolymerized product was a tedious process and hence was not practised and hence we used ethylene diamine which was easily separated by distillation.
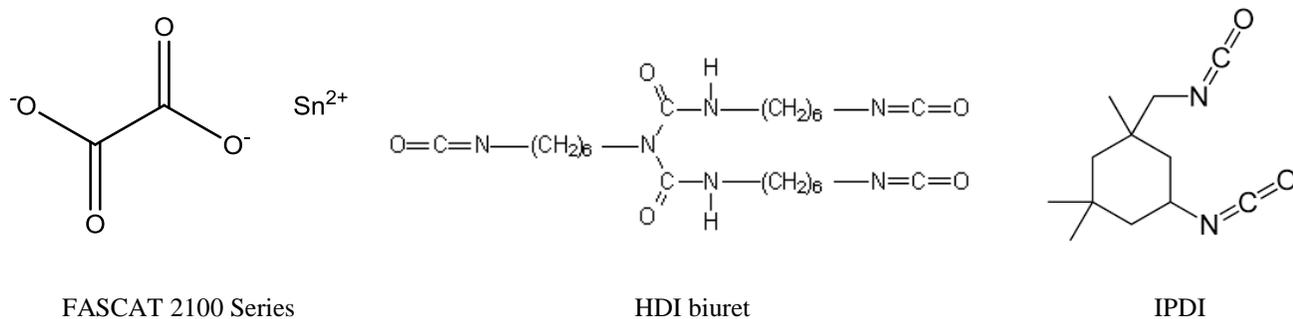
FASCAT 2100 Series   HDI biuret   IPDI

Fig. 4: Chemical structures of FASCAT 2100 Series/HDI biuret/ IPDI
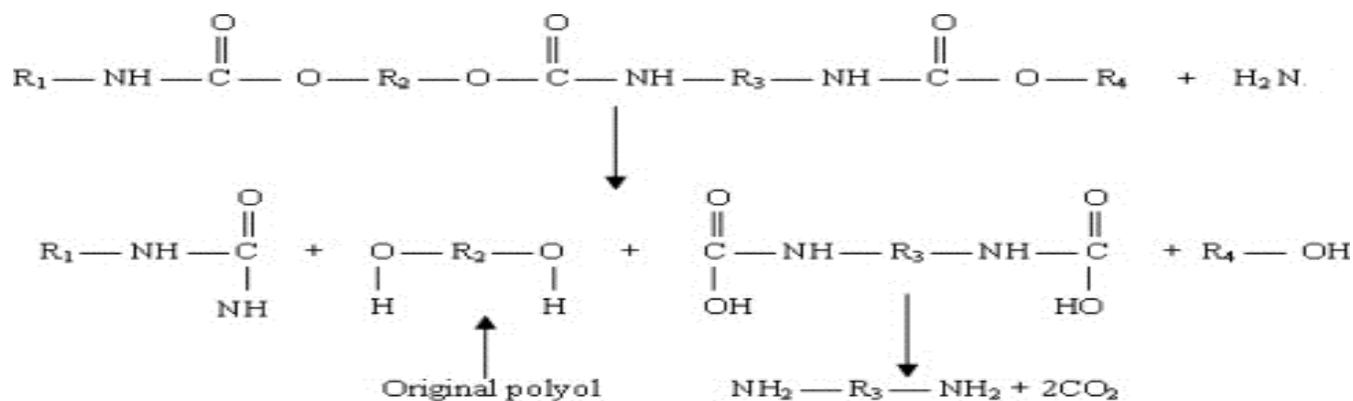
Scheme 1: Aminolysis of Polyurethane Foam
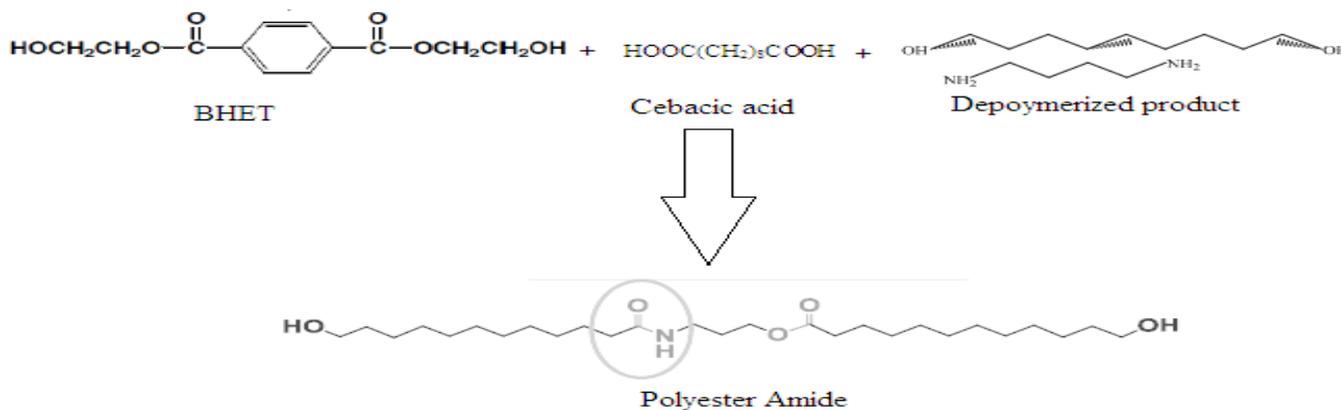
Scheme 2: Preparation of polyester amides

