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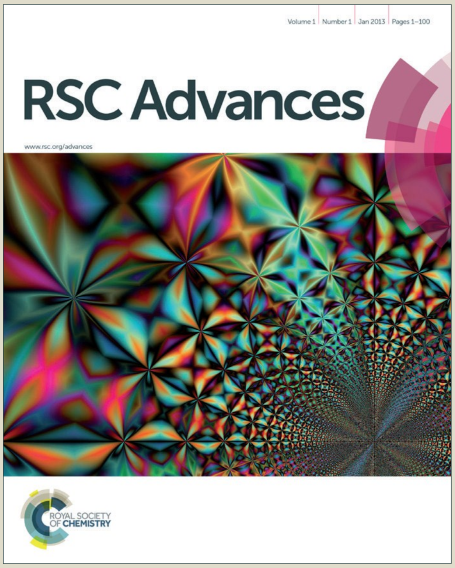

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ARTICLE

Utilization of renewable bio-based resources *viz.* sorbitol, diol, and diacid in the preparation of two pack PU anticorrosive coatings

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Present research work reveals the use of renewable ingradients to synthesize polyester polyol part of polyurethane as a modification different from traditional pattern via melt condensation technique. The difunctional acid used in the preparation of polyester polyol was selected according to their chain length and molecular weight sequentially. Both renewable and non-renewable difunctional acids were used for comparing the coating properties in each formulation. Chemical and corrosion resistances were also studied with respect to their effects on final coating properties on behalf of their structural parameters for sustainable production of 2K PU coating. Synthesized coatings were further characterized by techniques like gloss, adhesion, flexibility, pencil hardness. Overall, sebacic acid based formulation was found to be most suitable among all as per their coating performance specially for anticorrosive property, gloss, and pencil hardness.

Introduction

Polyurethane (PU) is a versatile class of tailor made polymers used in paint and coating sectors since very long time due to high resistivity against chemicals along with excellent mechanical properties.[1-2] It is also used in day to day life for manufacturing of shock absorbers, elastomers, sealants, foams, automotives, roofs, biomedical materials, appliances in thermoplastic PUs, etc.[3-6] Till the date, maximum utilized applications of PU are based on conventional materials, which have severe drawbacks towards environment and human health along with economical point of view. To overcome aforesaid problems, now a days, an increasing demand on renewable source base technology has observed in the preparation of paints and coatings.[7-9] Some applicable reasons for this approach is concerned to prevent greenhouse gas emission, nontoxic by product, good biocompatibility, higher sustainability of raw materials, etc.[10-13] Two ways needed to apply the phenomenon, first one is the raw material used for formulation should have renewable or derivative of renewable material and next is to minimize the use of organic solvent or to prefer green solvent.[14-15] A new trend in current scenario is to use sugar alcohol and vegetable oil based ingredients in coating sector. Hence lot of experiments are being carried to apply this loom via eco-friendly approach[16-19] because as per commercial requirement in industrial sector, PU possesses robust physical properties in respect of other formulations. Among all available renewable sources, maximum efforts are taken to use vegetable oil for preparation bio-based PU[20-23] and very less work is carried on sorbitol due to phase separation and brittle nature of polymeric resins based on it.[24] Therefore, it was decided to proceed the synthetic work related to sugar alcohol based building block preparation in the form of protective coating and find remedy on related problems. Purpose for the said coating is to develop a barrier for restricting the contact between metals with exterior exposures to prevent from deterioration in the form of corrosion by atmospheric contaminants. This is also non-economical for commercial sectors to bear a huge loss day by day caused by corrosion of substrate and maintenance of the same.

Developing research and increasing technological trend diminished the alternative way for utilization of one of the hexa functional sugar alcohol i.e. sorbitol in coating sector rather than its limited use as artificial sweetener. The technology for enzymatic and chemical conversion of polysaccharides to sorbitol is very well established and reported in literature.[25-26] One of the promising features of carbohydrate can be to form cross-linking network like interpenetrating polymer network in PU coatings due to strong interfacial bonding.[27] Another reason in considering sorbitol for preparation of renewable based polyols was presence of superior physical properties i.e. thermal stability, solvent resistance, and mechanical properties due to its polyhydroxy structure.[28]

To generalize such aforesaid proposal, the research and modifications presented in resin formulations are based on renewable raw materials viz. sorbitol, diacids, and 1,4-butanediol. Sorbitol comprises maximum part in formulation to prepare polyester polyol than others. The process was optimized via melt condensation and further preceded for preparation of PU coatings with consideration that the molecular structure of PU depends upon the compound used, polymerization techniques, stoichiometric ratio of selective compounds, etc.

