Advancements in polyurethane coating: Synthesis and characterization of a novel hyper branched polyester polyol

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CHRONICLE	ABSTRACT
	Hyperbranched polyester polyols have emerged as a promising candidate for polyurethane coatings due to their unique structure and properties. In this context, this paper aims to synthesize a new hyperbranched polyester polyol and evaluate its potential as a polyol for polyurethane coating applications. In this study, the synthesis of hyperbranched polyester polyol involves the reaction between a multifunctional alcohol and a multifunctional carboxylic acid or anhydride. It is further modified by incorporating 2-hydroxyethyl methacrylate and styrene. The properties of the polyester polyol were characterized using various analytical techniques, including FTIR, NMR, SEM and TGA. This paper also provides a discussion on the potential applications of the synthesized hyperbranched polyester polyol in several industries such as automotive, aerospace and construction.

1. Introduction

Polyurethane coatings have gained significant attention in recent years due to their excellent mechanical, chemical, and thermal properties. The performance of polyurethane coatings largely depends on the properties of the polyol used in their synthesis. The synthesis of polyester polyol for polyurethane coating has been reported in several studies[1-7]. Polyester resins are widely used due to their versatile applications such as elastomers[8-9], coatings[10], polyurethane foam[11-12] and sealants and adhesive[13]. The demand for polyurethane coatings has led to the importance of manufacturing polyester polyols[14-16]. In Europe alone, over two million tons of polyurethanes are produced annually[17]. Polyurethanes, due to their excellent mechanical and chemical properties, high resistance to weathering and solvents, toughness, and low temperature flexibility have been widely used in coatings[18-26]. The reaction between polymeric isocyanate and a polyol such as polyester resin for manufacturing polyurethanes[27-28] in the absence of catalysts is slow and requires a long time to reach equilibrium. To accelerate reaction rates, various catalysts have been reported in the literature, including amine catalysts and organometallic compounds[29-30]. The final properties of the polyester polyol such as crystalline structure, degree of phase separation and mechanical properties depend on the molecular structure of polyester polyol[31-32]. This structure is affected by factors such as percentage of ingredients, production conditions, impurity content, glycol ratios, etc. Various new methods have been developed for synthesizing different types of polyester polyols with unique structures. These include Jatropha-Oil-Based Polyester Polyol[33], Polyester Polyol from Cyclohexanone plant wash water[34], isosorbide-based polyester polyols[35], polyester polyol from Direct conversion of waste polyesters[36], polyester polyol based on epoxidized soybean oil[37], and other works reported in the literature[38-40]. Recent investigations on polyurethane have revealed that vegetable oil fatty acids can serve as a suitable replacement for petroleum-based raw materials[41-43]. This study focuses on the synthesis of a new hyperbranched dehydrated castor oil fatty acid (DCOFA) based polyester polyol, utilizing 2-hydroxyethylmethacrylate (2-

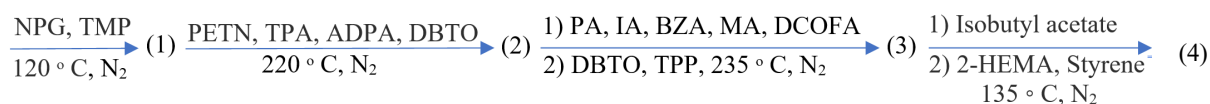HEMA) and styrene, for use in the production of polyurethane-based materials. The DCOFA used in this study cannot react directly with polyisocyanate and remains intact during the reaction. So, it requires functionalization with hydroxyl containing molecules to incorporate hydroxyl groups into its structure[44]. The presence of hydroxyl groups in the polyester polyol structure, as well as in the 2-HEMA co Styrene copolymer bound to the fatty acid of DCO and maleic anhydride (MA), reacts with cyanide groups in polyisocyanate to form a multi-branched and three-dimensional cross-linked structure between polyester resin and polyisocyanate in the presence of catalysts. However, synthesizing polyester polyol from DCO fatty acid modified with poly (2-HEMA co Styrene) is a new field that has not been widely explored. In this study, we prepared wood coating polyurethane through the reaction between new modified polyester polyol and polyisocyanate.

