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Research Article

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Study on Influence of Reaction time and process environment conditions on Heterogeneous Hydrogenation of HTPB using a Pd-Zr-charcoal catalyst

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Abstract

This paper outlines the influence of reactor environment conditions in synthesizing hydrogenated HTPB (HHTPB) using Hydroxyl-terminated polybutadiene (HTPB) polymer by catalytic hydrogenation method using bi-solvent system using iso-propyl alcohol and toluene as active solvent media. A novel synthesis approach to understand the effect of various reactor environment conditions such as nitrogen gas, H_2 gas and hydrogen-air environments to hydrogenate HTPB using a catalyst made up of palladium and zirconium as base metals supported on activated charcoal was demonstrated. Experiments were conducted in a 100 mL Inconel made batch type reactor with a magnetically driven variable speed impeller. Optimization of process time is demonstrated and fixed as 6 h for the study. HTPB and HHTPB polymers were characterized by NMR, FTIR, and chemical analysis. The results showed that the degree of hydrogenation of HTPB is ~87.5 % which is a waxy solid under hydrogen-air environment conditions for the given reactor volume with the chosen operating conditions. After hydrogenation of HTPB, no significant change in hydroxyl value was noticed, and the HHTPB formed is of vinyl-type functional isomer in H_2 environment. A marginal increase in molecular weight was observed after hydrogenation in all cases. HTPB and HHTPB were subjected to TG- DSC studies and it was found that the thermal stability of HHTPB marginally increased.

Keywords: Reactor environment, hydrogenated HTPB, degree of hydrogenation, Pd-Zr-charcoal catalyst, catalytic hydrogenation

1. Introduction:

Hydroxyl-terminated polybutadiene (HTPB) was prepared using a free-radical polymerization method, with hydrogen peroxide as an initiator and IPA as a solvent. HTPB contains unsaturated double bonds, which can potentially degrade during aging by oxidation. This oxidative

degradation will lead to a reduction in structural properties [1]. The presence of olefinic double bonds in HTPB causes some drawbacks with respect to the physicochemical and mechanical properties, such as poor oxygen resistance and weatherability, limiting its applications in high-end fields. The polymer hydrogenation technique has become increasingly commercially viable due to the growth of research in this field and the demand for high-performance polymeric materials. The selective hydrogenation of C=C double bonds is a significant process to obtain HHTPB which possesses excellent oil and fuel resistance properties improved heat, ozone and weathering resistance. Homogeneous and heterogeneous catalytic hydrogenations are the two primary techniques for hydrogenating polymers. Tonson Abraham [2], reported a homogeneous catalytic hydrogenation process to reduce unsaturation in liquid mono-functional and di-functional-terminated conjugated diene polymers, to achieve 80 % hydrogenation with noble-free metal catalysts using functional blocking agents. Hydroxyl-terminated poly-isoprene was hydrogenated over Ni-diatomaceous earth in hexane and treated with alcohols to separate highly-hydrogenated polymers from low or non-hydrogenated polymers and claimed that the IPA layer contained 97 % hydrogenated polymer [3]. Hydrogenation of polybutadiene polyol was attempted using Raney Ni catalyst using iso-propyl alcohol as a solvent and achieved a hydrogenation degree of 63.8 % [4]. The presence of hydroxyl groups was found to inhibit the hydrogenation process and the degree of hydrogenation mainly depends upon the catalytic system used [5]. Podesva et al., [6] described a method to hydrogenate OH-telechelic polybutadienes using di-imide (N_2H_2) and achieved a 95 % conversion with conventional Ziegler-Natta catalyst using elemental hydrogen. HTPB was hydrogenated with hydrazine dispersed in water using carboxylic acid to synthesize a white powder with a degree of hydrogenation of 99 % [6]. Hydrogenation was carried out using cobalt acetyl acetonate- di-isobutyl aluminium hydride (DiBAL-H) as the catalyst system, and the ^{1}H-NMR technique was used to confirm the hydrogenation of the polymeric material [7]. Palladium of 1% and 0.5 % on activated charcoal were used for hydrogenation of HTPB wherein toluene was used as a solvent media, and reported a degree of hydrogenation of 95 % [8]. Sabata et al. [9] estimated the rate constants of the hydrogenation process with vinyl polybutadienes in the presence of homogeneous Ziegler Ni catalysts. Several research articles were briefed on hydrogenation of various polymers [10-19]. The research on heterogeneous catalysis of HTPB hydrogenation has attracted more attention due to the easy catalyst-product separation after the hydrogenation reaction, which results in lower production cost and better product quality that of the products obtained from homogeneous hydrogenation [20-26]. Hence, this research is highly focused on the development of a novel heterogeneous process and also to study the influence of process time & the reactor environment conditions

which are required for the futuristic process methodology to scale-up the synthesis of HHTPB. This process significantly improves HTPB's oxidative and UV stability, making it ideal for use in demanding environments. A quantitative assessment of estimating degree of hydrogenation was done using ^{1}H-NMR. Generally, the homogeneous catalyst has a high activity and selectivity under mild reaction conditions. In homogeneous catalytic process, it is difficult to separate a catalyst from the reactant mixture, and is difficult to reuse, leads to the increase the catalyst cost. The significant advantages of heterogeneous hydrogenation are the catalyst separation, re-usability, and the absence of metal contamination in the produced polymers. Both Pd and Zr significantly favors the catalytic hydrogenation process. The presence of hydroxyl groups was found to inhibit the hydrogenation process and the yield of hydrogenation depends upon the catalytic system used.

This invention uses a binary solvent system comprising isopropyl alcohol and toluene for producing HHTPB with the catalyst. Although either solvent can independently facilitate HHTPB production, their combined use in a specific proportion provides the distinctive solvent environment central to the invention. This paper also briefed how HHTPB was synthesized using different reactor environments. Choosing the appropriate catalyst system and the optimum process conditions are highly important for the development of a novel process. As the cost of palladium based precursors is very high, a suitable substitute precursor of ZrO_2 with similar characteristics is also added along with activated charcoal during synthesis to make a cost-effective catalyst Similar work with other catalysts were carried out by us and the studies employ a similar experimental platform, certain aspects of the experimental procedures including the reactor configuration, operating conditions, characterization techniques, calculation of degree of hydrogenation (DH), and data-analysis methodology are necessarily similar. However, we would like to clarify that the similarity in the experimental methodology does not imply that the experimental results or scientific findings are same. We chosen the heterogeneous process using a bi-metal catalyst with Pd and Zr supported on activated charcoal to study the effect of process conditions. The present study was conducted as a separate experimental investigation, and the experimental datasets reported in this manuscript are newly generated and have not been reported in our previous research articles [21-23]. In particular, the measured experimental results, comparative performance data, and corresponding interpretation presented in the current manuscript are distinct from those previously published. This work is aimed at (a) whether hydrogenation is possible without H_2 gas (b) Influence of admittance of air along with H_2 gas (c) spectroscopic analysis of all the experiments.

2. Materials and methodology:

2.1 Materials: HTPB was prepared by standard free radical polymerization using butadiene and H_2O_2. HTPB that was used in this invention possessed hydroxyl value of 40.8 mg KOH/g, number average molecular weight (Mn) of 6150 g/mol, poly-dispersity of 2.25, intrinsic viscosity of 0.14 dl/g, viscosity of 6 Pa-s at 30^0C and cis, trans and vinyl isomer ratio as derived from FTIR, being 28.9%, 50.4% and 20.7% respectively. Synthesis of Pd-Zr-charcoal catalyst using Palladium nitrate hydrate, Zirconium (IV) oxy nitrate hydrate and activated charcoal. A fine blend of two solvents, iso propyl alcohol (IPA) (or 2-propanol) and toluene is used as solvent system in this invention, even though both the solvents can independently produce HHTPB with this catalyst. These are procured from M/s Merck and used as received. Nitrogen and hydrogen gas were procured in cylinders of 320 bar pressure from a commercial vendor with a purity > 99.5 %**.**

2.2 Catalyst synthesis

Palladium nitrate hydrate, Zirconium (IV) oxy nitrate hydrate and activated charcoal which is dispersed in 50 ml of distilled water and stirred all the contents for 12 h at room temperature. The precipitate was collected by vacuum filtration, washed thoroughly with deionized water to remove residual precursors, and then dried at 105 °C for 12 h in a hot air oven. Any residual moisture was subsequently removed under vacuum using a rotary evaporator. The catalyst was calcined at 300^0 C at a heating rate of 2 ^{0}C/min, under a nitrogen environment for 3 h, then exposed to hydrogen for 3 more hours with continuous flow at 30 ml/min. This high-temperature calcination and reduction yielded a Pd-Zr-activated charcoal catalyst. The catalyst composition as palladium, zirconium, and activated charcoal content of 2.4 ± 0.4 %, 4.9 ± 0.5 %, and 83.3 ± 1.1 % (w/w/w), respectively as major constituents and was confirmed by EDS.