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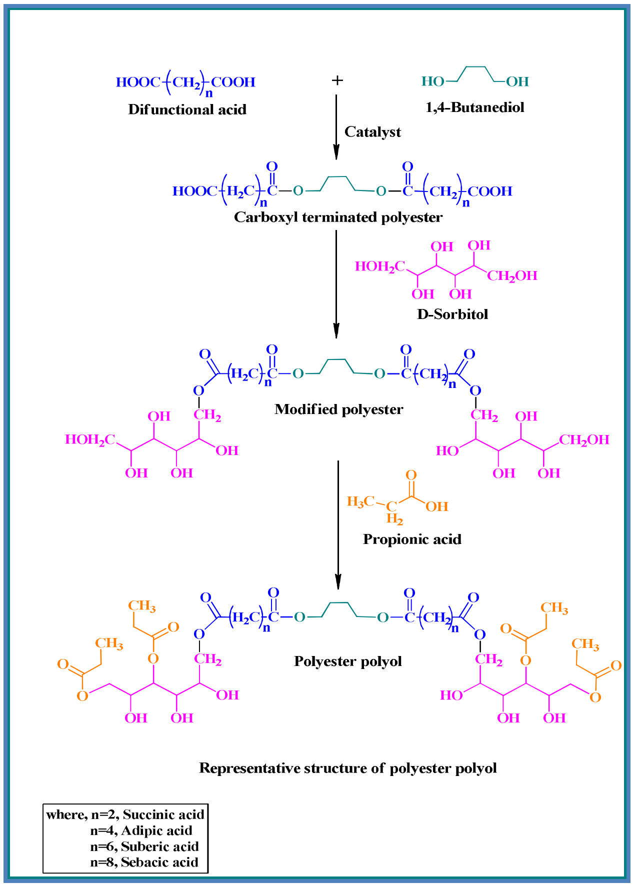
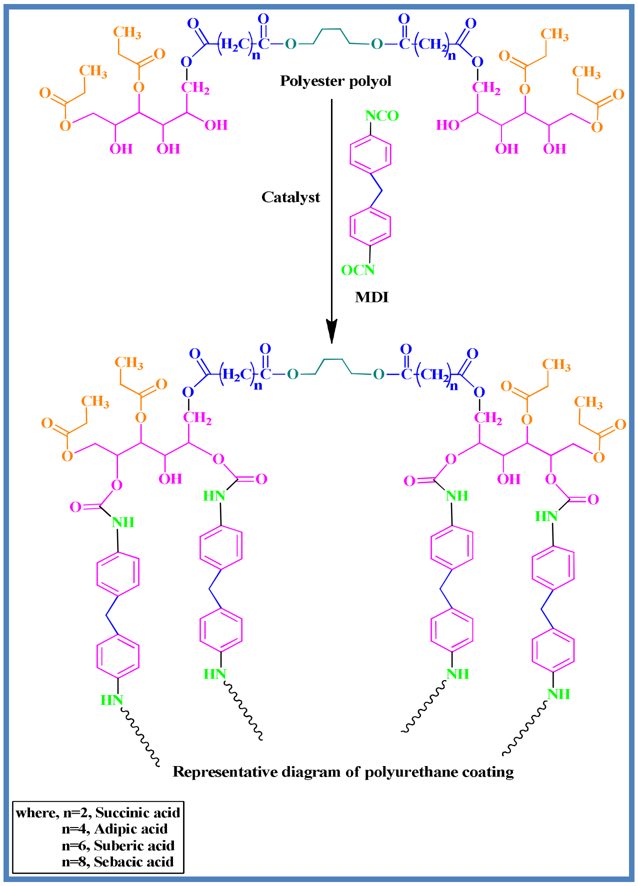


Scheme 1 General reaction scheme for synthesis of polyols.



Scheme 2 General reaction scheme for synthesis of PUs.

A series of polyester polyols was prepared comprising of five components i.e. one difunctional acid (succinic acid, adipic acid, suberic acid, sebacic acid), one mono functional acid (propionic acid), two multifunctional hydroxyl compound (sorbitol and 1,4-butanediol) with p-toluene sulphonic acid (PTSA) as a catalyst. Different aliphatic dicarboxylic acids and 1,4-butane diols were used to introduce flexibility to the polyols and all of them can be of renewable origin except adipic acid as a non renewable ingredient. The whole reaction was performed in three steps. The purpose of different steps was to add a new ingredient successively on different reaction temperature for a specific purpose. In first two steps, our aim was to increase the chain length along with molecular weight of prepolymer. In final step, few of the excess hydroxyl groups of sorbitol were blocked by propionic acid as capping agent to avoid more consumption of diisocyanate due to economical and health purpose as well as to control hard segment and cross linking sites.

The prepared polyester polyols were further reacted with 4-4’ methylenebis (phenylisocyanate) i.e. MDI for preparation of two pack PU coatings. The prepared PU coatings were characterized for their gloss, flexibility, adhesion, pencil hardness, mar resistance, etc. The final material comprises the hard and soft segment[29-30] and needs to study the effect of the change in difunctional acid on soft and hard segments.