Polyurethane chemolysis by reaction with amines has been described in the literature. A process based on polyurethane foam decomposition using Diethanolamine in an extruder and the resulting decomposed product could be used as an alternative virgin polyol in reclaiming polyurethane elastomers was proposed by Watando et al., (2006). A reheating process for the products in the chemical recycling of rigid polyurethane foam by an extruder with diethanolamine as a decomposing agent was effective for improving the product stability was experimented by Fukaya et al., (2006). In another experiment rigid polyurethane foam scrap was depolymerised by aminolysis using diethylene triamine as a degrading agent and sodium hydroxide

as both a reactant and catalyst, resulting in 4,4′-methylenedianiline was proposed by Chuayjuljit et al., (2012). A system wherein flexible foams were decomposed by alkanolamines without a catalyst at 150ºC and decomposed products were completely separated into two layers, the upper liquid layer being a polyol and the lower liquid layer of methylene diphenyl amine was demonstrated by Kanaya et al., (1994). Aminolysis of rigid polyurethane using diethylene triamine and studied the application of aminolysed products as hardeners of epoxy resins was carried out by Lee et al., (2001). A process based on polyurethane decomposition with ethanolamine at 120ºC, ammonia and ammonium hydroxide at 180ºC, diethylene triamine at 200ºC and other basic reagents was initiated by Sheratte et al., (1978). In all cases the process involved simultaneous or subsequent reaction with propylene oxide which allowed the different amines obtained to be quantitatively converted into polyols. The polyols derived from this process were used in the reformulation of new polyurethanes by polymerization with corresponding isocyanate and were suitable for application in rigid foams.

In the present study, ethylene diamine (EDA) was used for aminolysis in optimized ratio of 1:2 (PUF: EDA) w/w and the reaction was carried out at 120ºC for 3 hours in presence of 0.2% NaOH on weight basis of PUF, as a transesterification catalyst. The aminolysed product was characterized for hydroxyl and amine value by conventional methods of ASTM D1957 and ASTM D2073. Polyester amide with excess hydroxyl and amine groups was successfully synthesized by polycondensation of aminolysed product/ bis (2-hydroxyethyl terephthalate) (BHET)-obtained after recycling PET and sebacic acid using 0.5% FASCAT 2100 series catalyst on weight basis of entire batch. FASCAT 2001 catalyst shortens cycle times, reduces consumption of chemical reactants, and reduces byproduct formation, while increasing product ester yield and purity. FASCAT 2001 catalyst reduces side reactions. Polyester amide urethane coatings were prepared by reacting Polyester amide with excess hydroxyl and amine groups with isocyanate curing agents. The coated films were evaluated for physical, mechanical and chemical properties.

EXPERIMENTAL

Materials

Rigid PUF waste obtained from Hamilton India Pvt Ltd, was grinded and converted into small pieces, Ethylene diamine, Sodium hydroxide and sebacic acid were of analytical reagent grade procured from SD Fine Chemicals Ltd, Mumbai. FASCAT 2100 a catalyst was obtained from Arkema, HDI biuret and IPDI Isocyanates cross linkers were obtained from Bayer Material Science Ltd, Thane.

Aminolysis of Polyurethanes (Conventional Method)

Calculated quantities of PUF, EDA and NaOH were charged in a four neck glass reactor equipped with stirrer, reflux condenser, temperature indicator and nitrogen inlet. PUF and EDA were reacted in 1:1 (PUED C1) and 1:2 (PUED C2) (w/w) ratios along with 0.2% NaOH catalyst on weight basis of PUF as per *scheme 1*. The details of batch to study Conventional aminolysis are presented in Table 1. The aminolysis reaction was carried out at 120ºC under reflux and nitrogen atmosphere for 3 hours. The depolymerised product was characterized by hydroxyl value with ASTM D 1957, amine value with ASTM D 2073 and Attenuated Total Reflectance [ATR] analysis.

Aminolysis of Polyurethanes (Microwave Method)

A comparative study of depolymerization of PU foam was also conducted using microwave radiation as against the conventional one. Depolymerization of PU foam was carried out by varying time and microwave power. The ratio of PUF to EDA was maintained 1:2 by weight and 0.2% NaOH on weight basis of PUF. The reaction conditions i.e. ratio of PUF to EDA, the percentage of catalyst, temperature were the same as applied for conventional method only difference was the time required for depolymerization as use of microwave reduced the time required for depolymerization. The details of the batch to study the effect of the time of microwave irradiation is presented in Table 2 and the effect of microwave power in Table 3.The ultimate aim of this comparison was to observe the difference in the hydroxyl and amine value using different source of energy so that reaction kinetics of the depolymerization of PU foam can be studied accordingly. By using microwave the time for depolymerization of PUF decreased from 3 hours to 0.5 hours with less side reactions.

Purification of Depolymerised Product of PU foam

The assembly comprised of normal distillation setup including 3-necked distillation flask, Condenser, distillation head, temperature controller, agitator, collecting flask. On continuously heating the depolymerized product with constant agitation, at about 130ºC a colorless liquid fraction was obtained, which was EDA with boiling point of 116ºC. After removal of EDA from depolymerised product, the unreacted foam was separated via filtration. The depolymerised product left after removal of EDA by distillation and unreacted foam by filtration was used for preparation of polyester amide.