2.3 HHTPB process methodology:

The hydrogenation of HTPB process is more complex by virtue of the higher molecular mass due to its poor segmental mobility, Hence, HTPB hydrogenation studies have been carried out on dissolving HTPB in an appropriate organic solvent system. IPA and toluene were chosen as solvents. Experiments were conducted in a 100 mL inconel autoclave (reactor) with a magnetically driven variable speed impeller and the schematic is shown in Figure 1. The required quantity of solvents i.e. toluene and IPA were added initially to the HTPB in the predefined ratio of HTPB: IPA: toluene in the ratio of 1:1:2 (w/w/w) into the reactor at room temperature. 2 % w/w of catalyst (percent with respect to HTPB) was added to this solution and then pressurized

the vessel to the desired operating pressure of 6 MPa. The reactants were heated to predefined temperature of 240^0C and continued the reaction for a specified ratio at a constant stirring rate of 800 RPM. The reactor is as 200 kg/cm^2 pressure-rated reactor with a continuous temperature and pressure monitoring, pressure relief devices, interlocks, controlled gas charging sequence, leak testing, ventilation, remote operation, etc. Safety interlocks are provided with high pressure trip (>100 kg/cm^2) interlock reaction system with manual de-pressurization vent system during reaction if any abnormality is noticed and a continuous water supply during the entire reaction to cool the reactants. The batch high pressure reactor was operated within its specified pressure and temperature operating limits, with pressure and temperature monitored during the experiment and the reactor operated using the applicable safety/interlock provisions of the system. The experimental procedure was conducted according to the established high-pressure reactor operating and safety procedures.

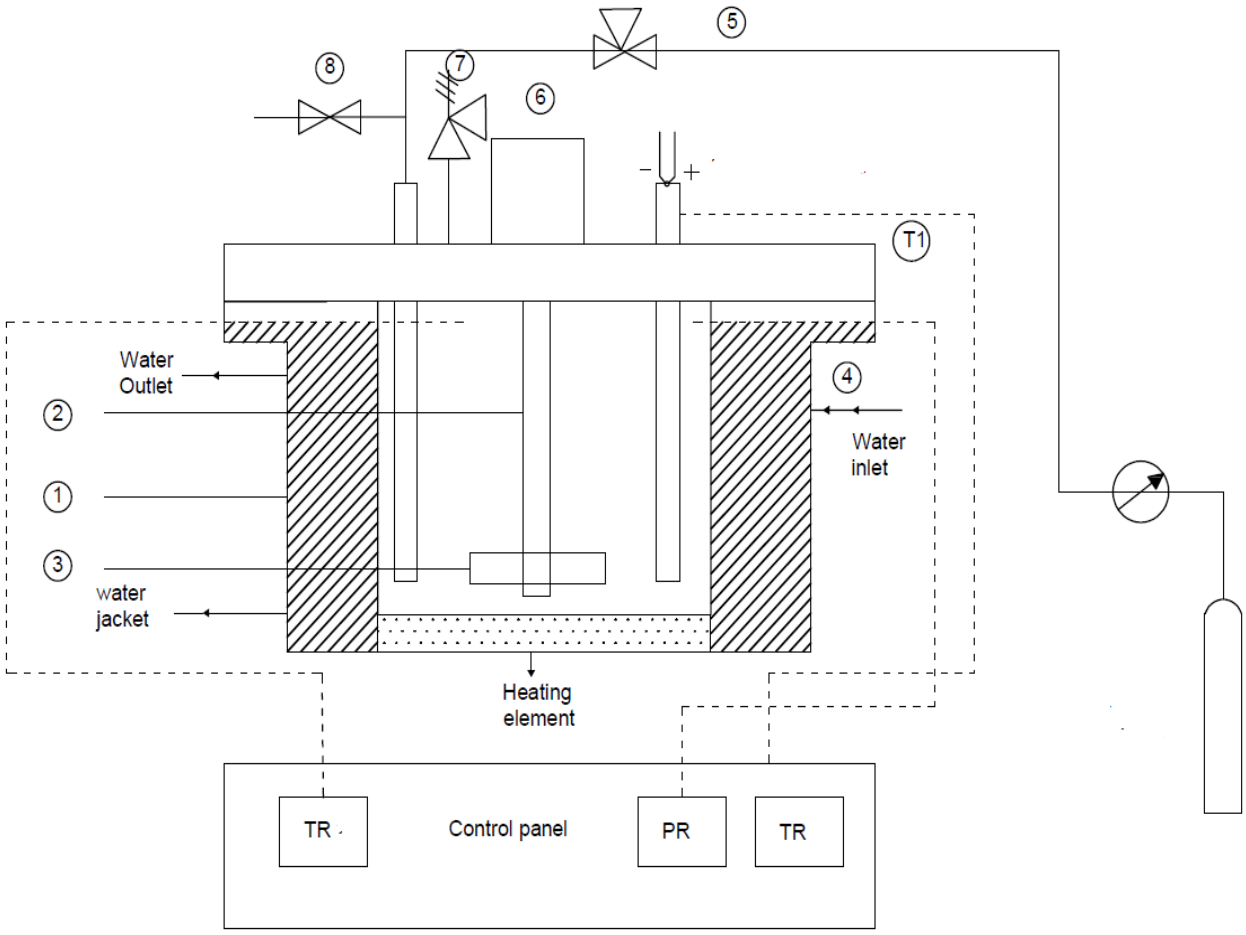

Figure 1. Schematic of hydrogenation reactor for HTPB hydrogenation

2.4 HHTPB Characterization:

The degree of hydrogenation of HTPB was estimated using ^{1}H-NMR spectra, and the data was complemented by ^{13}C-NMR and FTIR (Bruker model) spectra. The samples were analyzed using ^{1}H-NMR of Model: Bruker Model Avance Z800701, equipped with a dual carbon/proton (CPDUL) cryoprobe in which $CDCl_3$ was used as a solvent. The degree of hydrogenation was estimated based on the disappearance of olefinic C=C double bonds. The gel permeation chromatography (GPC) technique (AGILENT, Model: 1260 Infinity using polystyrene as reference) was used for estimating the molecular weight distribution, average molecular weight, and poly-dispersity of both HTPB and HHTPB. Thermal behaviors of HTPB and HHTPB were analyzed using TG-DSC (thermogravimetry - differential scanning calorimeter) of model Netzsch STA 449F3 with N_2 as inert carrier gas at a flow rate of 20 ml/min and a heating rate of 10^{0}C/min. The acetylation method estimated the hydroxyl value (-OH value). HTPB reacted with dried acetic anhydride in the presence of pyridine, which was used as a catalyst, and the liberated -COOH was titrated by acid-base titration.

3.Results and discussion: Study on the influence of process parameters

3.1 Influence of process time

Extensive studies were carried out to optimize the process time initially based on the degree of hydrogenation. The other influential parameters, the schematic representation of hydrogenation reactor set-up and the synthesis process of HHTPB, catalyst and its characterization were detailed by Devi vara prasad et. al [20]. The catalytic hydrogenation process of HTPB is influenced by several factors. Optimizing these environmental factors is essential for achieving efficient, selective, and economically viable catalytic hydrogenation of HTPB. By carefully controlling these factors, the catalytic hydrogenation process of HTPB can be made more efficient, selective, and cost-effective. The use of catalytic hydrogenation of HTPB requires high temperatures and pressure, longer reaction times. As the reaction progressed because of increase in polymer chain stiffness causes even greater restriction of chain mobility. The process time in hydrogenation of polymers plays a major role in achieving the desired level of hydrogenation. In general, more the process time, higher the degree of hydrogenation. In case of reversible reactions, the degree of hydrogenation increases up to the optimum time and then decreases with time. Hence, it is always essential to find an optimum time for the reaction. A set of four experiments were carried out at different process times of 2, 4, 6 and 8 h to assess the required process time. A process temperature of 240 ^{0}C, a feedstock ratio of HTPB: HTPB: IPA: toluene ratio of 1:1:2 (w/w/w), catalyst weight of 0.2 g i.e. the catalyst loading of 2 wt % relative to the initial HTPB mass was selected based on the preliminary experiments and our previous studies [21-23], where this

loading provided sufficient catalytic activity to avoid the use of an unnecessarily high catalyst concentrations. The Pd concentration in the catalyst = 2 % of the catalyst weight, which means the Pd concentration is 4 mg. The initial H_2 gas pressure of 6 MPa was maintained as reaction pressure condition for all experiments.