Experimental

Materials

Dibutyltindilaurate (DBTDL) and PTSA were received from Himedia and Molychem, respectively. Sorbitol, succinic acid, suberic acid, sebacic acid, and 1,4-butanediol were supplied by S D fine Chem. Ltd., Mumbai, India. MDI, adipic acid, and propionic acid were provided by Merck. All chemicals were used as received and without any further purification.

Preparation of polyester polyol

The esterification of renewable ingredients was carried out by following the experimental procedure as reported in our previous attempts.[24] A three neck round bottom flask was equipped in the assembly set up for preparation of polyester polyol with a nitrogen inlet, thermometer, distilling bridge, and overhead stirrer. Initially it was charged with one of the difunctional acid (as per the formulation) like succinic acid, adipic acid, suberic acid, sebacic acid (1 M), and 1,4-butanediol (0.5 M) by maintaining 120-140 ^{0}C temperature in the presence of PTSA (0.1 % of total mass of ingredients) as a catalyst to accelerate the esterification reaction. Sorbitol (2 M) was added within 60-90 min after increasing the temperature to 160 ^{0}C, when first intermediate product attained acid value half of initial. After this, stoichiometric amount of propionic acid (4 M) was added to the reaction mixture as a third step addition for desired product. The final temperature was adjusted in between 180-190 ^{0}C and time to time acid value was monitored throughout the experiment (Scheme-1). Reaction was stopped, when acid value fell near to 10, indicated consumption of maximum numbers of carboxylic moiety. Another details regarding the yield/conversion, acid value and hydroxyl value for each resultant product and different successive steps are mentioned in Table S1 (ESI).†

Preparation of PU coatings

By mixing of polyester polyol and MDI in accordance to a stoichiometric ratio of 1.1:1 for NCO/OH, ingredients were used for preparation of two pack (2K) PU coatings.[31] A series of coatings were prepared using different polyester polyols synthesized from renewable and non-renewable acids (Scheme-2). Use of cyclohexanone as a moderate solvent with 75 wt. % of polyol part was utilized for complete dissolution of polyester polyol in the presence of DBTDL catalyst for prevention of the problems related to phase separation and proper mixing to reduce viscosity of medium. Then coatings were applied on mild steel panels having a size of 3 × 6 inch by means of brush or bar applicator. For next 48 h, panels were cured at room temperature under observation and were kept at normal conditions.

Characterization

^{1}H-NMR spectra were scanned at 300 MHz on a Varian Mercury YH-300 FT-NMR in $CDCl_3$ using TMS as an internal standard. The chemical shift values are on δ scale. FT-IR spectra was scanned by means of a Shimadzu-8400 FT-IR spectrometer in the range of 4000 to 450 cm^{-1} by NaCl thin plate method using nujol as a solvent. Molecular weight of sample was measured by an Agilent GPC 1260 infinity, USA, with Agilent PL gel 5µm mixed-C column 300*7.5 mm, 5 µm. Tetrahedrofuron (THF) was used as an eluant at 1 mL per min flow rate at 30 ^{0}C using polystyrene as a standard reference. A thermogravimatric analyser (TGA) and differential scanning calorimetric (DSC) analyzer were of Perkin Elmer-4000 series for studying thermal stability and behaviour of PU coatings, respectively. The samples were analysed using N_2 at flow rate of 20 mL/min for inert atmosphere with heating rate of 10 ^{0}C/min. Temperature range for TGA was 30-800 ^{0}C while for DSC, it was within -20 to 170 ^{0}C.

An electrochemical analyzer PGSTAT 30 differential electrometer manufactured by Metrohm, India was used to execute the electrochemical study and determination of the corrosion rate. An electrochemical cell with three electrodes *viz.*, a saturated calomel electrode as a reference electrode, platinum wire as a counter electrode, and coating panel as a working electrode was used for electrochemical study in 3.5 % NaCl solution as electrolyte. Prior to examination, panels were polished with sand papers, followed by thorough rinsing with solvent and double distilled water with exposure in air to dry. Epoxy adhesive (Araldite) was applied over the PU sample panels with attachment of conductive wire from another side to restrict the defect arises due to salt solution and to provide current, respectively. Coated panels having size of 1cm × 1 cm area were immersed in solution for at least 20 min before analysis.

