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Synthesis of Polyurethanes From Acetyl Acetone Induced Polyols In Soybean Oil

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Abstract: Polyols were generated by reaction between epoxidised soybean oil and acetyl acetone which produced excess of polyols after reduction with $NaBH_4$ the resulting product was made reacted to HDMI (di-isocynate) to generate the resulting polyurethanes. The resulting polymers and the intermediate products were characterized with FT-IR which suggest the generation of the desired product from the used reactants.

Keywords: Polyols, epoxidised oil, soybean oil, polyurethanes, isocynate

Introduction: Polyurethanes (PU) are repeating urethane groups which are planned by certain chemical reaction taking place among an alcohol (-OH, di/poly) and an isocyanate (-N=C=O, di/polyol) group, this reaction befalls in presence of a chain extender, reaction catalyst or various other additives [1, 2]. The nature of Polyurethanes is supposed to be of thermosetting, when heated at higher temperature undergo loss of minor molecular mass structure instead melting, accredited to weak bond which breaks undergoes under thermal decomposition [3-5]. Extended chained polyols having flexible segments, are found to results in the soft and elastic polymer and whereas high volumes of crosslinking (due to crosslinkers) results in generation of rigid polymers. So as to augment the properties and applicability of the synthesized material, meticulous information of the above concept must be with the investigator to bring up significant reforms in PU.PUs are found to have their application in diverse fields viz. in paints, glues/adhesives, extraordinary flexibility foam, packaging foam,synthetic fibres, rubbers to be used in medical technology, etc., attributed to their astonishing, bio-durability, bio-compatibility,processibility and mechanical assets (viz. flexibility). Apart Pus also find their applicability in the arena of solid fuel rockets, blow-up boats, statuaries and adornments [6-9].

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Epoxidation, hydroxylation and purification are the basic steps to generate polyols from vegetable oils, epoxidation of oil is done at by various methods like, by regulated temperature in presence of peroxide, via acid ion-exchange resin method,via enzymatic method, viausing metal catalyst, followed by neutralization (with water)leading to hydroxylation. Purification of polyol synthesized by rotatory vapourto limit the impurities like water, heptane etc. [10-13]. PUs are chemically inert and combustible in which on decomposition results in the generation of CO and HCN, NOx, NCO and other toxic products [4]which could be prove dangerous to human health, hence precautions are obligatory during use of PUs [14]. This article describe the generation of polyols from soybean oil (SBO) and attempt of generation of PU from it.

Material and method: Soybean seeds were used for extraction of SBO, sulphuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), hexane, diethyl ether, sodium borohydride ($NaBH_4$), Iodine Monochloride (ICl), Iodine Monobromide (IBr), acetyl acetone ($CH_3.CO.CH_2.CO.CH_3$), Hexamethylene di-isocynate (HMDI), Dibutyltindilaurate (DBTDL), 1,4- Butanediol,were purchased from Merck India.

Extraction of SBO and determination of Iodine number:Soyabean seeds were taken and grinded (200 g), and was extracted with SBO with the help of Soxhelet apparatus.Iodine number/value was determine the amount of unsaturation in SBO (eq. 1).Oilwas treated with the solution of iodine monobromide (IBr) and iodine Monochloride (ICl). Number of iodine sensitive groups were calculated by knowing the amount of iodine required to make the solution retain its original colour. The unreacted iodine is reacted to which is further convert this into iodine whose concentration was known after titration with sodium thiosulphate.

$$\mathrm{IV} = \frac{(b-a)\times 0.01269\times 100}{w} \qquad \text{------- (1)}$$

where “a” and “b” are volume of ICl and thiosulphate (in mL) respectively while “w” is weight of oil (g) and “IV” is iodine value. IV for soybean oil was observed to be 130.