The hydrogenation reaction is favourable at high pressures and because H_2 gas is consumed during the hydrogenation reaction, the instantaneous H_2 pressure during the reaction may differ from the initial pressure and may decrease as hydrogenation proceeds. Therefore, the possibility of changes in H_2 availability during the reaction is vital during the reaction. It was observed that a decrease in DH at extended reaction time potentially arises from several factors, including reversible hydrogenation/dehydrogenation, catalyst deactivation, changes in H_2 availability or pressure, and mass-transfer limitations associated with the polymeric hydrogenation reaction system. The hydrogenation of an unsaturated polymer can potentially be accompanied by processes such as chain scission, chain coupling/crosslinking, or other structural changes. Therefore, the decrease may not be exclusively due to reversibility. Therefore, it is interpreted that the DH value used is as evidence that hydrogenation reaction occurring with possible side reactions, which can be considered as potential factors to influence the recovered polymer properties. The contact between polymer and heterogeneous Pd catalyst, changes in catalyst activity and gas–liquid/polymer mass transfer may influence the apparent hydrogenation behavior at prolonged reaction times. Similarly, any change in effective H_2 availability during the experiment could contribute to the observed decrease. These possibilities cannot be independently distinguished and using DH values. These are the possible reasons can be attributed to decrease in DH with extended time of reaction after 6 h. The results are given in Table 1.

Table 1. Influence of process time on hydrogenation of HTPB and the product characteristics

Time, h	OP, %	%DH	Geometrical isomer content (relative) from FTIR analysis (%)					-OH Functionality Distribution (%) (^{1}H-NMR		
			Cis	Trans	Vinyl	K	C	G	H	V
2	18.06	48.51	68.1	16.0	15.9	25.1	1212.7	14.1	60.6	25.3
4	17.57	49.92	66.9	15.7	17.4	27.2	1248.0	9.4	62.2	28.4
6	8.84	74.79	54.0	5.7	40.3	161.2	1869.7	0	0	100
8	14.24	59.39	72.7	9.9	17.4	49.3	1484.7	0	68.4	31.6
HTPB-ref	35.10	---	28.8	20.8	50.4	---		14.6	52.7	32.7

OP-olefinic protons; DH- degree of hydrogenation, Functionality distributions: G-geraniol (4.2 ppm); H-hexane-1-ol (4.1 ppm); V-vinyl (3.4-3.65 ppm); Isomer distribution: C-cis (723 cm^{-1}); T-trans (965 cm^{-1}); V-vinyl (911 cm^{-1}) from FTIR; K_{app} - Apparent rate constant, L/ (mol), C, Pd-normalized productivity, g Pd^{-1} h^{-1}

To provide a more meaningful comparison of catalytic performance, it is also calculated the Pd-normalized activity/productivity, where the available experimental data permit such calculation. The productivity can be expressed as

Pd-normalized conversion (C) = DH* mass of hydrogenated HHTPB / (mass of Pd *100) with units such as g HHTPB g Pd^{-1} h^{-1}. C is found be higher for 6 h process time.

Degree of hydrogenation (DH) reflects the conversion of C=C bonds to saturated C–C bonds, whereas the recovered HHTPB yield represents the amount of polymer recovered after the reaction relative to the initial polymer amount. Here we considered DH only estimating apparent rate constant and Pd-normalized conversion. For a relevant Pd loading and normalized performance information for the selected 2 wt% total catalyst loading, 6 h process time condition is as an experimentally optimized value. The optimum time was fixed as 6 h for the reactions to study the impact of reactor environment conditions to estimate the degree of hydrogenation and the product characteristics. The process time is chosen with respect to higher degree of hydrogenation which is the desired product characteristic for its applications. At 6 h of process time, there was a maximum hydrogenation of vinyl isomers took place followed by trans and cis isomers. The degree of hydrogenation of HTPB was found to be increased up to 6 h and beyond this, it decreased drastically and also a sudden increase in isomer content was noticed as shown in the Table 1, which summarizes the HHTPB polymer characteristics. Geraniol and hexene-1-ol contents of HTPB were totally converted into vinyl functionality at 6 h of hydrogenation time. The results are illustrated in Figure 2.

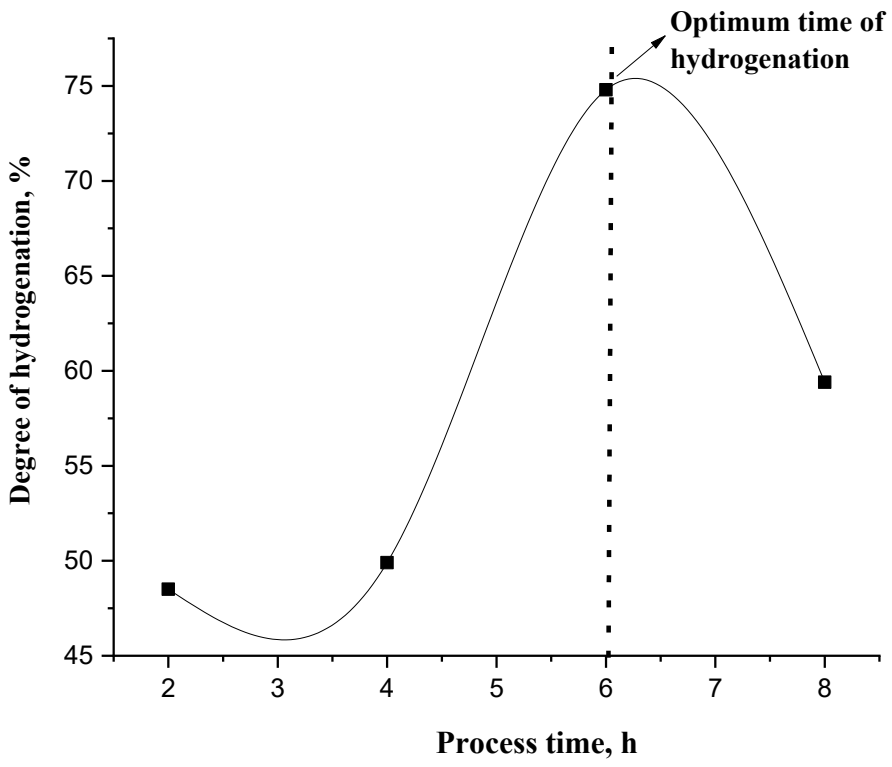

Figure 2. Influence of process time on degree of hydrogenation of HTPB

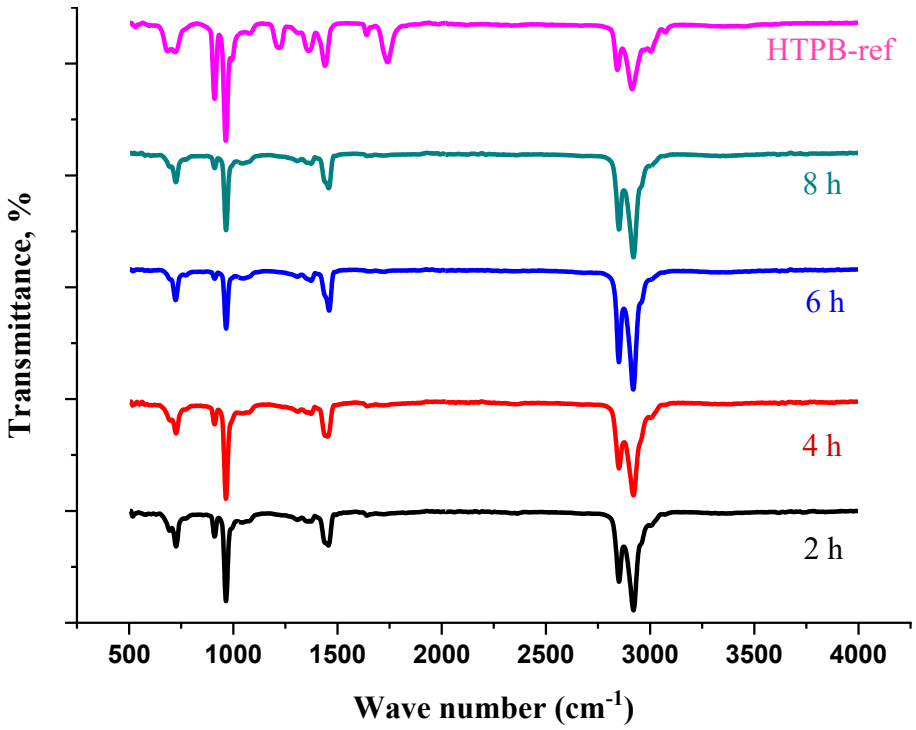

Figure 3. FTIR spectra of influence of process time on hydrogenation of HTPB

With the optimized time of 6 h, hydrogenation of Pd-Charcoal was carried out and the degree of hydrogenation was 37% [23]. Hence, bi-metal supported with charcoal was chosen to increase the extent of reaction.