Preparation of BHET by recycling of PET bottle

The glycolysis reaction was carried out using ethylene glycol at molar ratio of 1:6 (PET: EG). PET flakes, EG and 0.5% (w/w) zinc acetate catalyst were charged in a three necked glass reactor equipped with stirrer, thermometer and reflux condenser. The glycolysis reaction was carried out at 190 ± 5 ^{o}C under reflux in nitrogen atmosphere. The reaction was carried out for different reaction times of 2, 4 and 6 hours. After the reaction was complete, the reaction mixture was cooled to room temperature and boiling water was added to the reaction mixture to dissolve BHET formed during the reaction while the oligomeric product was precipitated. The mixture was then filtered under vacuum to separate the oligomeric product. The filtrate solution was then cooled under ice bath for crystallization of BHET formed. The crystalline BHET was then filtered and dried. It was then purified by recrystallization and dried in an air circulating oven at 60 ^{o}C for 2 hours. The percent yield of BHET obtained was 80 percent.

Preparation of Polyester amide

Table 1: Conventional Batch of EDA/PUF

BATCH	PUED C1	PUED C2
PU Foam (g)	20	20
EDA (g)	20	40
NaOH (g)	0.04	0.04
Yield (%)	50	60
@120ºC for 3hours		

Table 2: Microwave assisted aminolysis- Batches with varying reaction time

BATCH	PUED T1	PUED T2	PUEDT3
PU Foam (g)	10	10	10
EDA (g)	20	20	20
NaOH (g)	0.02	0.02	0.02
Time (min)	10	20	30
Yield (%)	70	75	77
@120ºC for 10,20,30 minutes at 400kW			

Table 3: Microwave assisted aminolysis- Batches with varying microwave power

BATCH	PUEDM1	PUEDM2	PUEDM3
PU Foam (g)	10	10	10
EDA (g)	20	20	20
NaOH (g)	0.02	0.02	0.02
Microwave Power (kW)	400	600	800
Yield (%)	77	80	80
@120ºC for 30 minutes			

Aminolysed product with hydroxyl value 557 mgKOH/g and amine value 300 mgKOH/g; bis (2-hydroxyethyl terephthalate) (BHET)-obtained after recycling PET; sebacic acid were charged

in a mole ratio of 0.9:0.5:1.5 and 0.5% of FASCAT catalyst on weight basis of entire batch (PEA1). The reaction was carried out in a four necked glass reactor equipped with stirrer, temperature indicator, nitrogen inlet and reflux set as per *scheme 2*. The detail of the batch for preparing polyester amide is presented in Table 4. Xylene was added as an azeotropic solvent for removal of water of condensation throughout the reaction. The polyesterification reaction was carried at 160ºC and progress of reaction was monitored by acid value determination. The reaction was stopped when the acid value of the reaction mixture reached 30 mgKOH/g. Polyester amide products was removed from the reactor and then cooled and later characterized for hydroxyl and amine values. It was also analyzed by FTIR spectroscopy for structural ilucidation.

Preparation of Polyester amide based coatings

Polyester amide with excess hydroxyl and amine groups prepared in the above steps was cured with isocyanate curing agent. DMF – MEK (70:30 v/v) mixture was used as solvent. The films were applied on mild steel panels (150mm x 100mm x 0.5mm) and cured at 120ºC for 30 minutes. The coatings were further evaluated for mechanical and chemical properties.

Characterization and Testing

Hydroxyl Value (ASTM D 1957)

The hydroxyl value is defined as the number of milligrams of KOH equivalent to the hydroxyl content of one gram of sample. Or it is the number of milligrams KOH required to neutralize acetic acid produced as a result of acetylation of one gram of resin.

Procedure

A known weight of the sample was taken and refluxed over a steam bath using air condensers with pyridine-anhydride mixture (3:1) for 2 hours. Then 10 ml of distilled water was added and reflux was further continued for 15 minutes after which the solution was allowed to cool to room temperature. 20 ml of 1-butanol was then added to wash down any water droplets into the solution. The resultant solution was then titrated against 0.5 N alcoholic potassium hydroxide solution, using phenolphthalein as the indicator. A blank titration was also performed.

Hydroxyl value = [56.1 × (*B-S*) × *N*] / *W*   *(mg of KOH/g of resin)*

Where,

N = normality of alcoholic KOH.

B = burette reading of blank.

S = burette reading of sample.

W= weight of sample.

Acetic anhydride reacts with hydroxyl ion to form acetic acid and acetate ion. Remaining anhydride react with water to form acetic acid. This acetic acid is titrated against KOH and the amount of hydroxyl ion can be calculated.

Amine Value (ASTM D 2073)