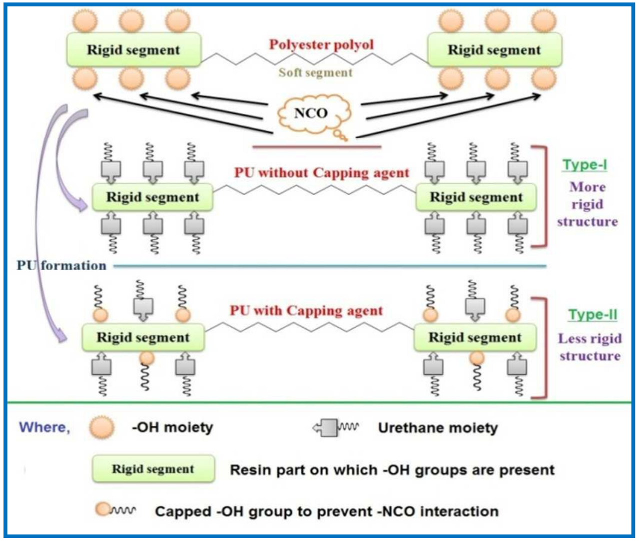


Fig. 1 Demonstration of capping in resin and PU.

Coating properties

The cross-cut adhesion test was carried out for adhesion test of PU coatings applied on mild steel panels as per ASTM standard D-3359-95B. An elcometer 107 X-hatch type apparatus was used to perform the test. A 1 mm × 1 mm size of cross cut mark was applied over the sample using 10 point sharp razor blades of cross hatch tester. Then after, an adhesive tape was adhered over the sectional surface. After few min, the tape was stripped off rapidly. The number of cubes removed by adhesive tape was compared with the remaining cubes on the surface. An automatic digital display gloss meter was used for testing the gloss of coated samples after calibrating with standard of polished black reference panel provided by manufacturer. Then gloss measurement of sample panels was carried out at an angle of 60 ^{0}.

A conical mandrel equipment manufactured by Raj Scientific Instruments, Mumbai was used to perform bending test. The sample panel was bent at different angles between 45 ^{0} to 180 ^{0} to observe any peeling or cracking on bent portion. A pencil hardness tester was used to evaluate the strength of coating film for their hardness by the pencil number from 1B (very soft) to 6H (very hard). Mar resistance was performed in the laboratory as per ASTM D-6279 standard on a mar resistance tester and it was denoted by 'g' in respect to the term of load and fails to mar the films. Dry film thickness (DFT) of coated panels was measured with ultrasonic DFT meter positector 200 instrument manufactured by Defelsko, USA.

Chemical resistance of PU sample plates was tested for reagents like organic solvent (xylene), acid, and alkali. These films were placed in 5 % solutions containing HCl, H_2SO_4, CH_3COOH, NaOH, and $NaHCO_3$. The coating plates were monitored and observed for time duration of one week for visual appearance after a regular interval of 12 h. Corrosion test was performed by immersing the sample panels in 3.5 % NaCl solution and by observing the deterioration on coating surface. For the study, two types of panels were used, one with 'X' shape cross cut mark and another without mark. To prevent the side corrosion, the side portion of panels was covered up by tape. The coated panels were tested for a total immersion time of 168 h by continuous inspection after each 24 h.

Results and discussion

A series of polyols was designed to have capping of few unreacted hydroxyl groups of sorbitol in final structure of polyester polyol. Purpose to use sorbitol was to introduce rigidity and manage the stoichiometric balance in oppose to flexibility generated by aliphatic chain of acid in addition with ester moiety. Sorbitol is also responsible to create higher cross-linking density in polymeric network due to its multiple secondary hydroxyl groups. The higher cross-linking density can impart higher thermal resistance to the resultant polymer. Moto behind capping of extra hydroxyl group was to keep minimum hydroxyl groups for further reaction with diisocyanate, which are intended to decrease isocyanate requirement and to reduce hard segment. Propionic acid was used as capping agent to consume some free hydroxyl groups in second intermediate product to minimize the consumption of –NCO in excess as well as to decrease rigidity in final coating properties. In this case, on reaction of propionic acid with unreacted hydroxyl groups of sorbitol, short side branches were introduced which were having $–CH_3$ as chain ends. It is clearly seen from the representative structure of polyester (Fig. 1/ scheme-1), that it contains diacid and 1,4-butanediol based soft segments, as well as propionic acid based capped side branches containing soft segment due to presence of ester and $–CH_2–$ groups. Presence of additional flexible part and reduction in hard segment (unavailability of –OH groups for formation of urethane as hard segment) would be able to balance soft and hard segments in the resultant polyol. On the contrary, for comparison purpose, modified polyester (without capping) was used to convert into PU coating. The coatings required higher diisocyanate and observed were of hazy, brittle, and without uniformity. Hence, capping of few hydroxyl groups included that resulted with PU coatings which were free from defects as in earlier case and as per our hypothetical requirement. Difference between both types of polyols are represented in scheme-1 as well as their structural changes were compared in ^{1}H-NMR section co-relation with Fig. S2 in the form of capped and uncapped structures. From the comparison, it was found that capped structure was more prominent and useful rather than uncapped.