3.1.1 Characterization details

3.1.1.1 NMR analysis

The peaks in ^{1}H-NMR from Figure 3(a) indicated the presence of (a) 4.8-6.0 ppm (-CH=) represents the olefinic region (1,4 cis and trans protons at 5.4-5.6 ppm and 1,2 vinyl protons at 4.8-4.9 ppm region) and (b) 3.4-4.0 ppm region represents the presence of –OH functionality distribution (geraniol(G), hexene-1-ol (H) and vinyl (V) groups) (c) 1.9-2.1 ppm shows =CH- 1,2- polybutadiene (d) 1.15 - 1.45 ppm shows aliphatic region (attributed to the saturated methyl protons in the main chains). ^{1}H-NMR spectra identified the increase in hydrogenation based on the decrease in C=C double bonds at 4.8-6.2 ppm region and the increase in saturated methylene protons at 1.3-1.6 ppm region [20]. The functional isomers (G-geraniol, H- hexene-1-ol and V-vinyl) were also estimated from ^{1}H-NMR data. The equations for the calculation of olefinic protons content (derived from ^{1}H-NMR data) and the degree of hydrogenation (%) were given below. ^{13}C-NMR is used for a qualitative assessment and supportive to ^{1}H-NMR.

Regarding the calculations, the equations and calculation procedures, including the determination of DH, are similar as reported [21-23]. This is because the same established definition and calculation methodology is appropriate for evaluating the corresponding reaction parameter in all the studies. The use of the same calculation equation should therefore be understood as methodological consistency of experimental data. Nevertheless, the numerical values used in the calculations in the present work were obtained from the new experimental measurements reported here.

$$\text{Olefinic protons (OP)} = \frac{(\text{NMR peak area under } 4.8-6.2 \text{ ppm region})}{\Sigma(\text{NMR data peaks})} \quad \ldots\ldots \ (1)$$

Degree of hydrogenation (DH), % =

$$\frac{(\%\ \text{Olefinic protons in HTPB} - \%\ \text{Olefinic protons after hydrogenation}) * 100}{(\%\ \text{Olefinic protons of HTPB})} \ldots(2)$$

DH represents the fraction of the original olefinic (C=C) groups in HTPB that have been hydrogenated. DH is used as the experimentally determined measure of the extent of C=C conversion. DH is not a measure of selectivity or yield. In the present study, DH is determined from the decrease in olefinic proton signals in the ^{1}H NMR spectrum.

The equation estimates the equillibrium constant (K_{app})

$$K = \frac{[HHTPB]}{[HTPB]*[H_2]} \quad \text{at constant process temperature (T)} \ldots\ldots\ldots\ldots (3)$$

The apparent rate constant was obtained by fitting the experimental hydrogenation data to the kinetic expression used in the present study. The apparent rate constant represents the overall observed rate of hydrogenation under the specified experimental conditions, including the effects of H_2 pressure, mass transfer, polymer properties, and other experimental factors. Specifically, the relationship between the concentration of products, reactants and pressure is used for computation of apparent rate constant.

Similarly, from ^{13}C-NMR data, a significant decrease in the peak intensity at 130 ppm region indicated the reduction of double bonds, i.e., an increase in the degree of hydrogenation as illustrated in Figure 4(b). ^{13}C-NMR data only used for qualitative estimation in this paper.

3.1.1.2. FTIR analysis

FTIR spectra were recorded in 500- 3500 cm^{-1} wave number range. As illustrated in the FTIR spectrum of HTPB and HHTPB (Figure 3), the characteristic peak at 723 cm−1 was related to 1,4-cis double bonds, at 965 cm^{-1} was related to 1,4-trans double bonds, and at 911 cm−1 was related to 1,2-vinyl double bonds. The concentration and distribution of different types of C=C in the polymer has a close relationship with the hydrogenation rate and reaction kinetics, due to the fact that the different types of C=C have different reactivities during the hydrogenation. The order of the reactivity of these three types of C=C is vinyl > cis> trans in the presence of a Pd-Zr-charcoal catalyst. Vinyl isomers are more reactive toward chemical modification reactions than cis and trans 1,4 units due to their lower steric hindrance. Thus, the overall reaction rate was controlled by the hydrogenation of trans C=C. The area under the peaks were computed for estimation of the above geometrical isomer content. There was a decrease in absorption peaks for cis, trans and vinyl double bonds (geometrical isomers) after hydrogenation was enumerated from FTIR analysis as shown in Figure 3. The absence of absorption peak at 1640 cm^{-1} indicated a reduction in C=C unsaturation, i.e., advancement of hydrogenation reaction. The geometrical isomer content after hydrogenation is given in Table 1.

3.2 Influence of reactor environment conditions on hydrogenation of HTPB

Hydrogen migrations might take place during solvent hydrogenation by transfer between identical donor and acceptor units. Since higher degree of hydrogenation was possible with the

combination of HTPB: IPA: toluene in the ratio of 1:1:2 (w/w/w), an attempt was made to study the influence of change in the reactor environment conditions. The same ratio of HTPB and solvents was ensured by changing the reactor environment alone during this study. Three experiments were carried out with N_2 gas, H_2 gas and H_2 gas-air (molar ratio of 60:1) respectively as reaction environment. Safe operation depends on the complete reactor design, rated pressure/temperature limits, gas-handling system, monitoring and protection systems, operating procedures, and the experimentally/engineering-defined safe operating envelope. The combination of H_2, O_2, elevated temperature, pressure, and a Pd-Zr- charcoal catalyst is not created any hazardous reaction environment and the reactor environment is intrinsically safe which is proved from the experiments. The figures 4(a) and 4(b) indicate the mechanism of hydrogenation of HTPB with H_2 and N_2 atmosphere.

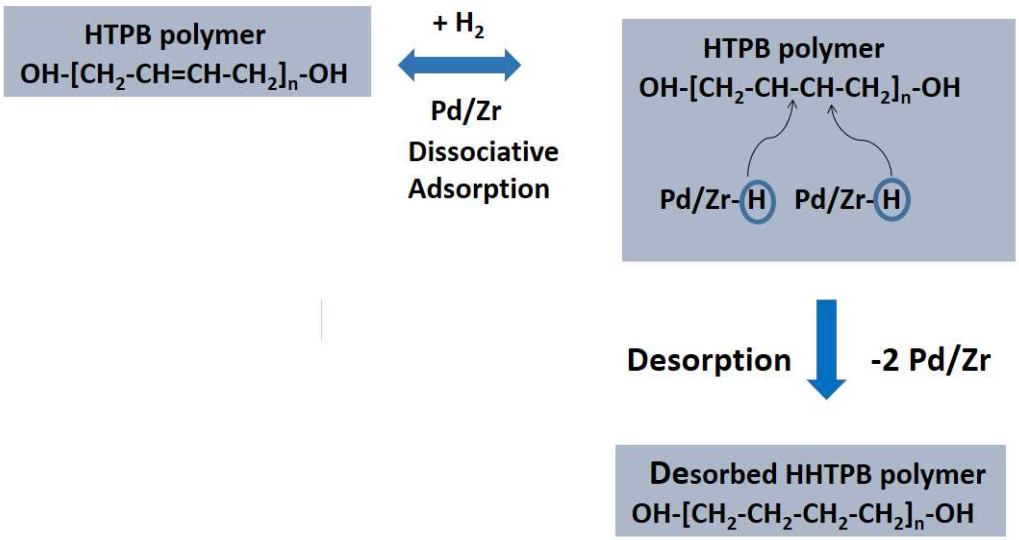

Fig. 4(a). Heterogeneous catalytic reaction mechanism of hydrogenation of HTPB using a Pd-Zr-charcoal catalyst