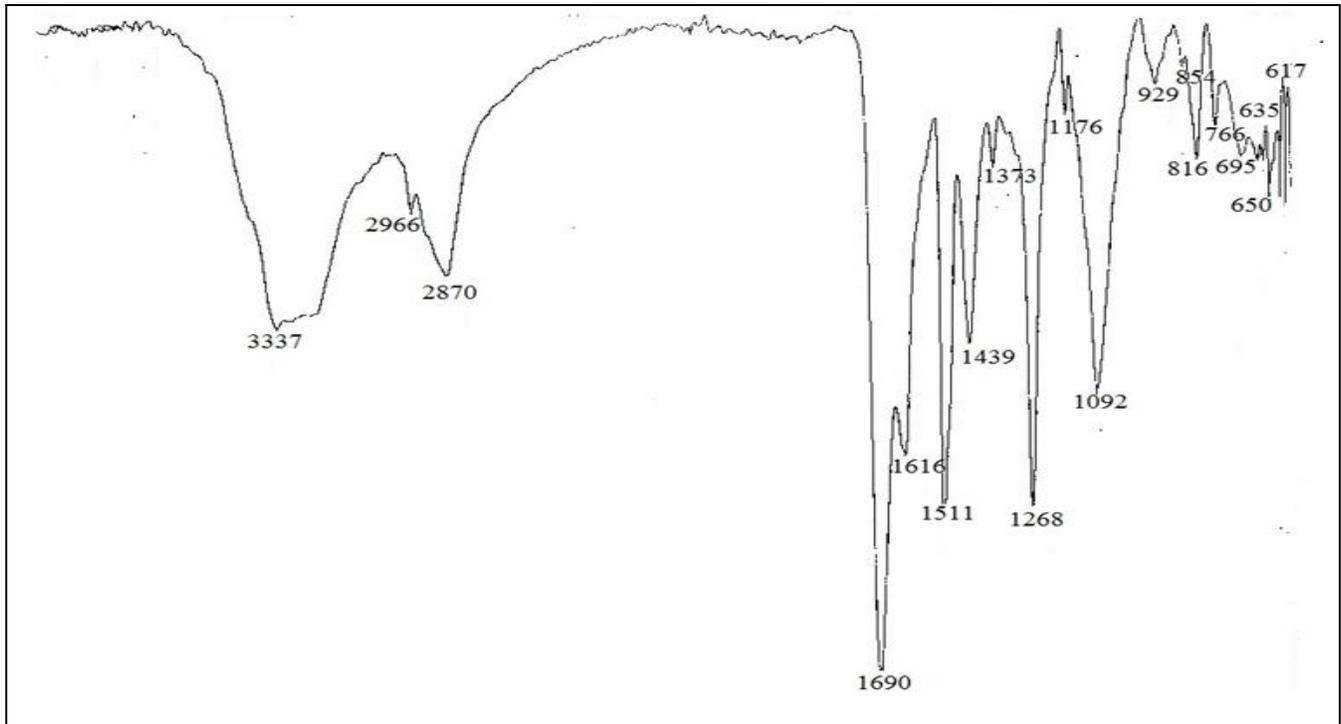**Fig. 5:** ATR Spectra of Conventional Aminolysed Product using EDA
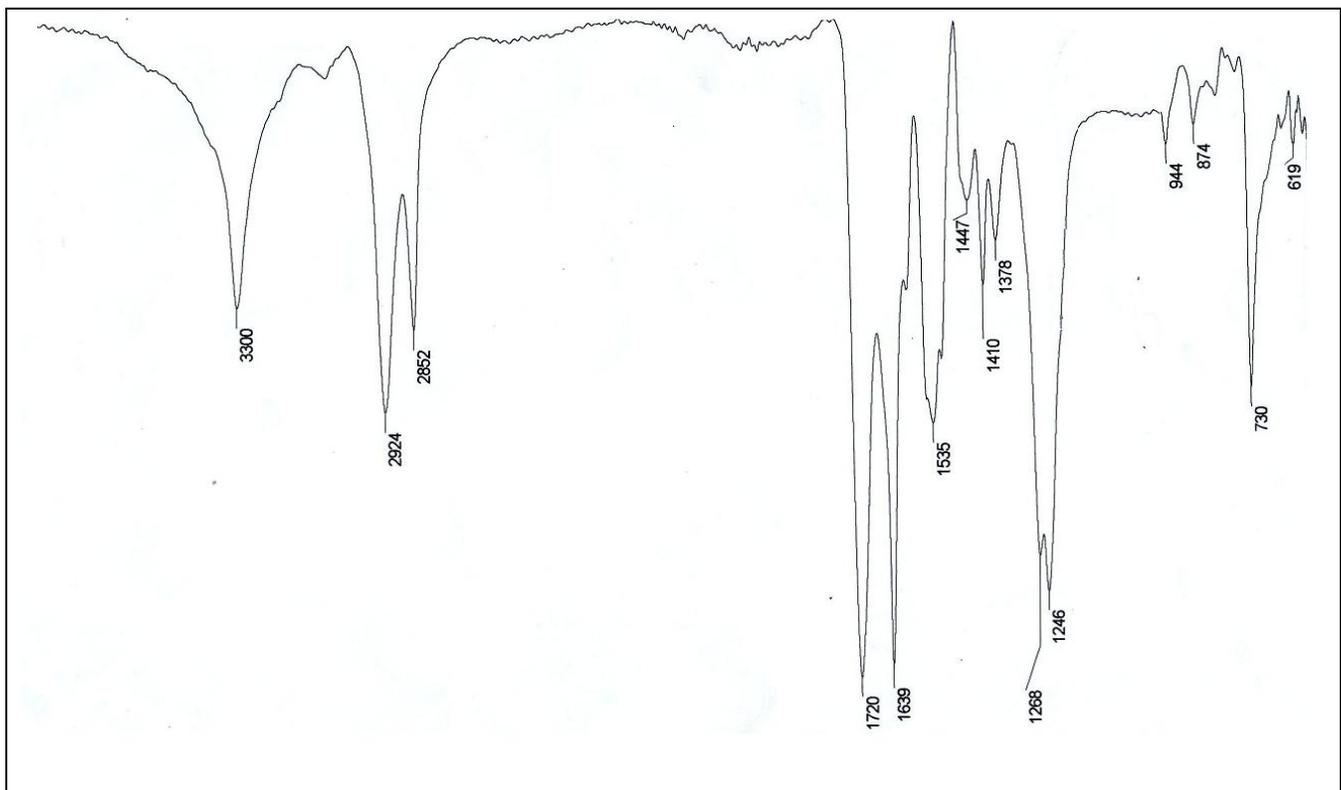

Fig. 6: ATR Spectra of Polyester amides

It is the number of milligrams of potassium hydroxide equivalent to the amine alkalinity present in one gram of the sample. The amine alkalinity can be regarded as the number of active hydrogen. These are considered alkaline because the amine group has a basic character.