FT-IR

The resultant peaks of reaction between difunctional acid, multifunctional alcohol, and mono functional acid have been studied by FT-IR spectra and the resulting diagram is shown as Fig. 2. The relative peak corresponding to each formulation are mentioned in the Table S2 (ESI).† The frequencies near to 3400 cm^{-1} corresponded to the presence of free –OH group in structure of polyester polyols. Absorption bands near to 2800 and 2900 cm^{-1} were due to symmetrical and asymmetrical stretching mode of vibrations corresponding to $–CH_2–$ and $–CH_3$ groups.[17] A strong band observed near 1730 cm^{-1} was attributed to >C=O group of ester

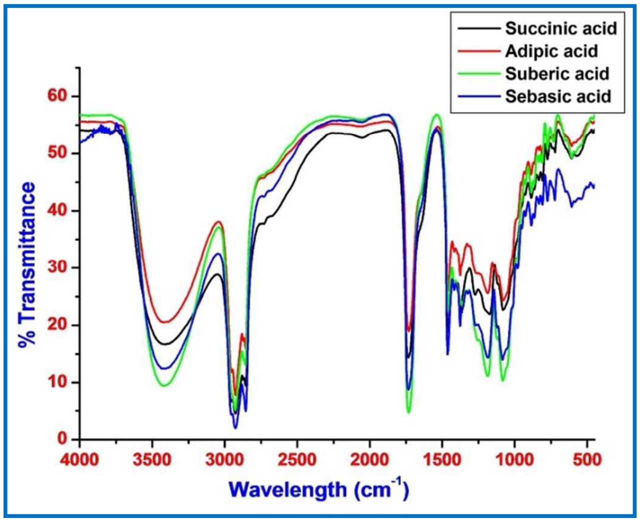


Fig. 2 FT-IR spectra of resins prepared from sorbitol.

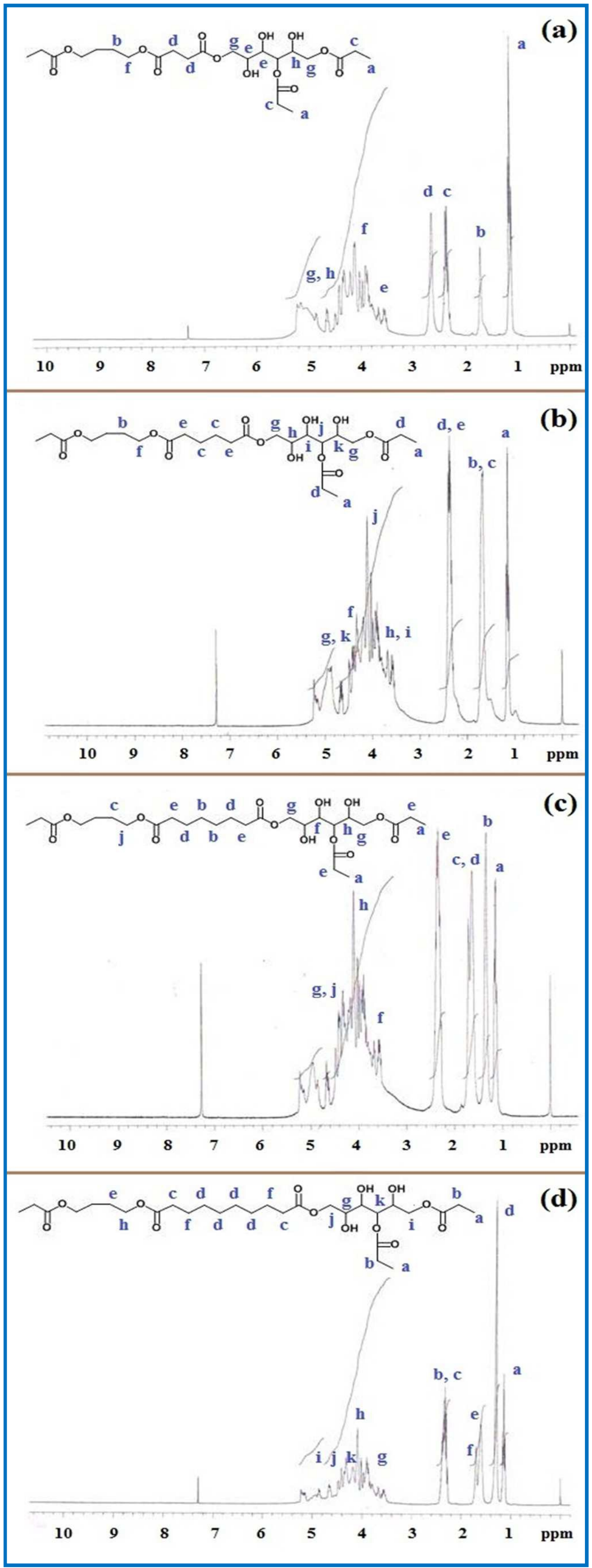


Fig. 3 ^{1}H-NMR of polyester polyols prepared with sequence – (a) succinic, (b) adipic, (c) suberic, (d) sebacic acid.

present in polyester polyol moiety. The bending vibrations for –CH_2– group revealed at frequencies in the range of nearly 1370 cm^{-1} and 1460 cm^{-1} for each successive formulations.