2. Results and Discussion

In this study, a novel hyper branched polyol polyester was successfully synthesized using DCO followed by radical addition of 2-HEMA and styrene. The synthesis process involved four steps of reactions: the first step is the melting step, by increasing the temperature of mixture to 150 degrees, Neo pentyl glycol (NPG) and Trimethylolpropane (TMP) become melt to form a liquid mixture. second step is an esterification reaction between Terephthalic acid (TA) and Adipic acid (ADPA) with Pentaerythritol (PETN) and other glycols in the presence of Dibutyl tin oxide (DBTO) as a catalyst. The molar ratio of glycols to carboxylic acid in this step is large because esterification of TA in the presence of glycols requires more time and higher temperature compared to other carboxylic acid/anhydrides.

In the third step Phthalic anhydride (PA), Isophthalic acid (IA), Benzoic acid (BZA), MA, DCOFA, DBTO and Triphenyl phosphite (TPP) are charged to the mixture. In the presence of extra hydroxyl group, esterification reaction is carried out. In the fourth step 2-HEMA and styrene are added gradually to the diluted mixture in the presence of Tertiary butyl per benzoate (TBPB) as an initiator. The type of reaction in this step is free-radical addition (Scheme1). The mixture of 2-HEMA and styrene with TBPB was prepared separately and gradually added from the funnel to the polyol polyester. This resulted in a highly branched polyester polyol resin with hydroxyl sites.

$$\xrightarrow[\text{120 ° C, N}_2]{\text{NPG, TMP}} (1) \xrightarrow[\text{220 ° C, N}_2]{\text{PETN, TPA, ADPA, DBTO}} (2) \xrightarrow[\text{2) DBTO, TPP, 235 ° C, N}_2]{\text{1) PA, IA, BZA, MA, DCOFA}} (3) \xrightarrow[\substack{\text{2) 2-HEMA, Styrene} \\ \text{135 ° C, N}_2}]{\text{1) Isobutyl acetate}} (4)$$

Scheme 1. Synthesis route for preparation of modified polyester polyol resin

IR spectra of the polyester polyol before (Intermediate A) and after addition of 2-HEMA and styrene (Intermediate B) were shown in Fig. 1. After reacting with 2-HEMA and styrene in the presence of TBPB, the unsaturated bonds in the DCOFA would be eliminated through radical polymerization. This would result in a decrease or complete absence of peaks corresponding to aliphatic C=C around 1600 cm^{-1}[45]. (**Fig. 1**).
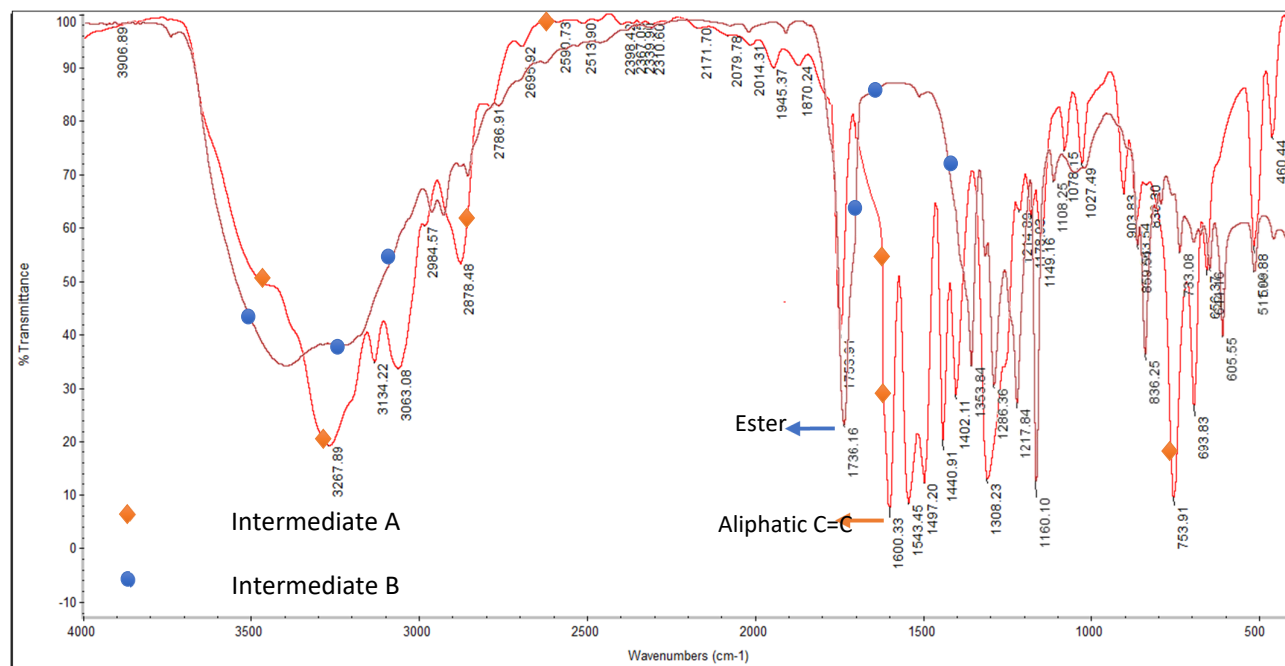