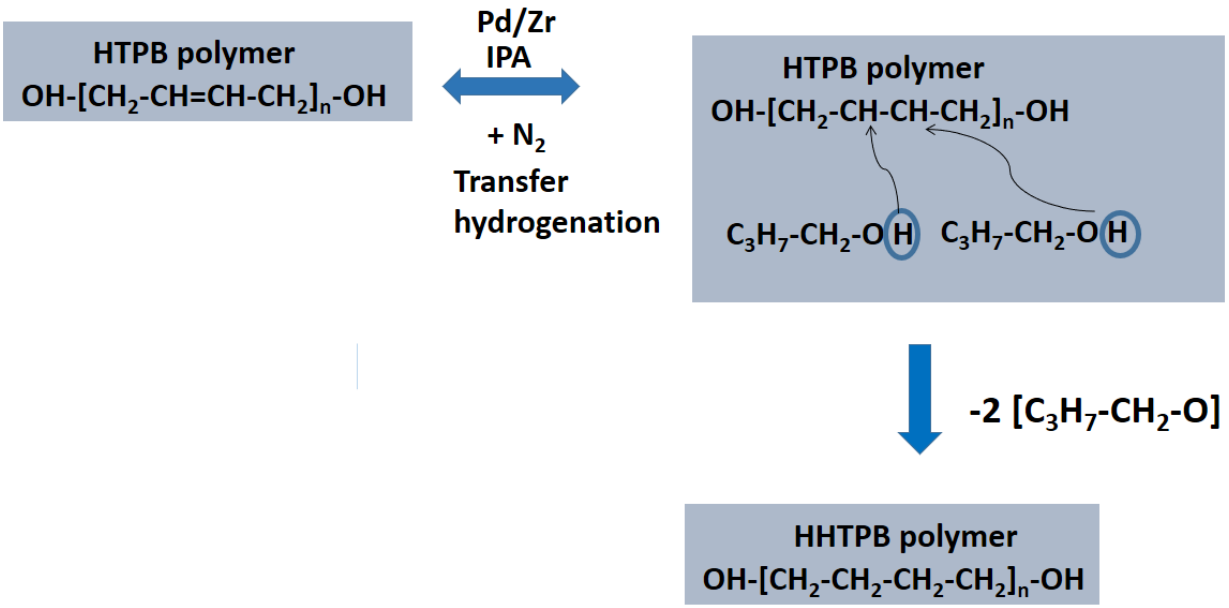

Fig. 4(b). Transfer hydrogenation reaction mechanism of hydrogenation of HTPB using a Pd-Zr-charcoal catalyst with solvent IPA

A process temperature of 240 ^{0}C, a feedstock ratio of HTPB: HTPB: IPA: toluene ratio of 1:1:2 (w/w/w), catalyst weight of 0.2 g and an initial H_2 / air gas pressure of 6 MPa were maintained as reaction conditions. Higher degree of hydrogenation and the apparent rate constant was observed for hydrogen-air (molar ratio of 60:1) environment in comparison to other reactor environments. It was observed that there was a maximum hydrogenation of vinyl isomers occurred when hydrogen-air environment was used. At higher temperatures, in the presence of catalysts, organic solvents such as isopropanol can donate hydrogen (catalytic cracking) and favors the hydrogenation reaction. The possibility of achieving reduction with the help of an organic molecule as the hydrogen donor in the presence of a catalyst is known as catalytic transfer hydrogenation. The same happened in case of hydrogenation of HTPB using IPA as solvent. This reaction is further favored by high pressure which is provided by N_2 gas supplied initially and this has yielded a lesser degree of hydrogenation during controlled synthesis. This is one of the possible reactions during hydrogenation irrespective of reactor. A degree of hydrogenation of 5.5 % was observed when N_2 gas is used as pressurizing medium, a transfer hydrogenation phenomenon might have been occurred. Hydrogen environment with high pressure favours the forward reaction and yielded a higher degree of hydrogenation

3.2.1 ^{1}H-NMR and ^{13}C-NMR analysis

The conformation of HTPB polymer molecules changes with the progress of hydrogenation which changes the microstructure (functional isomer distribution) of HHTPB and is well

characterized using NMR spectroscopy. The ^{1}H-NMR and ^{13}C-NMR analysis results are shown in Fig. 4(a) and 4(b) respectively.

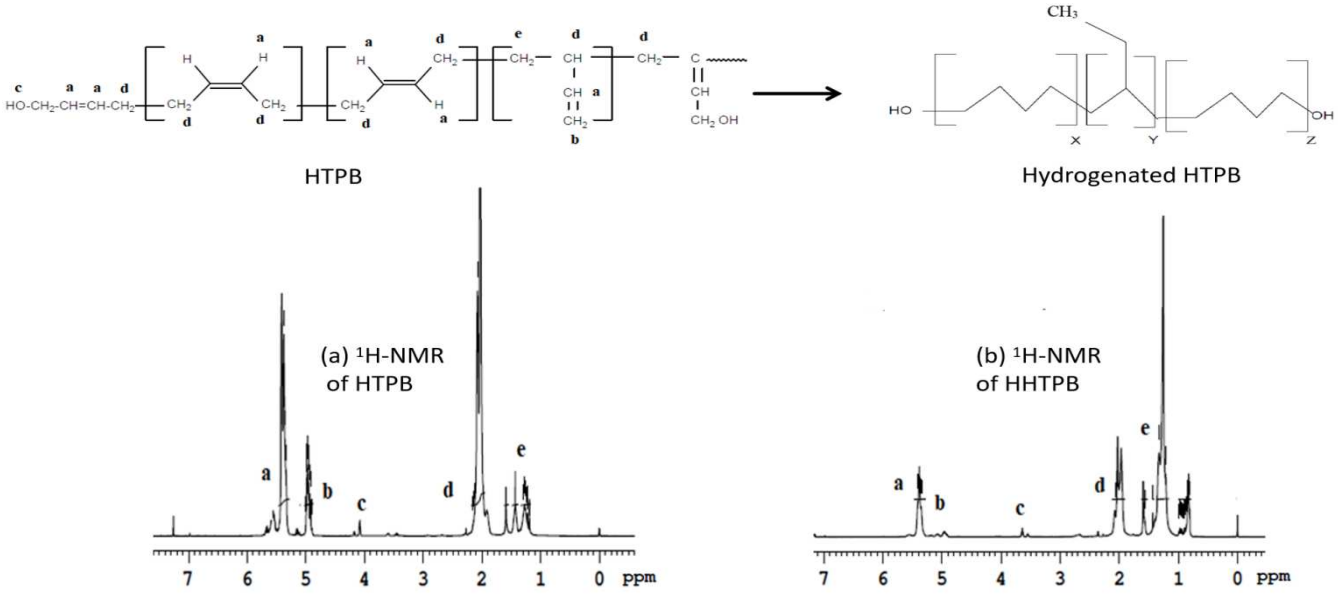

Figure 5(a). ^{1}H-NMR spectrum of HTPB and HHTPB

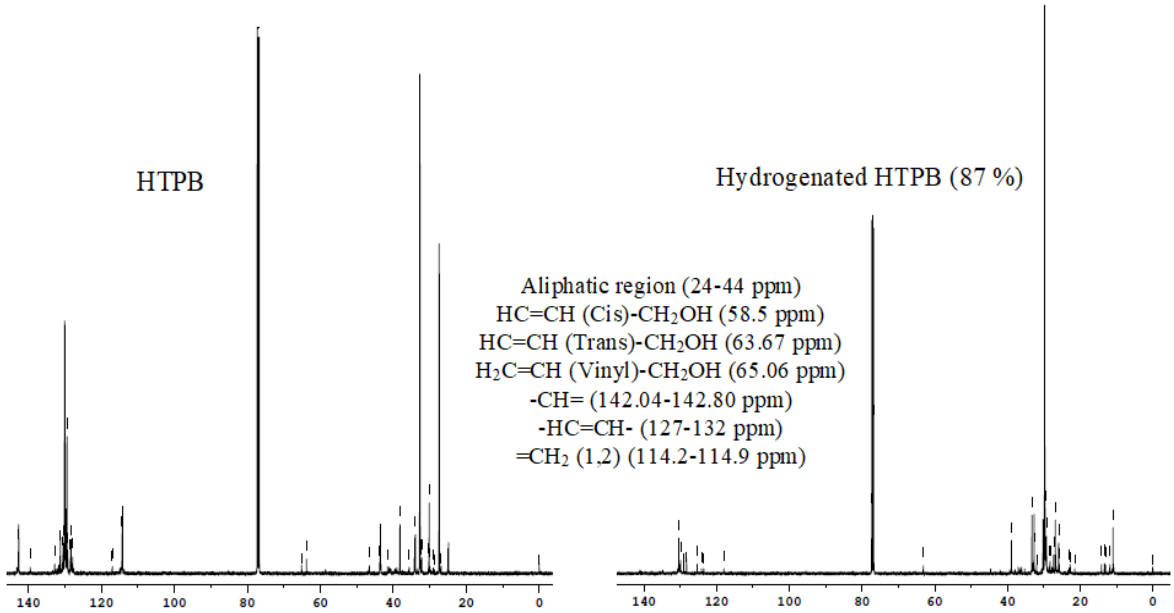

Figure 5(b). ^{13}C-NMR spectra of HTPB and HHTPB (87%)