Procedure

Table 4: Batch for preparation of Polyester amide

BATCH	PEA 1
Depolymerised Product of PU Foam (g)	90.64
BHET (g)	63.56
Sebacic acid (g)	151.38
FASCAT (g)	1.54
Yield (%)	80

Table 5: Classification of Adhesion Test Results

Classification	Nature of grid
5B	The edges of the cuts are completely smooth, none of the squares of the lattice is detached
4B	Small flakes of the coating are detached along the edges and at intersections of the cuts, 5% of the area is affected.
3B	Small flakes of the coating are detached along the edges and at the intersections of cuts. The area affected is 5 to 15% of the lattice.
2B	The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35% of the lattice.
1B	The coating has flaked along the edges of the cuts in large ribbons and whole squares have detached. The area affected is 35 to 65% of the lattice.
0B	Flaking and detachment is worse than grade 1B

Table 6: Hydroxyl Value and Amine Value of Conventional Batch

Batch No	PUED C1	PUED C2
Hydroxyl Value (mgKOH/g)	460	557
Amine Value (mgKOH/g)	239	300

Table 7: Hydroxyl Value and Amine Value of Microwave Batch with varying reaction time

Batch No	PUED T1	PUED T2	PUED T3
Hydroxyl Value (mgKOH/g)	278	445	480
Amine Value (mgKOH/g)	239	122	110

A known weight of the sample was taken in a conical flask and dissolved in Isopropanol. The mixture was then titrated against 0.5 N HCl, using bromocresol green as an indicator.

Amine value = $[56.1 \times N \times R] / W$

(mg of KOH/g of resin)

Where,

N = normality of HCl.

R = burette reading of sample.

W= weight of sample.

Acid Value (ASTM D 1639)

Acid value is defined as milligrammes of potassium hydroxides required to neutralize the free carboxylic acid (alkali reactive groups) present in the one gram of resin.

Procedure

A known weight of the sample was taken in a conical flask and dissolved in benzene-toluene mixture. The mixture was then titrated against 0.5 N alcoholic potassium hydroxide solution, using phenolphthalein as an indicator.

Acid value = $[56.1 \times N \times R] / W$ *(mg of KOH/g of resin)*

N = normality of HCl.

R = burette reading of sample.

W= weight of sample.

Spectroscopic Analysis

The ATR spectra were evaluated on CIL 15 spectrophotometer. The spectrum for depolymerised products was evaluated using transmittance technique. In case of coating films, the spectrum was taken of the respective films casted on metal panel, and conditioned at 100ºC in an air circulating oven.

Surface preparation, coating deposition and curing of coating

Mild steel panels were manually cleaned before application. Cleaning involved degreasing, hand scrubbing using emery paper (120 no.) followed by methanol cleaning. The application viscosity of all the coating solutions was maintained using mixture of solvents. The coating solutions were deposited onto prepared substrate followed by 10 minutes flash-off time and was then thermally cured at 120ºC for 30min. The coated panels were conditioned at room temperature for 24 hours before testing.

General Test Methods for Film Properties:

All tests were carried out at room temperature and a relative humidity. Before any tests were conducted, the specimens were pre conditioned under atmospheric conditions for a time period sufficient to allow the films to reach a stable condition with the environment.
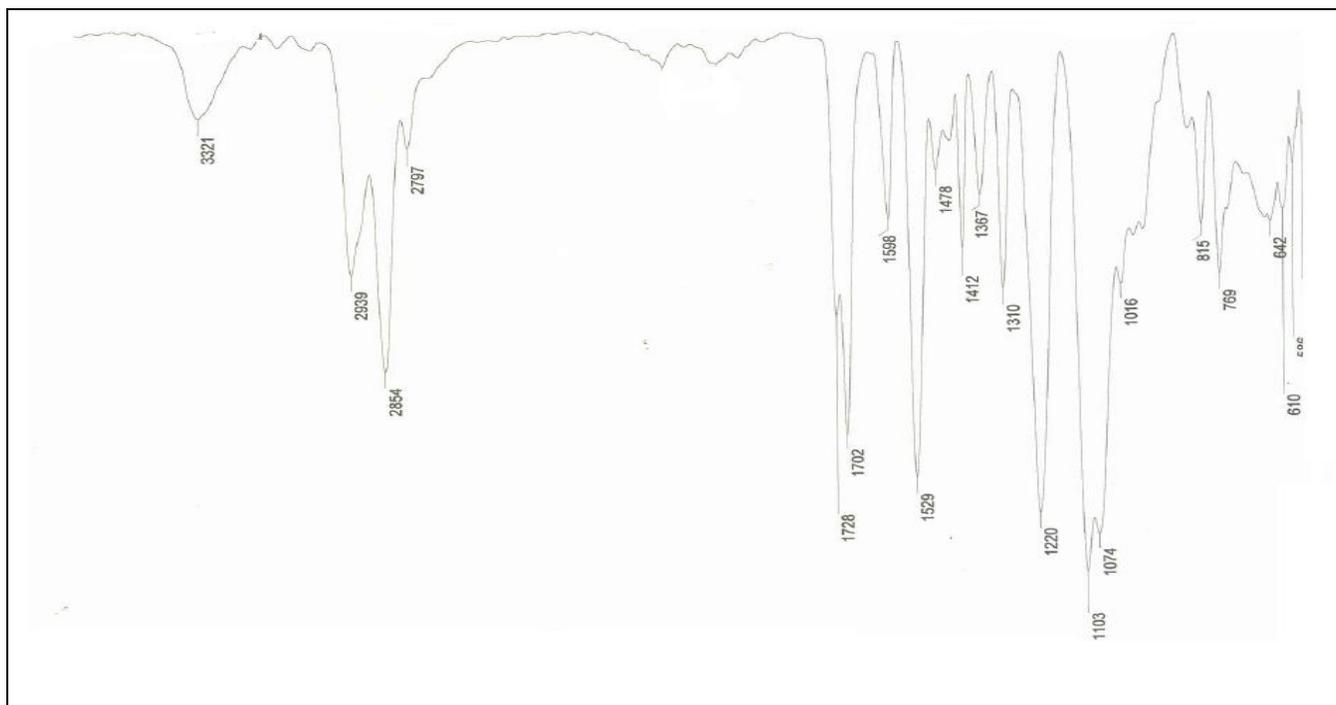
Dry Film Thickness