Fig. 1. FTIR spectrum of intermediate A and B

Polyurethane is a polymer that is formed by the reaction of polyol and isocyanate. In the case of polyurethane made from toluene diisocyanate (TDI) and polyester polyol, the reaction takes place between TDI and hydroxyl groups in the polyester polyol. This results in the formation of urethane linkages, which are responsible for the polymerization of the material.

The IR spectrum of polyurethane made from TDI and polyester polyol shows characteristic peaks at around 3420 cm-1, which correspond to the stretching vibrations of N-H bonds in urethane linkages[46]. The peak at around 1759 cm-1 corresponds to C=O stretching vibrations in ester groups present in the polyester polyol[47]. The peak at around 1505 cm-1 corresponds to N-H bending vibrations in urethane linkages[48]. (**Fig. 2**)

Overall, the IR spectrum of polyurethane made from TDI and polyester polyol shows characteristic peaks that are indicative of the presence of urethane linkages and ester groups. These peaks can be used to identify and characterize this type of polymer.
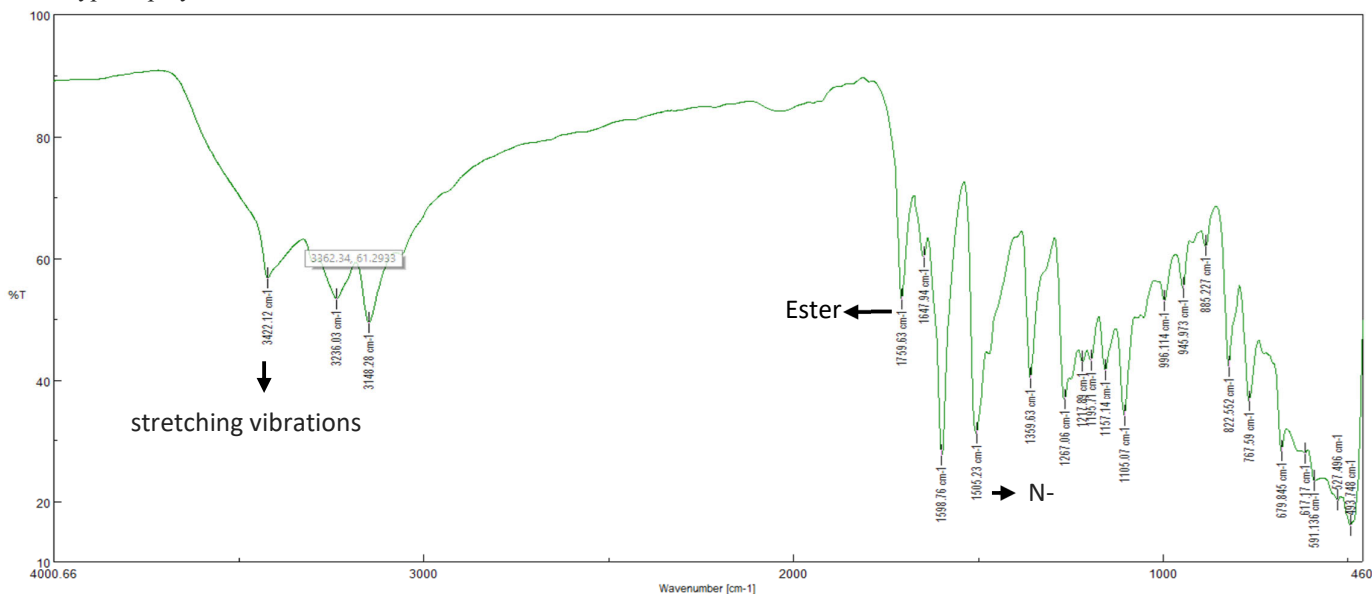