Table 2. Influence of nature of reactor environment on HHTPB polymer characteristics

Time, h	OP, %	%DH	Geometrical isomer cont from FTIR analysis						-OH Functionality Distribution (%) NMR)		
			Cis	Trans	Vinyl	K	k	r x 10^{-5}	G	H	V
N_2 atm	33.1	5.5	60.3	4.6	35.1	0.848	0.009	0.288	14.1	60.6	25.3
H_2 atm.	9.3	73.5	31.2	2.2	66.7	161.16	0.23	6.98	9.4	62.2	28.4
H_2-air(60:1)	4.3	87.8	65.6	0.7	33.7	813.58	0.35	10.6	0	0	100
HTPB-ref	35.10	---	28.8	20.8	50.4	---			14.6	52.7	32.7

OP-olefinic protons; DH- degree of hydrogenation, Functionality distributions: G-geraniol (4.2 ppm); H-hexane-1-ol (4.1 ppm); V-vinyl (3.4-3.65 ppm); Isomer distribution: C-cis (723 cm^{-1}); T-trans (965 cm^{-1}); V-vinyl (911 cm^{-1}) from FTIR; K – equilibrium constant, l/ (mol), k-rate constant, h^{-1} ; r-rate of reaction, $(mol/l)^2$/ h

The kinetic rate constant is estimated using the equation (4) and the values are given in Table 2.

$$k=\ln\left(\frac{1}{[1-\%DH]*t}\right) \quad \text{---------- (4)}$$

$$r= k\,[HTPB][H_2] \quad \text{……. (5)}$$

The kinetic rate constant (k) is proportional to the DH. The rate of reaction estimated for each reaction for N_2 atm, H_2 atm and H_2-air atm is 2.88 x 10^{-6}, 6.98x 10^{-5} and 10.6 x 10^{-5} $(mol/L)^2$ /h respectively.

Since air contains oxygen, therefore, the increase in DH from 73.5% under H_2 to 87.8% under H_2-air cannot be attributed solely to the effect of pressure alone. DH may involve the combined effects of H_2 partial pressure, total system pressure, and the presence of O_2. In particular, the hydrogenation rate is expected to depend primarily on the availability of molecular H_2 at the catalyst surface; therefore, the H_2 partial pressure, rather than total pressure alone, is an important parameter. The difference in DH is more appropriately discussed in terms of the changed gas composition and the possible influence of the small amount of O_2/N_2 introduced with air. Hence, the result as an experimental observation under a different gas composition and pressure condition,

with the increased DH potentially reflecting the combined influence of the changed H_2 partial pressure, total pressure, and O_2-containing atmosphere.

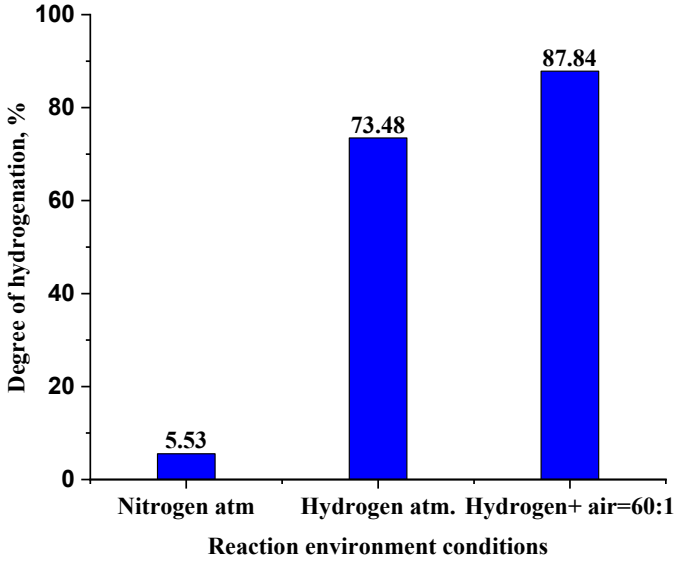

Figure 6. Influence of reaction environment on degree of hydrogenation

The present experiments were not specifically designed to independently determine the effect of O_2. A dedicated comparison at identical H_2 partial pressure and total pressure, with controlled O_2 concentrations, would be required to establish whether the increase in DH is directly associated with O_2. Therefore, the observed increase from 73.5% to 87.8% DH is reported as an experimental difference between the two gas atmospheres rather than being conclusively assigned to pressure or O_2 alone. H_2 gas is dissolved in the reactant mixture and reduced the pressure during reaction, whereas Nitrogen continues to be an inert in the system. This also might be caused an additional degree of hydrogenation during H_2-air environment and favoured the process further.

The functional isomers of geraniol, hexene-1-ol type were totally converted into vinyl-type after hydrogenation with both hydrogen and hydrogen-air environment conditions as illustrated in Figure 5(a) & 5 (b). Significant increase in degree of hydrogenation was noticed by including air in the system. The results are tabulated in Table 2. The degree of hydrogenation is illustrated in Figure 6.

3.2.2 FTIR analysis

The isomer conversion of HTPB followed the conversion in the order of vinyl > cis > trans whereas in N_2 atmosphere and H_2-air atmosphere the conversion followed vinyl > trans > cis. This could be due to the additional pressure exerted by nitrogen during the reaction made trans isomers to convert more than cis isomers. The FTIR spectra is given in Figure 7. The disappearance of isomers and the degree of hydrogenation had a close match. Hence both 1H-NMR and FTIR are considered as the useful tools for estimation of degree of hydrogenation.

However, we limited to 1H-NMR analysis as it more promising and qualitative and quantitative both.

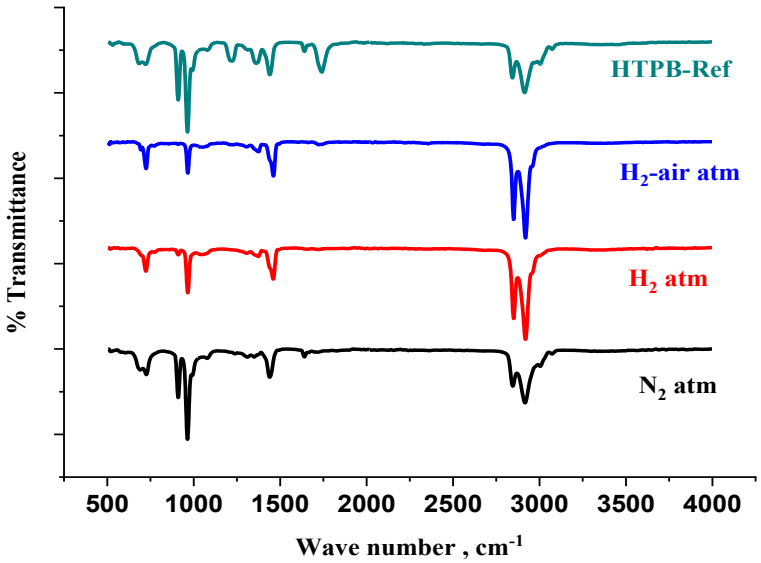

Figure 7. FTIR spectra of influence of reactor environment on degree of hydrogenation of HTPB

3.2.3 Thermal Characterization studies of HTPB and HHTPB

The decomposition behavior of HHTPB is studied using thermogravimetry- differential scanning calorimetry (TG-DSC) analyzer, wherein N_2 as inert gas carrier at a flow rate of 20 mL/min) for evaluating the thermal stability of HHTPB and compared with HTPB.