^{1}H-NMR

^{1}H-NMR spectra of different polyester polyols shown the signal for terminal –CH_3 at δ= 1.15 as represented in scheme-1 for the final stage product of capped polyester polyol. A different value for –CH_2– was observed within a range of δ= 1.2 to 4 due to the neighbouring moiety in which value ranges 1.2 to 2.7 corresponded to –CH_2– moiety present in between ester groups. H attached to C next to >C=O shown its peak towards downfield region near to 2.5 ppm.[32] Due to compact structure and less interparticle distance, the peaks of H atom of the C, attached with –OH group gave peaks in multiplet. All the NMR spectra are presented in Fig. 3 as per sequence related to increasing number of difunctional acid based polyester polyols. ^{1}H-NMR of polyester polyols prepared with sequence – (a) succinic, (b) adipic, (c) suberic, (d) sebacic acid and each peak in NMR were corresponded with the prepared polyol structures and positions of protons are denoted by alphabetic characters for better understanding the structure of capped polyester polyol. In requirement of more consistent data, ^{1}H-NMR of each intermediate product were also taken. ^{1}H-NMR graph for the first intermediate product i.e. carboxyl terminated polyester and second intermediate product i.e. modified polyester are shown in Fig. S1 and S2 (ESI).† ^{1}H-NMR from Fig. 3 and Fig. S2 was compared to find out side branches introduced by propionic acid in final polyester. Peak observed at 1 ppm in ^{1}H-NMR of final polyester was assigned to terminal –CH_3 groups. The peak for terminal –CH_3 is absent in ^{1}H-NMR of second intermediate product showed that terminal –CH_3 groups were absent as shown in Fig. S2. The overall results indicated presence of terminal –CH_3 may be due to introduction of side branches as a part of propionic acid. Presence of non-reactive –CH_3 groups in replacement of –OH group can reduce consumption of isocyanate part and reduce rigid segment of urethane, which matched with our requirements.

Molecular weight

The comparative differences in molecular weights (Mw) of different formulations are represented in Fig.S3 (ESI),† by means of schematic diagram, which shows the gel permeation chromatographic curve for polyester polyol and also summarized in Table S3(ESI).† Mw of polyester polyols was in the range of 2582-3462, which is substantial high molecular weight as a soft segment that can increase flexibility to whole moiety. Simultaneously in the series i.e. from succinic acid to sebacic acid, the shape of GPC curve changed from narrow to broad molecular weight distribution.

Thermal analysis

It has been found that in agreement with the literature, sample shown multistep degradation to PU samples as shown in Fig. 4. It also shown those dicarboxylic acids used in polyol part do not influence the basic mechanisms of thermal degradation in the prepared bio-based PU. The shape of the TGA curves remain unchanged even change in the dicarboxylic acids due to a very minute difference in chain length of acids.

Initial weight loss observed in TGA curves up to the temperature of 120 ^{0}C was about 1.797, 1.507, 1.099, and 0.897 % for succinic acid, adipic acid, suberic acid, and sebacic acid based formulations, respectively due to moisture or solvent entrapped in the prepared coatings. Remaining part of TGA curve of each formulation thermally degraded in three major successive steps consisting of urethane bond breaking along with degradation of ester moiety, and aliphatic hydrocarbon chains.[33-34] Thermal degradation observed in the first step was associated with internal minute steps. It was observed in the temperature range of 229-269, 221-287, 223-290, and 214-279^{0}C with weight loss of 9.45, 11.01, 10.51, and 8.13 % for PU coatings based on succinic acid, adipic acid, suberic acid, and sebacic acid formulation, respectively in accountable for bond breaking of urethane moiety. In the next part of TGA, thermal degradation was observed for breakdown of ester moiety and linear hydrocarbon chains in the temperature range between290-590 ^{0}C with weight loss about 62.02-67.97 %. In general, among all samples, PU based on succinic acid based polyester polyols showed highest thermal stability. The reason for higher thermal degradation to succinic based PU may be due to high cross-linking as it possess highest hydroxyl value and thus required more energy to degrade.

In support of aforesaid thermal degradation data DSC curve as shown in Fig. 5. The Tg values for the formulations containing succinic, adipic, suberic, and sebacic acids based formulation was found near 48.71, 67.06, 50, and 90.77 ^{0}C, respectively. Except adipic acid based formulation, rest of the others shown increasing value of Tg with increasing number of C atoms in their backbones.