Fig. 2. FTIR spectrum of PU

The molecular structure of hyper branched polyester polyol is characterized by a dense network of interconnected branches, which results in a high degree of cross-linking and three-dimensional structure. This unique structure gives the polymer its desirable properties such as high viscosity, low volatility, and excellent mechanical strength.

The size and shape of the hyper branched polyester polyol molecules can vary depending on the degree of branching and the length of the polymer chains[49]. Overall, the molecular structure of hyper branched polyester polyol plays a crucial role in determining its physical and chemical properties, making it an important material for various industrial applications such as coatings, adhesives, and composites. As shown in **Fig. 3**, all unsaturated bonds of DCOFAs are bonded together by P(2-HEMA-Styrene) and the formation of these bonds between DCOFAs by P(2-HEMA-Styrene) has a great effect on the drying time of the resin film.
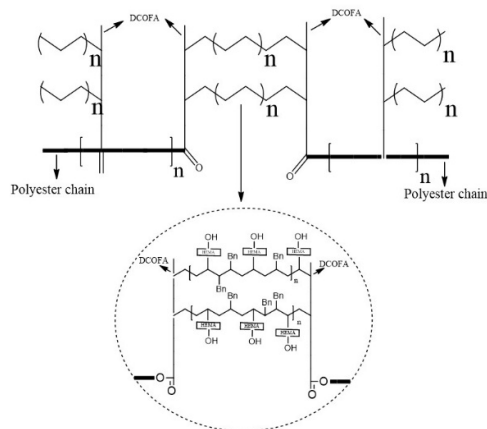