Fig. 7: ATR Spectra of Polyester amide urethane coatings

The dry film thickness is one of the most important parameters when testing the properties of paint films. A measuring gauge based on principle of electromagnetic induction should be used.

Gloss @60º (ASTM D523)

A Rhopoint-Novoglass glossmeter (Serial No 26135) was used to test the light reflection properties of the specimens according to ASTM D 523. The instrument was first calibrated for zero and then for the two standards supplied by the manufacturers. The coated steel panel was then placed with the coated surface facing upwards and the gloss measurements were determined. The average of the gloss measurements was taken as the specular gloss of the film.

Cross Cut Adhesion Test (ASTM D 3359)

Table 9: Hydroxyl and Amine Value of Polyester amides

Batch No	PUED M1	PUED M2	PUED M3
Hydroxyl Value (mgKOH/g)	480	550	565
Amine Value (mgKOH/g)	110	105	87

Table 8: Hydroxyl Value and Amine Value of Microwave Batch with varying microwave power

Batch No	PEA 1
Hydroxyl Value (mgKOH/g)	123
Amine Value (mgKOH/g)	58

The test was carried out on coated steel panels. The test was done using commercially available adhesive tape and is hence results obtained can only be used as an internal standard within the resins of those films applied. A grid marking of 1 sq.cm was made on the film taking care that the film was cut till the surface was exposed. An adhesive tape was then applied over the grid. To ensure good contact the tape was rubbed using an eraser. The tape was then rapidly and in single motion removed from the film at an angle close to 180^0 as possible. The grid was examined for any loss of the squares from the grid. The performance of the coating was graded as shown in the following Table 5.

Flexibility (ASTM D 522)

The flexibility of the coating was measured in terms of the "crack resistance" and the tests were carried out on a standard conical mandrel using coated steel panels. The panels were fixed before the rotator arm of the mandrel with the coated surface facing away from the cone. The rotator was then smoothly rotated through 180º causing the panel to deform. The coated panel was then immediately observed for any crack formation. If a crack formed then the length of the crack from the narrow end of the cone to the opposite edge of the crack was reported, if no crack was observed then a value of "0" was reported.

Falling Ball Impact Test (ASTM D 2794)

The definition of the impact resistance of a coating can be defined as the number of inch pounds required to produce cracking in the deformed coating. The test was carried out on steel panels. The test was carried out by dropping a 2 lb weight from maximum height of 60 cm. The weight dropped onto the coated surface or "intrusion" and on the reverse of the panel with reference to the coated surface or "extrusion".

Pencil Hardness (ASTM D 3363)

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Table 10: Peaks for conventional aminolysed product using EDA (Refer Figure 5)

Sr.no	Frequency, cm^{-1}	Assignment of peak to functional group
1	1092cm^{-1}, 1176 cm^{-1}and 1268 cm^{-1}	which corresponds to aliphatic ether group of polyether polyol formed after microwave depolymerization
2	1373 cm^{-1}	Bending vibrations of methylene groups appear in the polyol chain
3	2966 cm^{-1} and 2870 cm^{-1}	Stretching Vibrations of CH bonds in aliphatic carbons
4	3337 cm^{-1}	Stretching Vibrations of OH groups
5	1616 cm^{-1}and 1511 cm^{-1}	primary amines
6	854 cm^{-1}, 816 cm^{-1},766 cm^{-1}, 695 cm^{-1}	NH wag of primary and secondary amines
7	1439 cm^{-1} and 929 cm^{-1}	OH bend in Carboxylic acid
8	1690 cm^{-1}	C = O stretch in Carboxylic acid
9	617 cm^{-1}, 635 cm^{-1}, 650 cm^{-1}	CH bend

Table 11: Peaks for synthesized polyester amides (Refer Figure 6)

Sr.no.	Frequency, cm^{-1}	Assignment of peak to functional group
1	3300 cm^{-1}	NH stretch in amides
2	1639 cm^{-1}	C = O stretch in amides
3	1535 cm^{-1}	NH bend in amide
4	1720 cm^{-1}	C = O stretch in esters
5	2924 cm^{-1} and 2852 cm^{-1}	CH stretch
6	1447 cm^{-1} and 1410 cm^{-1}	C – C stretch in aromatic rings
7	730 cm^{-1}	CH bend in aromatic ring
8	874 cm^{-1}	CH stretch in aromatic ring
9	1268 cm^{-1}	Unreacted Carboxylic acid group
10	1246 cm^{-1}	C – O stretch in carboxylic group
11	944 cm^{-1}	OH bend in carboxylic group
12	1378 cm^{-1} and 619 cm^{-1}	CH bend

The pencil hardness of the film was evaluated on steel coated panels using a range of pencils from 6B to 6H. The nature of the pencil point and the method of holding the pencil were as per the standards. The test is carried out starting with the hardest pencil and the test is continued till a pencil is found that will neither cut nor scratch the surface of the film, this pencil is reported as result.