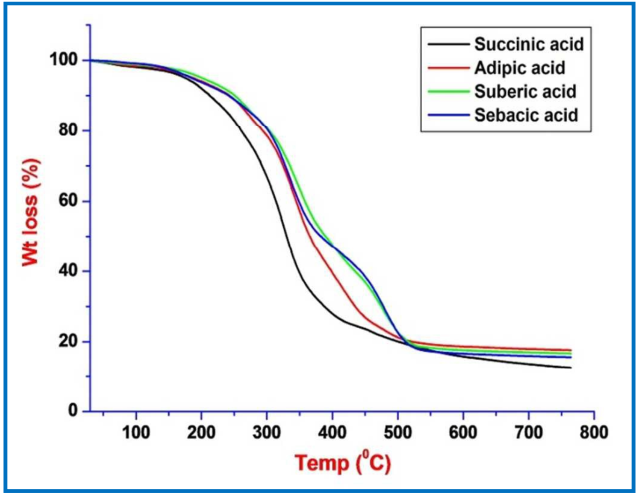


Fig. 4 TGA curve of PU coatings.

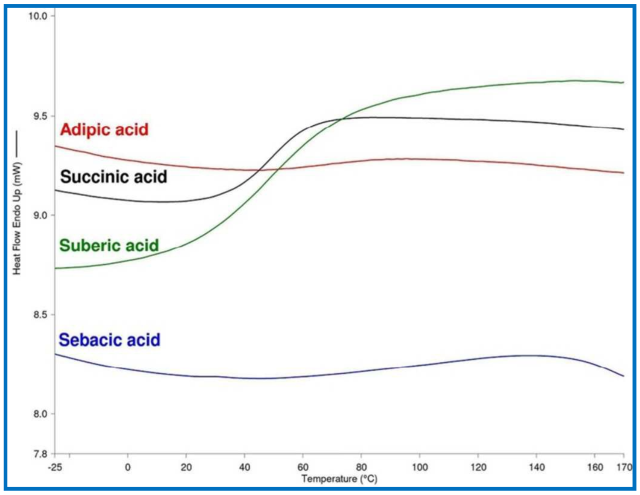


Fig. 5 DSC curve of PU coatings.

Coating properties

The coating properties tested for prepared PU samples included gloss, bending test, adhesion test, pencil hardness as well as mar resistance. All the prepared coating samples shown excellent flexibility, adhesion properties, and pencil hardness. This may be due to introduction of long aliphatic chain from difunctional acids as well as the stoichiometric ratio of soft moiety in accordance with rigid moiety, which plays a key role in the form of superior property. All the formulations have high resistance for pencil hardness parameter and better gloss property. It was observed that as the length of difunctional acid increased, the pencil hardness and gloss values also increased due to presence of more number of soft methylene units from succinic to sebacic acid formulations. The mar resistance property shown increase in sequential pattern from succinic acid to sebacic acid, however the value for suberic acid and sebacic acid were found likely to the same. This was because both the formulation passed the 800 g load successfully but failed for 1000 g load. The observation revealed that the strength for mar resistance may be within the range of 800-1000 g load for both the formulation one behind another. The summarised results are shown in the Table S4 (ESI).†

Chemical and solvent resistances

A summarization of exposure effects of selected chemicals including acid (mild & strong) and alkali (mild & strong) along with solvent on formulated two pack PU coating systems prepared from renewable sources and difunctional acids is shown in the Table 1. From the table it was cleared that the exposure in alkali has a tendency to reduce the adhesion property which is same for all the formulations i.e. lifting. The most sustainable and less effectible formulation among all comprises of nearly same results for suberic and sebacic acid based resin may be because of presence of higher length of –CH_2–.

Corrosion test

The formulated coatings were with film thickness within the range of 50-55 µ. It was found that the PU coating samples containing sebacic acid shown highest resistivity against corrosion among all formulations as shown within Fig. 6 along with Fig. S4 and S5 (ESI)† represented the appearance of coated panels in before and after 72 h of immersion, respectively. The formulation with suberic acid also has nearly same resistivity i.e. renewable formulation has higher resistivity rather than non-renewable adipic acid based formulation. This is because of highest molecular weight and longest chain length of sebacic acid based formulation contained more number of methylene unit. Anticorrosive property increased as they go through a sequence from adipic acid to sebacic acid, however, PU from succinic acid faced a problem of paint defect named blistering due to low molecular weight formulation with less resistivity.

Chemical / PU coatings	Succinic acid	Adipic acid	Suberic acid	Sebacic acid
H_2SO_4 5%	lifting	lifting	side lifting	softening
HCl 5%	softening	lifting	no effect	lifting
CH_3COOH 5%	slight discoloration	lifting	no effect	side blistering
$NaHCO_3$ 5%	lifting	lifting	lifting	lifting
NaOH 5%	lifting	lifting	lifting	lifting
Xylene	slight discoloration	no effect	no effect	no effect

Table 1 Chemical resistance test of PU formulations.