Fig. 3. Molecular structure of hyper branched polyester polyol

NMR-Spectroscopic Analysis

The structure of the synthesized polyester polyol was investigated using ^{1}HNMR and ^{13}CNMR spectroscopy techniques. **Fig. 4** presents the ^{1}HNMR spectrum of the polyester polyol. The aromatic protons are observed in the range of 6.2 to 6.6 ppm, while the aliphatic saturated protons appear as multiplet peaks in the range of 0.5 to 2.1 and 3 to 5 ppm. A broad singlet at 1.27 ppm indicated the presence of hydroxyl group. Fig. 5 shows the ^{13}C NMR spectrum of the polyester polyol. The carbonyl group (ester) of the synthesized polyester polyol is observed at 164.4 and 160.1 ppm, while aromatic carbons are seen at 133.9, 133.8, and 133.6 ppm. Aliphatic carbons are clearly visible at 31.1, 29.5, 24.2, 20, 16.5, and 16.3 ppm in the spectra[50].
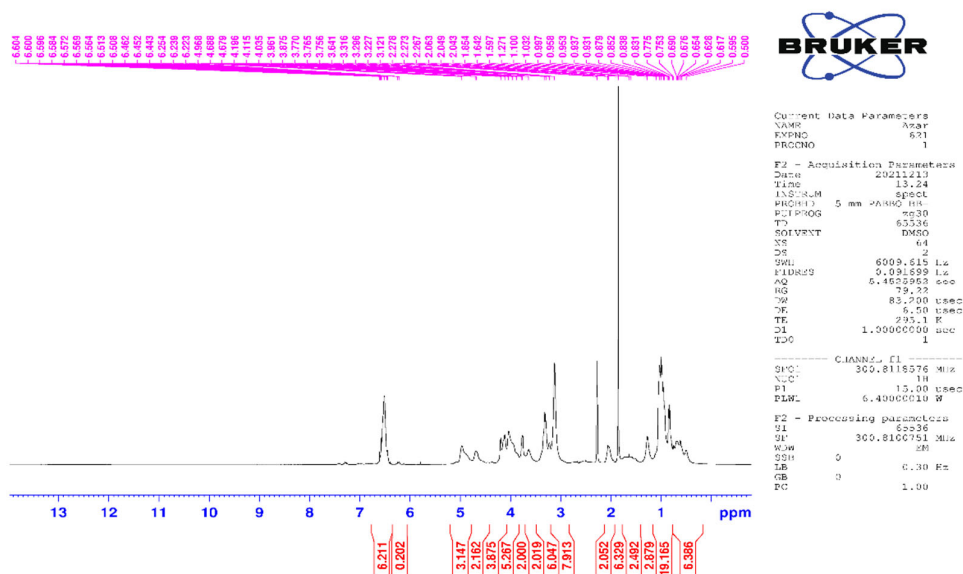
Fig. 4. ^{1}HNMR of synthesized polyester polyol
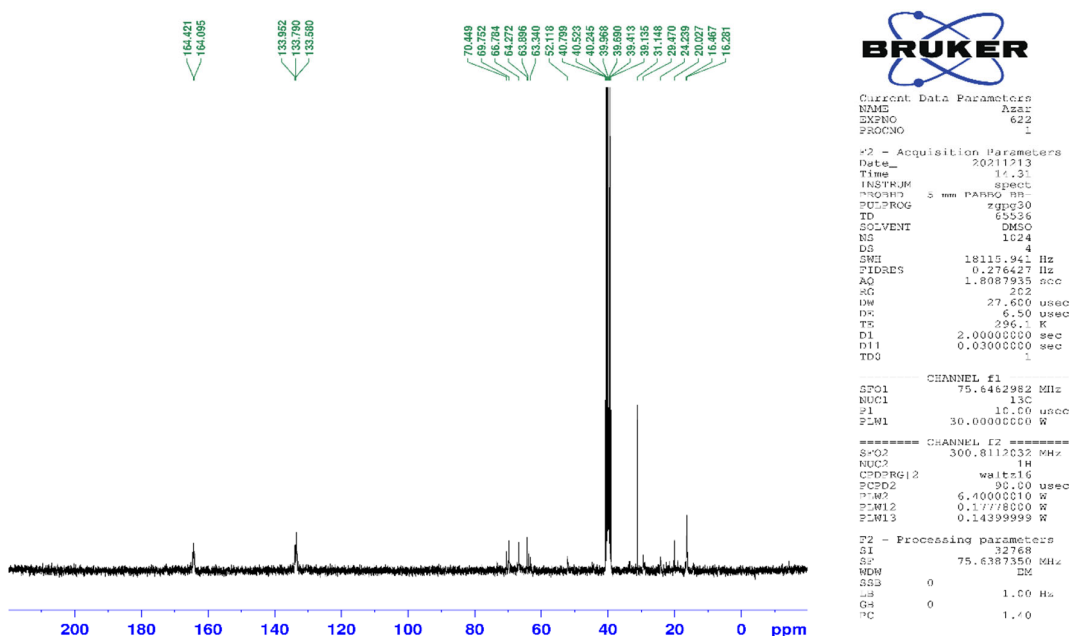
Fig. 5. ^{13}CNMR of synthesized polyester polyol

Thermogravimetric Analysis (TGA)