Table 3. Influence of reactor environment on HHTPB polymer thermal characteristics

Reactor environment	DTG peak, ^{0} C	T $_{10\ \%\ mass\ loss,}$ ^{0} C	Decomposition enthalpy, J/g	DSC 1st peak, ^{0} C	DSC 2nd peak, ^{0} C
HTPB	468	400	1662	372	449
N_2 atm	460	415	1569	373	447
H_2 atm	460	405	3957	405 (single peak)	
H_2-air atm	459	408	4068	401 (single peak)	

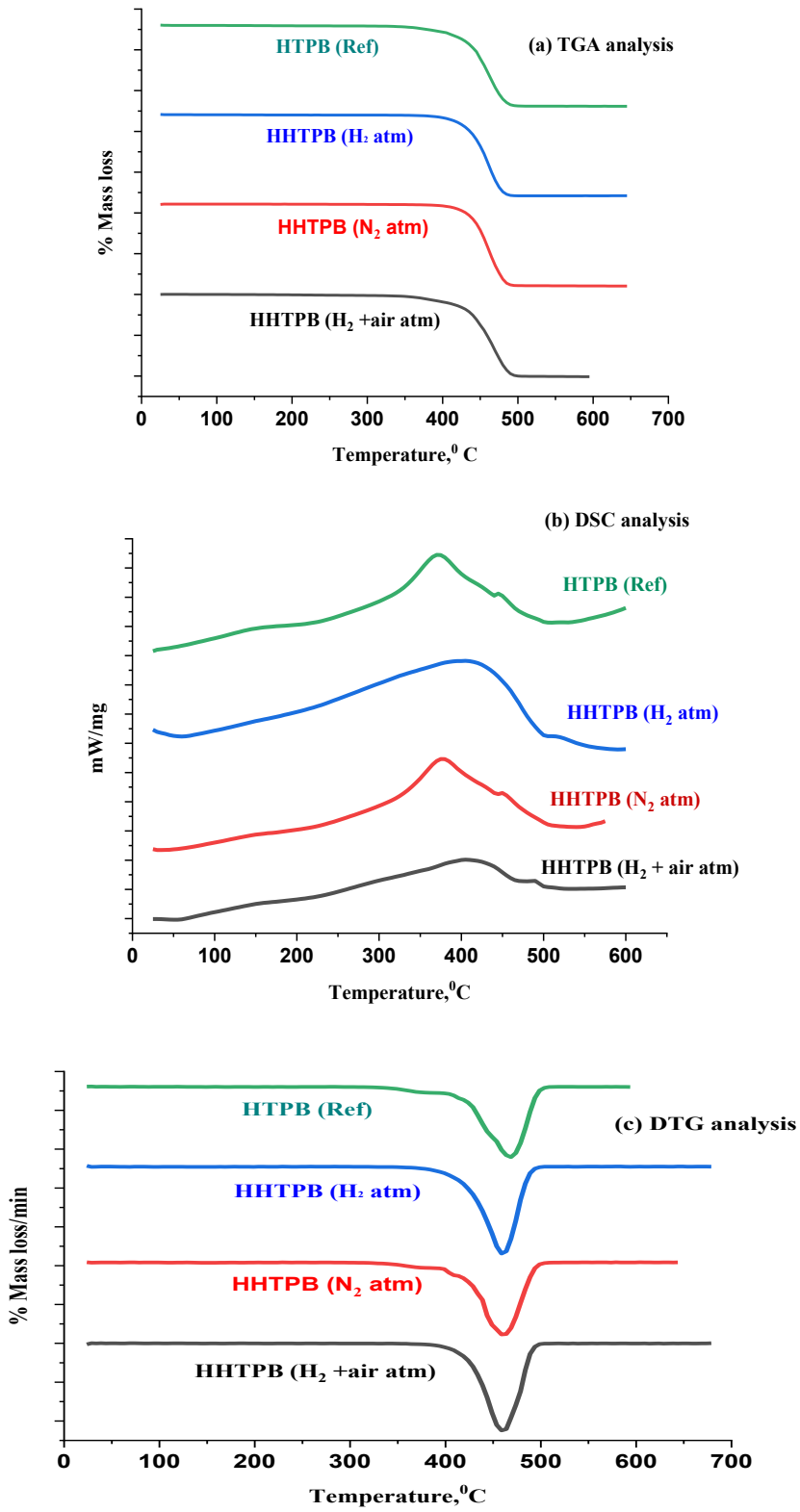

Figure 8. Influence of reactor environment on HHTPB polymer thermal characteristics (a) thermo-gravimetric (TGA) analysis (b) DSC analysis (c) DTG analysis

The samples were heated from room temperature to 600^0 C at a heating rate of 10^0C/min. The results indicated that the decomposition temperature of the HHTPB is comparable with HTPB, as

indicated in the TG-DTG graphs shown in Figures 8(a) and 8(c). However, a significant increase in $T_{10\ \%\ mass\ loss}$ was noticed for HHTPB in comparison to HTPB which showed that the thermal stability was marginally higher. Similarly, DSC was carried out under a nitrogen atmosphere at a heating rate of 10^0 C/ min up to 600^0 C, and it was observed that the decomposition enthalpy (which was derived from the area of the DSC peak) was relatively higher for HHTPB in comparison to HTPB as illustrated in Figure 8(b). The results are tabulated in Table 3. HTPB showed two major weight-loss stages. The first stage occurred due to de-polymerization, cyclization, cross-linking, and partial decomposition of the cyclized products, around 372 ^{0} C, and the primary gaseous products for the first stage were produced due to the volatilization of low molecular weight hydrocarbons such as 1,3-butadiene, cyclo-pentene, cyclo-hexadiene, etc. and the second stage occurred at around 449 ^{0}C, primarily due to the decomposition of the cyclized products whereas HHTPB showed single DSC peak at ~401^0 C which is comparatively higher than HTPB. After the hydrogenation of HTPB, the net increase in decomposition enthalpy (from the DSC peak area) indicated that the energy released from the formation of new bonds was greater than the energy absorbed for bond scission during the homolysis because of reduced double bonds in HHTPB.

Table 4. Influence of reactor environment on HHTPB polymer thermo-physical characteristics

Reactor environment	-OH value, mg KOH/g	M_n g/mol	M_w, g/mol	Poly-dispersity	T_g, ^{0}C	Intrinsic viscosity, dL/g
N_2 atm	40.4	5998	14349	2.39	-45.6	0.15
H_2 atm	40.9	7500	17320	2.31	-49.6	0.15
H_2-air atm	40.5	7540	16625	2.20	-49.0	0.16
HTPB(Ref)	40.8	6060	13400	2.20	-45	0.14-0.15

Mn- number average molecular weight; M_w- weight average molecular weight

The polymer characteristics of hydroxyl value, molecular weight, T_g and intrinsic viscosity details with respect to change in reactor environment are given in Table 4. GPC and structural characterization results indicate that no significant alteration of the polymer backbone was detected under the investigated hydrogenation conditions. However, a substantial change in the distribution of geometrical and functional isomers occurred in HHTPB with respect to the reaction environment. The hydroxyl values of HTPB and HHTPB are estimated using the acetylation method, the hydroxyl values remained broadly comparable after hydrogenation for the hydrogenated samples. The overall hydroxyl functionality was largely retained under the

investigated hydrogenation conditions. T_g is measured using DSC analysis, and observed that a marginal reduction after hydrogenation. The intrinsic viscosity is measured using toluene, is not changed after hydrogenation.