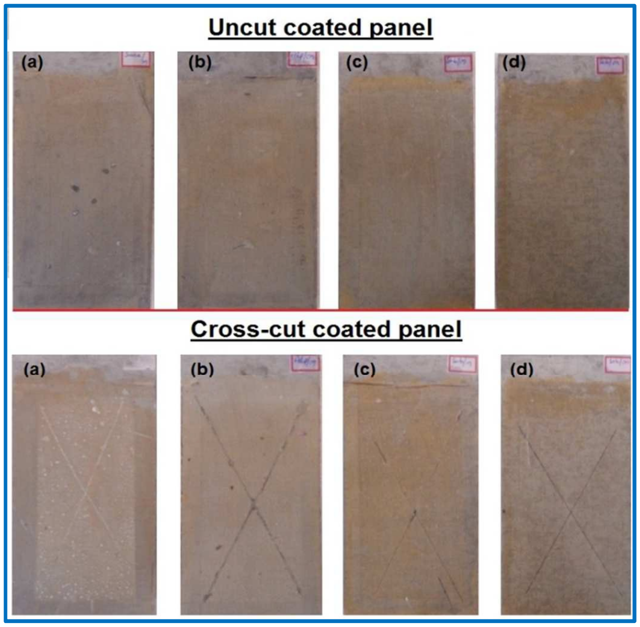


Fig. 6 Corrosion showing on coating plates after 168 h with sequence – (a) succinic, (b) adipic, (c) suberic, (d) sebacic acid.

Electrochemical study

The corrosion resistances for all the PU coatings were assessed by a technique, potentiodynamic polarization which is universally used for this purpose.[35] The Tafel curves were obtained by scanning the potential from a value of -1 V to +1 V above the corrosion potential with scan rate of 10mV/sec to attain the Tafel polarization measurements for electrochemical analysis of prepared PU samples. Two types of coated panels were monitored for corrosion rate (CR), corrosion potential (E_{corr}), and corrosion current density (I_{corr}). The panels consisted (a) without any coating, (b) PU coatings of different formulations. Final, results are summarised in Figure 7and Table S5.

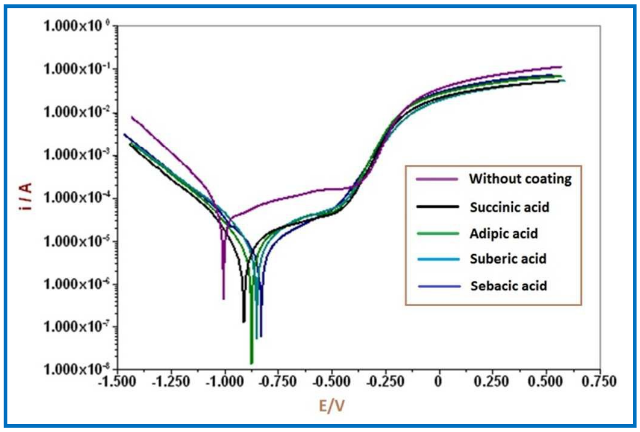


Fig. 7 Taffel curve for PU coatings.

Blank panel was found with lowest anticorrosion property because of absence of additional media to prevent corrosion i.e. existence of express contact of coated panel with salt solution, while the results revealed positive performance of all the coating medias as compared to panel without coating.

In a sequence of formulation in series of succinic acid to sebacic acid, the I_{corr} value was found to decrease, while the E_{corr} value was increased. Simultaneously, CR decrease for the PU coatings in series. The relation obtained between CR and E_{corr}/I_{corr} was as per the previous observations.[36] The results of electrochemical study indicated that sebacic acid based formulation was more susceptible with least corrosion. Despite, the variation in CR, E_{corr}, and I_{corr} values of prepared renewable source based PU coatings; the difference within all the formulations was very minute.

Finally, sebacic acid induced formulation was found with highest anticorrosive property while formulation of succinic acid was with lowest resistivity.

Conclusions

Sorbitol and sequential difunctional acids based two pack (2K) PU coatings were prepared successfully and characterized by proper techniques. The wide scope of selection for raw material made it possible to provide enormous significant properties in respect of each formulation and revealed satisfactorily results. Even in the case, any of the formulation can be used separately for coating purpose but overall conclusion in regards of comparative manner, came with the results positively approached towards specific moiety which contains higher chain length in its chemical structure. It was concluded that sebacic acid based formulation is the best among all resin formulations on the basis of properties shown for gloss, pencil hardness, corrosion resistance, etc. The same is most sustainable, suitable, and durable for coating application regarding their physical and chemical properties. This indicates favourable structure and property of sebacic acid based formulation as most prominent formulation and tends towards.

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