Epoxidation of SBO: Soyabean oil (2g) and H_2SO_4(0.5g) was charged in the two neck round bottom flask.The whole reaction mixture was magnetically stirred. Thermometer was also equipped and the temperature was maintained at 323K. H_2O_2 along with acetic acid wasadded drop wise within first 4 hours. H_2O_2 acts as donor of oxygen atom and while glacial acetic acid

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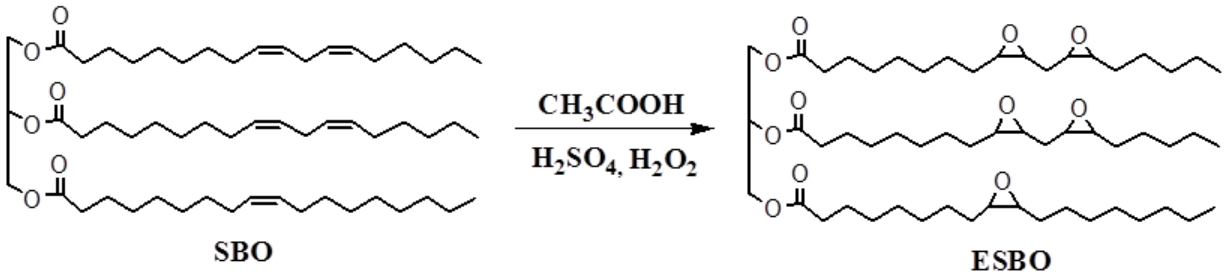
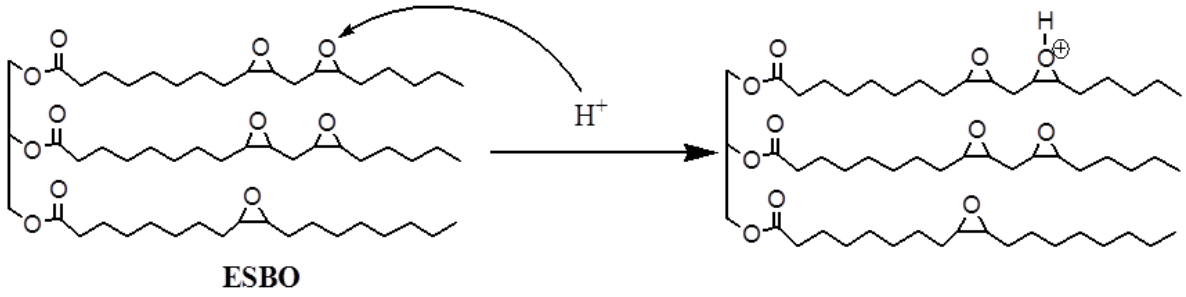
acts as carrier of oxygen in presence of inorganic acid (H_2SO_4). The reaction was further continued for 3 hours so that the complete epoxidation of mixture can takes place. The epoxidised oil (ESBO) was separated from the reaction mixture [15].

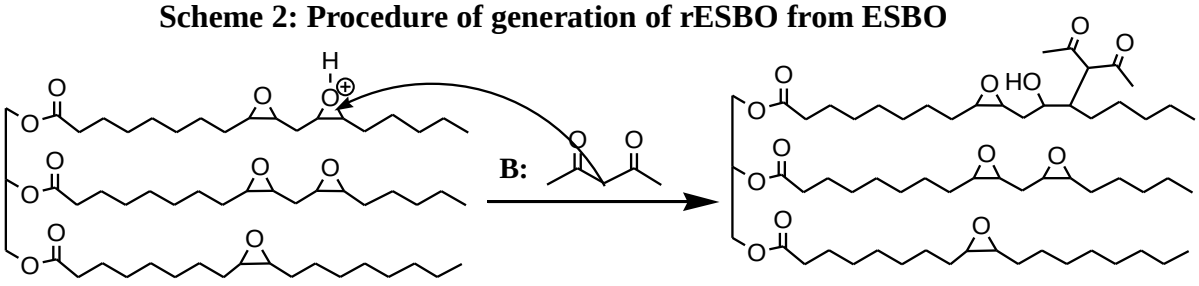


Scheme 1: Epoxidation of SBO

Reduction of ESBO:Reduction of ESBO was done with the help of acetyl acetone (scheme 3) followed by reduction with $NaBH_4$(0.5 g, scheme 4) was charged in the two neck round bottom flask. Epoxidised oil (2 g) was dissolved in diethyl ether (15 ml). It was added dropwise to the round bottom flask which undergoes mechanical stirring maintained at a temperature of 0° C [16].



Scheme 2: Procedure of generation of rESBO from ESBO



Scheme 3: Acetyl acetone on reaction with Epoxidised center generates –OH and diketone groups.