The first region, which occurs at low temperatures, represents the evaporation of any residual moisture or volatile compounds that may be present in the sample (0-150 ⁰C). The second region of degradation involves the decomposition of urethane bonds[51], where they dissociate into isocyanate and alcohol, primary and secondary amines, a terminal olefinic group on the polyester chain or CO_2 (230-330 ⁰C)[52]. The subsequent region of degradation is attributed to the decomposition of ester bonds through chain scission (330-450 ⁰C)[53-54]. In the instance of polyurethanes derived from DCOFA polyol, an additional phase of decomposition takes place at elevated temperatures (approximately 470 °C), potentially because of the cleavage of C-C bonds [55]. Based on the mentioned decomposition temperatures in Thermogravimetric Analysis, it is evident that obtained polyurethane is stable below than 230 ⁰C (**Fig. 6**).
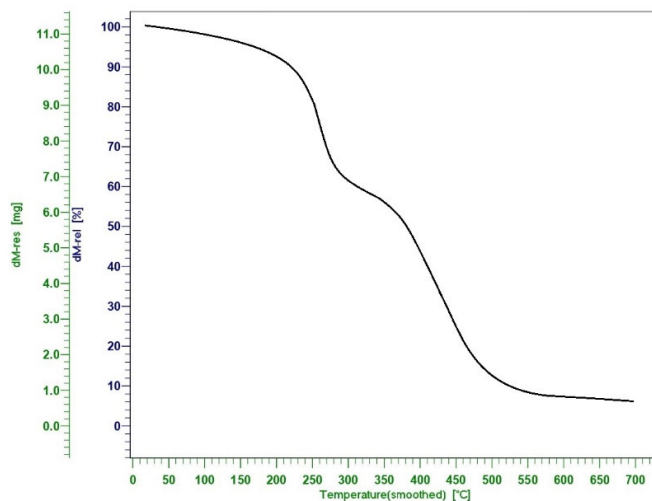

Fig. 6. Thermogravimetric analysis of polyurethane coating

Scanning Electron Microscopy (SEM)

The SEM image shows a polyurethane coating, which appears as a smooth and uniform layer covering with some irregularities on the surface, which could be due to the application process or the substrate's texture the surface (**Fig. 7**). The polyurethane coating is composed of interconnected polymer chains that provide excellent resistance to abrasion, chemicals, and weathering. Overall, the SEM image demonstrates the high-quality and durability of polyurethane coatings in protecting surfaces from damage and degradation.
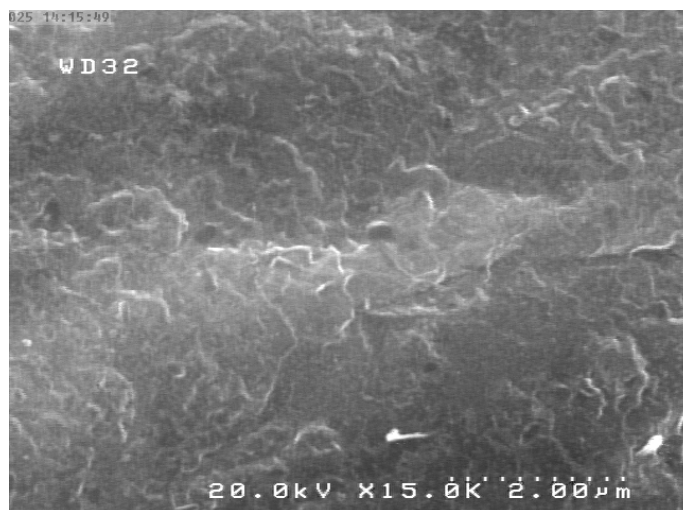

Fig. 7. Scanning electron microscopy of polyurethane

3. Conclusions

In conclusion, the synthesis of hyper-branched polyester polyol for polyurethane coating offers numerous advantages and potential applications in various industries. The unique structure of hyper-branched polyesters provides enhanced properties such as improved mechanical strength, chemical resistance, and thermal stability. Additionally, the synthesis process allows for control over the molecular weight and branching degree, enabling customization of the polyol to meet specific coating requirement. The results indicate that the use of 2-HEMA and styrene in the presence of initiator can lead to the formation of highly branched polyols with improved mechanical and thermal properties.