Scratch Hardness (IS 104)

The test was carried out on steel panels. The steel panels were fixed onto a movable base with the coated surface facing upward. A needle rests on the coated surface with a provision made for the placement of weights on it. The panel is moved for one cycle to and fro once with the needle resting on the coating. If the coating is scratched and the needle makes contact with the metallic substrate then the coating is said to have failed at that point for that weight. The weight is increased on the needle till a failure is observed. Every cycle is carried out on a different area on the coating surface.

Solvent Resistance (ASTM D 4752-10)

The solvent resistance was carried out using a piece of white cotton cloth. The solvents tested for were Xylene and Methyl Ethyl Ketone and double rubs were done. The result reported was the number of double rubs at which the films was observed to fail or else 100, which was maximum number of double rubs carried out.

Alkali Resistance and Acid Resistance (ASTM D1308-2)

These are the immersion tests carried out on coated metal panels. The edges of the steel panels were coated with wax to prevent creep. A 5% (w/v) aqueous sodium hydroxide solution was used in the test. The coated panels were immersed in the alkali bath so that the level of the alkali solution came up to approximately half the length of the panel. The test was carried out for 24 hours at ambient temperature and observations were made at 6 and 24 hours. The films were analyzed for any visible defects like blistering, discoloration, visual change in gloss, etc.

The acid resistance test was also carried out by same manner using 5% (w/v) hydrochloric acid and the films were analyzed for any visible defects like blistering, discoloration, visual change in gloss, etc.

RESULTS AND DISCUSSION

Successful depolymerisation of PU foam was achieved using EDA and the confirmation of depolymerisation was done by calculating the hydroxyl value and amine value of the depolymerised product.

Hydroxyl Value/ Amine Value

The hydroxyl and amine value obtained in the study increase as the ratio of EDA to PU foam increases. This could be due to the ability of EDA to break down PU foam polymeric network structure into low molecular weight oligomers and monomers. Increase in Amine Value is due to the side reactions that occur

during depolymerisation reaction; hence in order to avoid side reactions during aminolysis microwave assisted aminolysis was carried out. The hydroxyl value and amine value of samples depolymerised by conventional method using EDA are presented in Table 6 (Refer Table 1 for details regarding batches).

In order to study the effect of reaction time in microwave assisted aminolysis on the hydroxyl and amine values, the reaction was carried out for 10, 20 and30 minutes. From Table 7 it is clear that as the reaction time increased, there was an increase in the hydroxyl value. This can be attributed to the breaking of polymer networks by microwaves resulting in low molecular weight oligomers and monomers (Nikje and Mohammadi, 2009). It was also observed that there was a decrease in the amine value which may be due to absence of side reactions in microwave assisted aminolysis. Further the effect of microwave power on depolymerisation reaction was also studied by carrying out reactions with varying power. The hydroxyl value and amine value of samples depolymerised by microwave method at varying reaction time are presented in Table 7 (Refer Table 2 for details regarding batches).

The power of Microwave radiation when increased from 400 to 600 and then to 800kW, also showed the similar trend as noted earlier with increasing reaction time. There was an increase in the hydroxyl value with increase in the microwave power. This increase in hydroxyl value could be due to the absorption of microwaves by the polymeric structured PU foam, which with the aid of EDA, disintegrates into low molecular weight oligomers and monomers. Decrease in the amine value is probably due to the less number of side reactions occurring in microwave assisted aminolysis using EDA (Nikje and Nikrah, 2007). The hydroxyl value and amine value of samples depolymerised by varying microwave power are presented in Table 8 (Refer Table 3 for details regarding batches).

Microwave assisted aminolysis proved to be advantageous compared to conventional method because the former took lesser reaction time and involved less side reactions. There is considerable saving of energy and time and improvement in atom economy of the reaction. Another advantage of the process was that the recovery of un-reacted EDA was possible, leading to reduction in material loss. Thus Microwave assisted aminolysis using EDA can be considered as a green process and a sustainable method for ecological balance.

Depolymerised product had adequate numbers of hydroxyl and amine groups, confirmed by hydroxyl and amine values as depicted in Table 8. With these two functional groups present in excess, the depolymerised product obtained was used to prepare polyester amide by reacting with sebacic acid and BHET (which was obtained after depolymerizing PET in the presence of FASCAT catalyst). The hydroxyl value and amine value of polyester amides are presented in Table 9 (Refer Table 4 for details regarding batches).The formation of Polyester amide was confirmed by decrease in acid value and the reaction was stopped when acid value reached 30 mgKOH/g. Polyester amide was further characterized by its Hydroxyl and Amine Values. There was a decrease in the hydroxyl and amine value which indicated that –OH and –NH$_2$ were consumed through condensation reaction. Further Polyester amide with –OH and –NH$_2$ was crosslinked using IPDI and HDI biuret crosslinkers and coatings

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Table 12: Peaks for polyurethane amide urethane coatings (Refer Figure 7)