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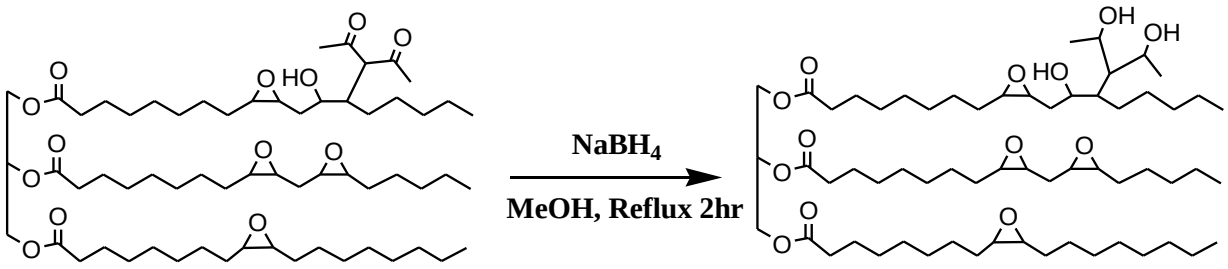
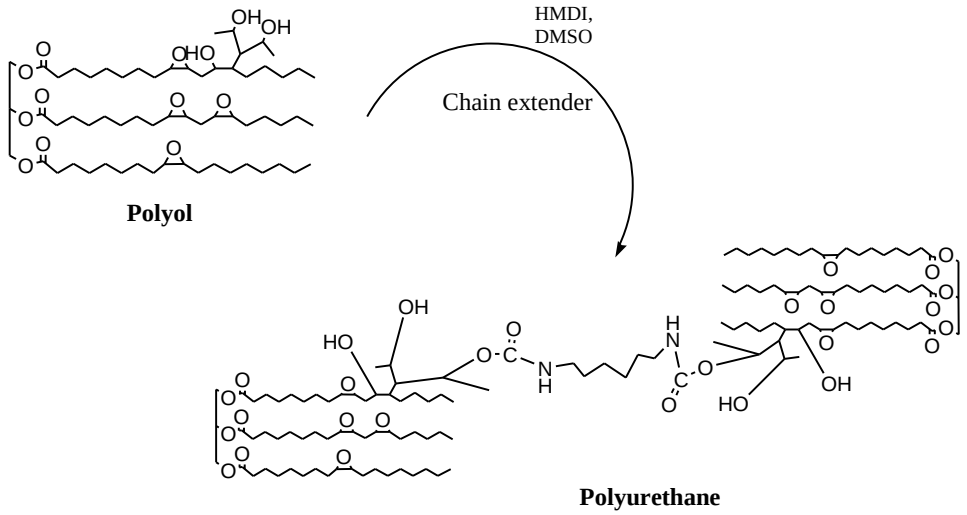


Scheme 4: Diketone further reduced by $NaBH_4$ to produce a polyols

Polyurethane Preparation from different Polyols: Polyurethanes were synthesized from as prepared polyols on reaction with –NCOs (isocynates). An approximately stoichiometry (2:1:1) of the reaction was maintained betweenHMDI: polyol : chain extender (1,4- Butanediol). In a 3-neck flask, HDMI(in DMSO) and polyols (in DMSO) solution containing 1%wt DBTDL (catalyst) weresupplied drop-wise at 65±1^{o}C. This resulting mixture was permitted to react for 2.5 to 3.0 hours and then was allowed to cool down to room temperature. To the resulting mixture 5% w/v chain extender (1,4- Butanediol, in DMSO) was added drop-wise to the pre-polymer solution under continuous stirring for near 12 hours. After theaccomplishment of the reaction, the PU containing solution was precipitated into deionized water for about 48 hours, then washed thoroughly with ethanol for about 5-6 hours at room temperature, followed by drying in a vacuum oven at 60^{o}C for anout48 hours before characterization.



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Scheme 5: PU synthesized by reaction between polyols (from SBO) and HDMI

Result and Discussion: All the samples were tested through FT-IR for their synthetic proof. The FT-IR of the sample was done to determine the functional groups of the raw materials and as prepared products. The FT-IR clearly proposes the basic structure of all the materials. The FT-IR of SBO shows it characteristic peaks, C=O (Ester) appears at 1750 cm-1, C=C(stretching) at 1651 cm-1 and C-O appears at 1302 cm-1 [17].