Acknowledgements

4. Experimental

4.1. Materials and Methods

DCOFA with an acid value of 198 mg KOH/g was supplied by Arvalli Castor Derivatives Private Limited, Gujarat. India. 2-HEMA was supplied by Jin Dun chemical. China. Other reagents and chemicals in this study were used as received and were not further purified (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany). FT-IR spectra were recorded on Thermo Nicolet Nexus 670 spectrophotometer using the KBr-pellet technique. Via a Bruker Avance 500 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany), ^{1}H-NMR and ^{13}C-NMR spectra were recorded on 500 MHz and 125 MHz, respectively. The tensile tests were performed on STM-20 at a fixed crosshead speed of 2mm min^{-1}. Samples were prepared according to ISO 527-2-2012. Flexural tests were done on STM-20 at a fixed crosshead speed of 2mm min^{-1}. Samples were prepared according to ISO 178:2019

4.2. General procedure

4.2.1. Preparation of Liquid mixture of alcohols

A 2 liter, 4 necked flask equipped with an agitator, an electric heating mantle, a nitrogen gas inlet, a thermometer, and a condenser charged with 44 gr of NPG and 13.2 gr of TMP under a nitrogen blanket to the flask with stirring. The mixture was heated from room temperature to 130 °C over 2 hours until all the solid alcohols become melt into a liquid.

4.2.2. Preparation of polyester polyol in the presence of DBTO as a catalyst with extra alcohol content

5.5 gr of PETN, 29.7 gr of TA, 5.5 gr of ADPA and 0.05 gr of DBTO as a catalyst are charged to flask and mixture was heated to 230 °C over 3 hours to continue the reaction. Reaction proceed to the point at which the acid value reach to below than 4 mg KOH/gr resin, then mixture is cooled to 80 °C.

4.2.3. Preparation of polyester polyol (Intermediate A)

14.3 gr of PA, 23.1 gr of IA and 11.55 gr of BZA, 0.66 gr of MA, 7.15 gr of DCOFA, 0.02 gr of DBTO and 0.02 gr of TPP are charged to flask and the reaction is carried out at a temperature of about 175-240° C, preferably 190-235° C. and it is continued until the acid value reach to below than 10 mg KOH/gr resin, then mixture is cooled to 80 °C.

4.2.4. Preparation of final polyester polyol modified with Poly (2-HEMA-co-styrene) in the presence of TBPB (Intermediate B)

25 gr of 2-HEMA, 20 gr of styrene, and 4 gr of TBPB are mixed at room temperature and charged to a dropping funnel. Then contents of the funnel were added slowly into the reaction mixture at 130 degrees over 2 hours in the reflux condition. mixture is then cooled to 50 °C. In the next step add 59 gr of iso butyl acetate as solvent to make 70% solution of polyester polyol.

4.2.5. Physical and spectral data of polyester polyol

Table 1. Physical data in liquid state at 25°C

Entry	Properties	Unit	Value	Test method	Ref
1	Appearance	----	Transparent	----	
2	Color	Gardner	1	ASTM D-1544-98	[56]
3	Viscosity	CPs	750	ISO 2555:2000	[57]
4	Acid number	mgKOH/g	10	ASTM D-1639	[58]
5	Solid content	% weight	67.2	ASTM D-1259	[59]

a (Brookfield RV, #3 60 rpm, 25 °C)

FT-IR (KBr), ν, cm^{-1}: 3400 (O-H), 1736 (C=O), 1353 (C-H, sp 3).^{1}H NMR (300 MHz, DMSO-d6), δ, ppm: 0.50-1.10 (m, 25H), 1.27 (bro. s, 3H, OH), 1.85 (s, 6H), 2.04 (bro. s, 2H), 3.12-3.31, (m, 14H), 3.64-4.19 (m, 13H), 4.68 (bro. s, 2H), 4.96 (bro. s, 3H), 6.43-6.60 (m, 6H), ^{13}C NMR spectrum (75 MHz, DMSO-d6), δ, ppm: 164.4, 164.1, 133.9, 133.8, 133.6, 70.5, 69.7, 66.8, 64.3, 63.9, 63.3, 52.1, 31.1, 29.5, 24.2, 20, 16.5, 16.3.

4.2.6. Preparation of polyurethane

To make a two-part polyurethane coating using polyester resin, first mix the resin with a poly isocyanate (Desmodur E14) according to the manufacturer's instructions. Then, add any desired pigments or additives to the mixture and stir thoroughly. Apply the mixture to the surface using a brush or roller, making sure to spread it evenly and avoid any bubbles or drips. Allow the first coat to dry completely before applying a second coat, if necessary. Once the final coat is dry, sand lightly and polish if desired for a smooth finish**.**

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