Sr. no	Frequency, cm^{-1}	Assignment of functional group
1	3321cm^{-1}	NH stretch in amides
2	2939 cm^{-1}, 2854 cm^{-1} and 2797 cm^{-1}	CH stretching
3	1728 cm^{-1}	C = O stretch in esters
4	1702 cm^{-1}	urethane carbonyl
5	1598 cm^{-1} and 1529 cm^{-1}	NH bend in amides
6	1478 cm^{-1} and 1412 cm^{-1}	C – C stretch in aromatic rings
7	1310 cm^{-1}, 1016 cm^{-1}, 1074 cm^{-1}, 1103 cm^{-1}	C – O stretch in esters
8	1220 cm^{-1}	Aliphatic amines
9	642 cm^{-1} and 610 cm^{-1}	CH bend
10	815 cm^{-1} and 769 cm^{-1}	CH stretch in aromatic ring

Table 13: Mechanical and Chemical Properties of Polyester amide urethane Coatings

	HDI biuret	IPDI
DFT (ASTM D1186)	50-60microns	55-70microns
GLOSS @ 60º (ASTM D523)	5.5 – 6.0	6.5 – 8.3
SCRATCH HARDNESS (IS 104)	1700g	1800g
PENCIL HARDNESS (ASTM D3363)	5H	5H
IMPACT RESISTANCE (weight x height) lb.cm (ASTM D2794)	120 lb.cm	120 lb.cm
CROSS CUT ADHESION (ASTM D3359)	4B	4B
FLEXIBILITY (mm) (ASTM D522)	0	0
ACID RESISTANCE (5% HCL w/v) (ASTM D1308)	Pass	Pass
ALKALI RESISTANCE (5% NaOH w/v) (ASTM D1308)	Minute cracks	Loss of Gloss

prepared thereof were further analysed for mechanical and chemical properties.

Spectroscopic Analysis

A digital electromagnetic thickness gauge instrument was used to measure the dry film thickness (DFT) of each coated panel. The DFT of all the coatings was in the range of 50 – 70 microns, there is variation in the thickness of the coatings from HDI biuret and IPDI and is negligible enough to reflect the difference in the properties observed in Table 10. Specular gloss was measured using a 60º Gloss meter. Coatings based on HDI biuret exhibited low gloss as compared to those based on IPDI. Gloss is directly related to the structure of raw materials used. HDI biuret has a linear structure and NCO groups are at the terminals and hence not much crystallinity was developed. IPDI has a cyclic structure with NCO groups in vicinity which increased the crystallinity and better gloss as compared to HDI biuret coatings was obtained. Pencil Hardness of the film is equated with the pencil that just fails to damage the coating and Scratch hardness of the film is equated with load at which needle penetrates the coating.

Pencil Hardness and Scratch hardness of HDI biuret as well as IPDI based coatings showed consent result. This is due to the fact that presence of polyurethane linkages in the films makes them tough and also difficult to notch off. Impact test is devised to determine the degree, to which a film on a metal surface can accommodate rapid deformation. The impact may be onto the coated surface or onto the back of the panel. The coatings based on HDI biuret and IPDI could pass the impact test (both on surface of coating and reverse impact) when the indenter was released from a height of 60cm. This may be due to the free volume available between the adjacent polymeric chains. The free volume in the polymeric backbone structure is due to the aliphatic structure of raw materials used in preparation of coatings. Performance in cross cut adhesion was good in case of HDI biuret and IPDI based coatings. It was observed that both the coatings had excellent flexibility. This could be due to the aliphatic nature of sebacic acid used during synthesis of polyester amide. Also aliphatic backbone of HDI biuret and IPDI helps in increasing the flexibility of final coating.

Solvent resistance of coatings was investigated according to ASTM D 4752. The coatings based on HDI biuret and IPDI showed good resistance to solvent rub in case of "Xylene" which could be due to highly cross-linked, dense and polar polymeric films polar nature of the polyester amide urethane coatings and showed poor resistance in case of Methyl Ethyl Ketone - 72 rubs for HDI biuret and 42 rubs for IPDI. This poor resistance towards MEK can be attributed to polar nature of the polymeric films. Acid and Alkali resistance were investigated according to ASTM D 1308, coatings based on HDI biuret as well as IPDI showed excellent acid resistance, wherein no visible damage was done to any of the films kept in acid solution for 24 hours. In alkali solution slight loss of gloss was observed for HDI biuret based coatings whereas minute cracks and loss of gloss were observed on IPDI based films. The defects observed in alkali exposure may be due to the ester linkages which are susceptible to saponification.

CONCLUSION

Aminolysis of waste PU foam was successfully carried out to generate oligomers having hydroxyl and amine functionality. The hydroxyl and amine value obtained in the study increase as the ratio of EDA to PU foam increases, in conventional method. As

reaction time increased in case of microwave method, there was an increase in the hydroxyl value. This can be attributed to the breaking of polymer networks by microwaves resulting in low molecular weight oligomers and monomers. As microwave power increases there was an increase in the hydroxyl value. This increase in hydroxyl value could be due to the absorption of microwaves by the polymeric structured PU foam, which with the aid of EDA, disintegrates into low molecular weight oligomers and monomers. Decrease in the amine value is probably due to the less number of side reactions occurring in microwave assisted aminolysis using EDA. Formation of polyester amide urethane coating attaining satisfactory properties showed that aminolysed product synthesized from waste PU Foam was a successful replacement for virgin polyols. Measured values of mechanical and chemical properties confirm that the polyester amide based urethane coatings as well as polyurethane urea based coatings exhibited overall good performance properties. Microwave assisted aminolysis proved to be advantageous over conventional method considering the time and energy required for depolymerisation reaction. The study mentioned here is a sustainable way to utilize waste PU foam in coating application leading to a green environment.

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