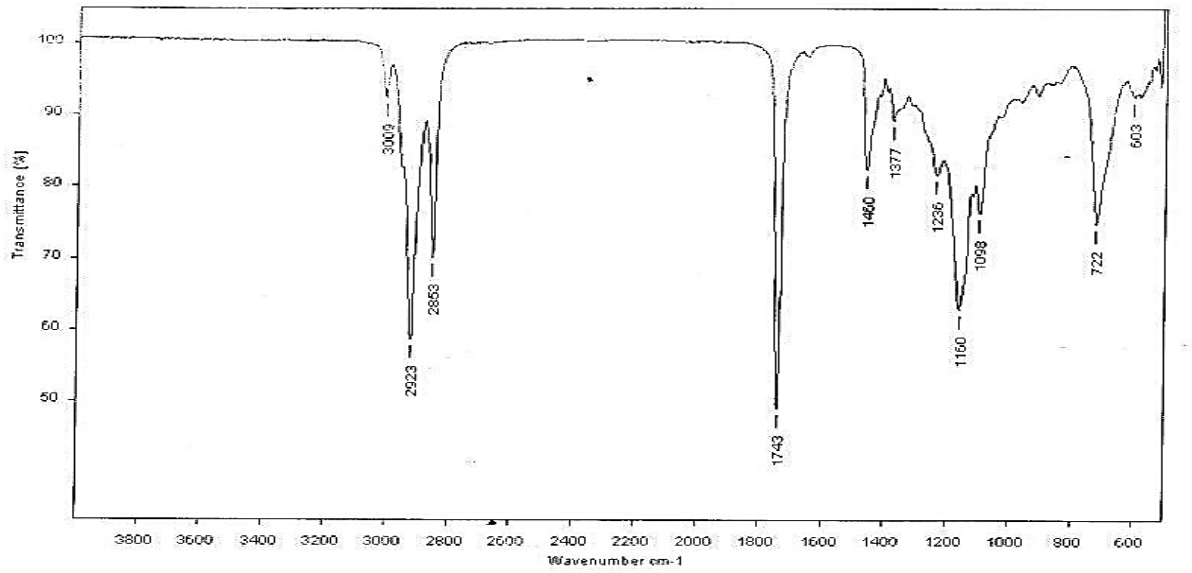

Fig 1. FT-IR of SBO

(a)

(b)

(c)

(d)

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Fig 2. (a) Process of extraction of Soybean oil (SBO) by Soxhelet apparatus, (b) extracted Soybean oil, (c) epoxidised soybean oil (ESBO), (d) reduced ESBO

FTIR of ESBO: FTIR spectra of ESBO, peaks of C-O-C appears at 1119 cm^{-1} , peak of C=O appears at 1743 cm^{-1}, peak of CH_2 appears at 1465 cm^{-1} [18].