4. Conclusions

This research work is oriented towards a development of a synthesis process of hydrogenation process and studied the influence of process time and various reactor environmental conditions against the degree of hydrogenation for a given reactor volume using Pd-Zr-charcoal as a catalyst. It was reasoned out the changes in apparent rate constant with four different times and three environmental conditions i.e. nitrogen gas, H_2 gas and hydrogen-air environments. During the process of HHTPB formation, no significant change in hydroxyl value was observed and HHTPB formed with maximum content of vinyl-type functional isomers at a higher degree of hydrogenation. Observed characterization results are consistent with the preservation of the principal polymer structure, while minor structural modifications. A minor increase in molecular weight was observed with respect to the degree of hydrogenation. Various techniques like NMR, FTIR, and chemical analysis were used to estimate the degree of hydrogenation; Our findings also provide a useful guidance for the design of efficient and low-cost bi-metal catalyst for the selective hydrogenation of HTPB polymer. The experimental results showed that HHTPB degree of hydrogenation is ~87.5 % for the selected operating parameters and reactor volume with hydrogen-air environment. However, it yielded a waxy solid which is difficult to use in further applications. Hence, it is not recommended to allow air for hydrogenation. The degree of hydrogenation increased with reaction time up to 6 h, reaching 74.79%. A further increase in reaction time to 8 h resulted in a decrease in DH to 59.39%. This decrease indicates a lower measured hydrogenation level at prolonged reaction time. However, the present data do not allow the decrease to be conclusively assigned to dehydrogenation or reaction reversibility. Other factors, including catalyst deactivation, changes in H_2 availability, mass-transfer limitations, or possible structural changes in the polymer during prolonged reaction, may also contribute. Further controlled kinetic and thermodynamic experiments would be required to establish the mechanism responsible for the observed decrease. Catalytic transfer hydrogenation also happened in inert gas atmosphere such as N_2 environment to a smaller extent. Hence, it is recommended to use H_2 gas environment to achieve a desired degree of hydrogenation and the chosen process variables to achieve a desired degree of hydrogenation are 240^0 C, 6 Mpa as initial

H_2 pressure, HTPB: IPA: toluene ratio of 1:1:2, and 2 % catalyst with respect to HTPB using Pd-Zr-charcoal as a catalyst. HHTPB and HTPB were subjected to TG-DSC and found that HHTPB is thermally stable similar to HTPB. The reported increase in thermal stability is only marginal and GPC and structural characterization results indicate that no significant change in the polymer molecular-weight characteristics or major structural features was detected under the experimental conditions investigated. As the batch size is restricted to a small size of max. 20 g with the available reactor system, future scale-up studies to be taken-up for estimating the mechanical, rheological and ballistic properties using hydrogenated HTPB and to make a comparative assessment in detail.

5. Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper and Ethics, Consent to Participate, and Consent to Publish declarations and Ethics declarations are not applicable.

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8. References

1. P. Sutton, O. Biblarz,, Rocket Propulsion Elements, John Wiley & Sons, Inc., Seventh Edition, A Wiley-Interscience publication. New York: Wiley, 2001.
2. Abraham Tonson. Highly hydrogenated functional terminated conjugated diene polymers. US patent 5266,653 (1993).
3. Catalytic hydrogenation of hydroxyl-containing polyisoprene polymers using Ni-diatomaceous earth catalyst, Japanese Patent 62151404 (1987).
4. Catalytic hydrogenation of -OH-terminated polybutadiene polyol polymers using Raney Nickel catalyst, Japanese Patent 53026890 (1987).

5. C.H. Lira, L.F. Nicolini, M.C.B. Dolinsky, Determination of the hydrogenation degree of telechelic polybutadiene by ^{1}H -NMR. Magn. Reson. 5 (2006), 22-27.
6. J. Podesva, P. Holler, Hydrogenation of low-molar-mass, OH-telechelic polybutadienes-1: methods based on di-imide. Institute of macromolecular chemistry, Academy of sciences of the Czech Republic. J Appl. Polym. Sci. 74 (1999), 3203–3213.
7. J.Pradel, N. Pierre, L. Christoph, Method for hydrogenation of polymers in dispersed medium, US patent 7148292 (2006).
8. S. Gopala Krishnan, A. Kavitha, S.K. Nayak, Hydroxy terminated polybutadiene: chemical modifications and applications. J.Macromol. Sci. 50 (2013), 128–138.
9. S. Sabata, J. Hetflejs, Hydrogenation of low molar mass -OH telechelic polybutadienes catalyzed by homogeneous ziegler nickel catalysts. J. Appl. Polym. Sci. 85 (**2002)**, 1185–1193.
10. K. Scariah, V. Sekhar, M. Rama Rao, Thermal degradation behaviour of co-polyurethanes based on hydroxy terminated polybutadienes and its hydrogenated analogs: thermo-gravimetric and pyrolysis-GC studies. J.Eur. Polym. 30 (**1994)**, 925-931.
11. V.Sekkar, V.N. Krishnamurthy, Mechanical and swelling properties of co-polyurethanes based on hydroxy-terminated polybutadiene and its hydrogenated analog. Propellants Explos. Pyrotech. 22 (1997), 289-295.
12. N.K. Singha, S. Bhattacharjee, S. Sivaram, Hydrogenation of diene elastomers, their properties and applications: A critical review, Rubber Chem. Technol. 70 (1997), 309–367.
13. K.Bronstert, V. Ladenberger, G. Fahrbach, Catalytic hydrogenation of polymers containing double Bonds. US Patent 3673281 (1970).
14. Qian, Zhang.; Yuanjie, Shu.; Ning, Liu.; Xianming, Lu.; Yao, Shu.; Hongchang. Hydroxyl Terminated Polybutadiene: Chemical modification and application of these modifiers in propellants and explosives. J. Energ. Mater. 16 (2019), 153-193.
15. M. Chmielarek, Paweł, Maksimowski., Tomasz, Gołofit, Katarzyna, Cieślak, Wojciech, Pawłowski, Waldemar, Tomaszewski. Modification of HTPB (α, ω-dihydroxypolybutadiene) by esterification, silanization, epoxidation and hydrogenation. High energy materials. 12 (2020), 203-220.
16. Sartomer. Hydroxyl terminated polybutadiene resin and derivatives. Sartomer product bulletin, http://www.rimworld.com/nassarocketry/msds/HTPB(R-45M), (2012).

17. J. Zhanga, Chena. Yao, Jing, Tana, H. Sanga, The synthesis of rhodium/carbon dots nanoparticles and its hydrogenation application, J.Appl. Surf. Sci. 11 (2016), 101-122.
18. Lakshmiprasad, Gurrala, M. Midhun Kumar, B. Shweta Sharma, Changyub Paek, Vinu, R. Selective production of C9 monomeric phenols via hydrogenolysis of lignin using Pd-(W/Zr/Mo oxides)-supported on biochar catalyst, Fuel. 308 (2022), 121818.
19. M. Midhun Kumar, Vallabh, Prabhudesai.; Ravikrishnan, Vinu. Lignin Depolymerization to Guaiacol and Vanillin Derivatives via Catalytic Transfer Hydrogenolysis using Pd-Lewis Metal Oxide Supported on Activated Carbon Catalysts, Molecular Catalysis, 549 (**2023)**, 113474.
20. Prine, N. Characterization and selection of hydroxyl-terminated characterization and selection of hydroxyl-terminated polybutadiene polymers for high-strain applications, Internal report, Univesity of Southern Mississippi. (2019).
21. CH. Devi vara Prasad, P.Kanaka Raju, Ravikrishnan, Vinu., Abhijit P Deshpande, The Impact of Different Catalysts on Heterogeneous Hydrogenation of Hydroxyl-Terminated Polybutadiene", Journal of Chemistry Select, Wiley-VCH GmbH publications, Research Article, doi.org/10.1002/slct.202401883, 9 (**2024),** 1-10.
22. CH. Devi vara Prasad, P.Kanaka Raju, Ravikrishnan, Vinu., Abhijit P Deshpande, Synthesis of HHTPB by partial hydrogenation of HTPB using copper chromite as a catalyst, Propellants, Explos., Pyrotech. 49(2024), 1-12, https://doi.org/10.1002/ prep.202300339.
23. CH. Devi vara Prasad, P.Kanaka Raju, Ravikrishnan, Vinu., Abhijit P Deshpande, Synthesis of propellant grade HHTPB by hydrogenation of HTPB using Pd-activated charcoal as catalyst, J. FirePhysChem, 2024, https://doi.org/10.1016/j.fpc.2024.05.001.
24. B. Orwat, R. Januszewski, M. Dutkiewicz, I. Kownacki, Efficient Transformation of Polybutadienes to Polyolefins: Systematic Studies on the Transition Metal-Catalyzed Hydrogenation of Synthetic Rubbers, Ind. Eng. Chem. Res.,62 (2023), 10309.
25. Sungyoung Yoon; Seulah Lee; and Jongbok Lee, Comprehensive Review on Post-Polymerization Modification of Hydroxyl-Terminated Polybutadiene (HTPB), Elastomers Compos. 59 (2024), 108-120.

Supplementary data