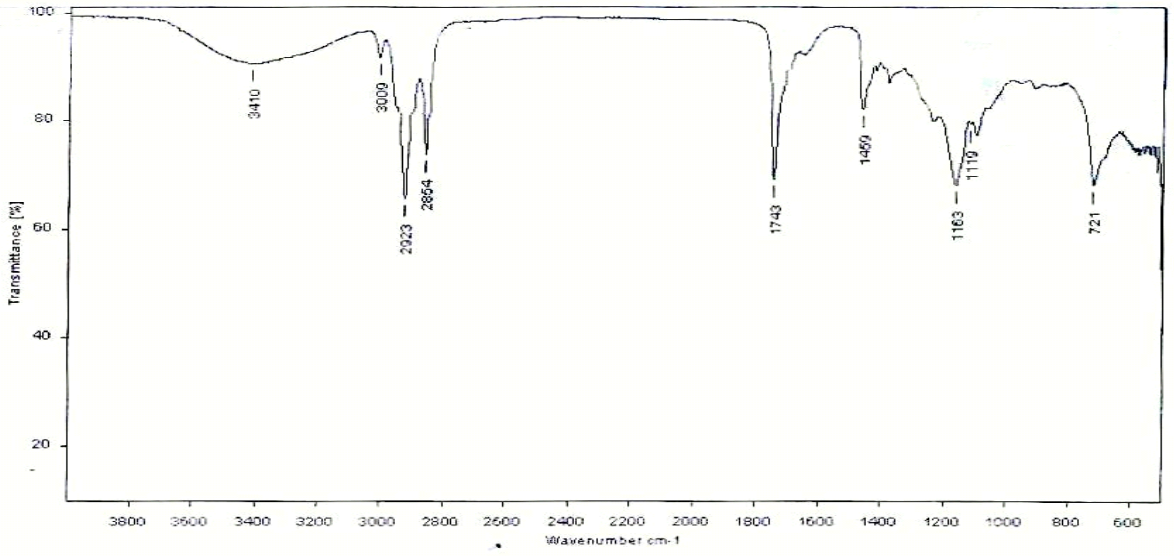

Fig 3: FTIR spectra of ESBO

FTIR of reduced ESBO (rESBO): Reduction of ESBO was done by $NaBH_4$(reducing agent) the FTIR of all the rESBO suggest efficient conversion of epoxide group to alcoholic group.The characteristic peaks comes around OH at 3500 cm^{-1} , C-H comes around 2903 cm^{-1} , C-O comes around 1126 cm^{-1}.

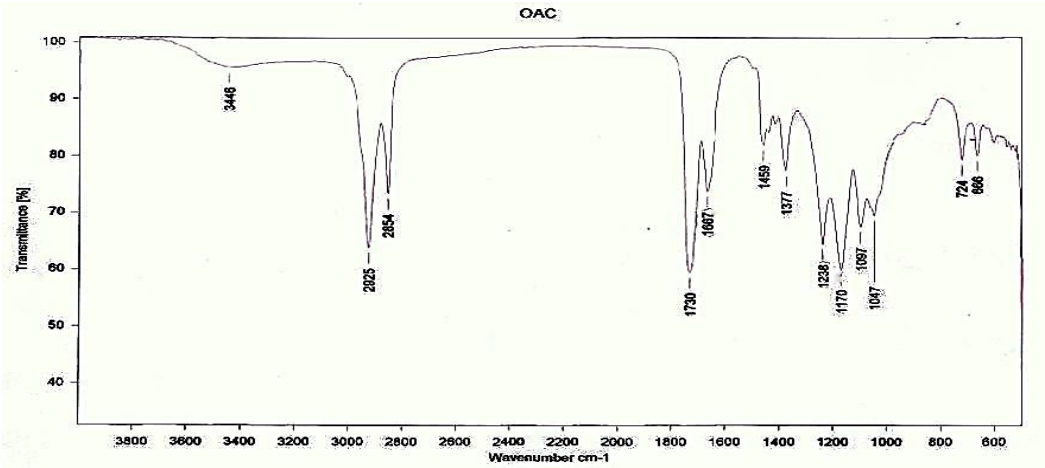

Fig 4: FT-IR of AcSBO

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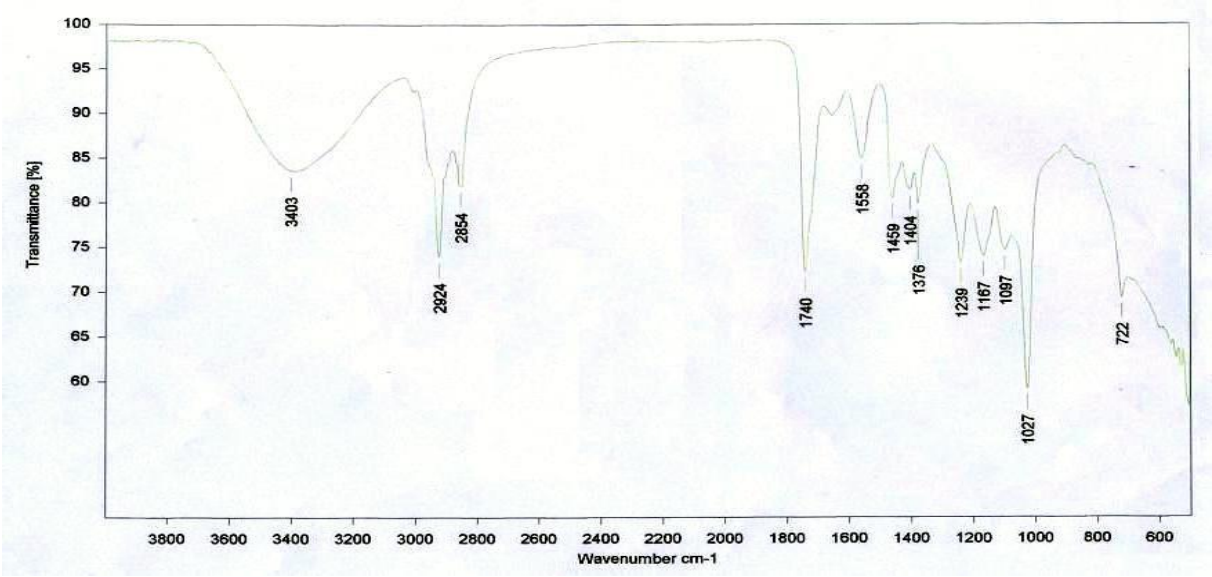

Fig 5. FTIR of rESBO by $NaBH_4$

FTIR of HDMI reacted to rESBO (Polyurethane): The rESBO reduced by reducing reagents was further reacted with HDMI to provide polyurethane molecules.The characteristic peak of N-H appears at 3343.71 cm^{-1}, C=N appears at 1635.79 cm^{-1}.

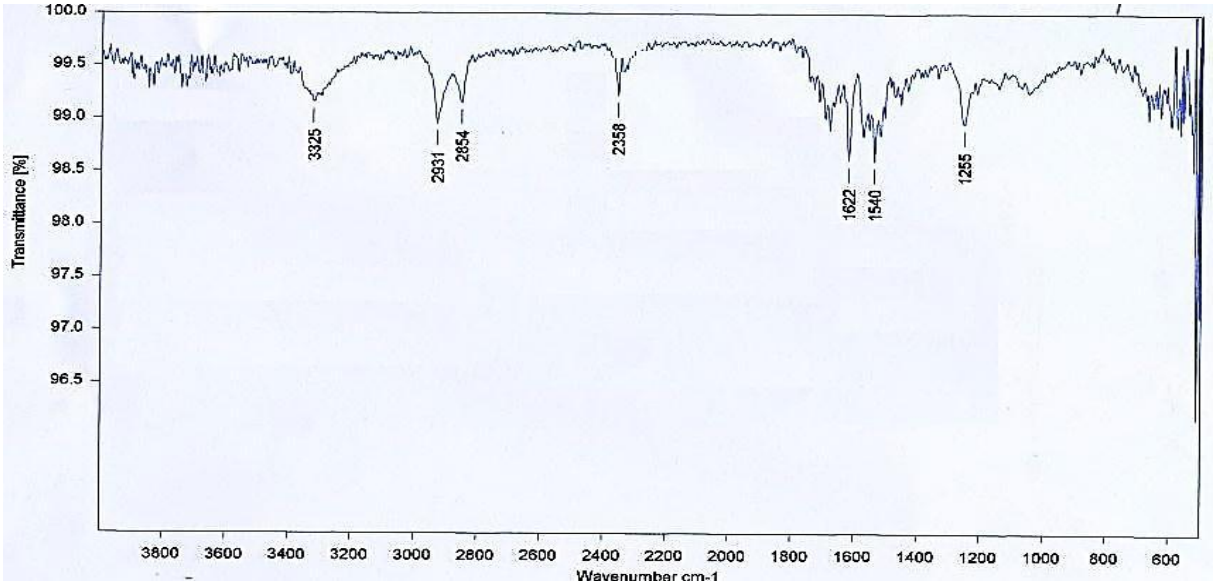

Fig 5: FTIR spectra of as prepared Polyurethane

Conclusion: Acetyl acetone was allowed to react to epoxidised SBO, which were further reduced by $NaBH_4$to generate polyol. These synthesized polyols were

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sucussfully converted to PU by reacting it with HDMI (a di-isocynate). Acetyl acetone was used as reagent to induce excess of –OH group in the backbone of SBO, which helps in higher degree of reaction between diol and di-isocynate.

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