

Hydroxyl Terminated Natural Rubber (HTNR) as a Binder in Solid Rocket Propellant

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Abstract. Controlled degradation of deproteinized natural rubber by oxidative method using cobaltous leading to the formation of telechelic liquid natural rubber (TLNR) has been the subject of study in the current work. Hydroxyl-terminated natural rubber (HTNR) having number-average molecular weights (M_n) below $10,000 \text{ gmol}^{-1}$ were synthesized at temperatures 60°C using Cobalt bis(acetyl acetonate) (Co) in the presence of ethanol and Sodium borohydride. The HTNR were characterized structurally by using Fourier Transform Infrared (FTIR) and Gel Permeation Chromatography (GPC). From the FTIR and GPC analysis, one hour reaction showed the lowest M_n around 6691 gmol^{-1} comparable to Hydroxyl terminated polybutadiene (HTPB) which were 7708 gmol^{-1} . As the reaction time increases the M_n also increase up to 8 hours of reaction. FTIR indicated that the synthesized HTNR contained hydroxyl end groups. The study showed the optimum percentage of Cobalt bis(acetyl acetonate) is 5% which produce the lowest molecular weight. Next, the HTNR underwent crosslinking reaction with isophore diisocyanate (IPDI). Then, metal fuel (aluminium powder, Al), oxidizer (ammonium perchlorate, AP) and HTNR were mixed together and went through compression process to produce solid rocket propellant. Burning rate obtained from HTNR samples were 2.78 mms^{-1} which were equivalent to HTPB samples which is 2.94 mms^{-1} .

Introduction

About four decades ago, the development of methods for the production of TLNR was started. Essentially, oxidative chain scissions which involve controlled degradation of natural rubber (NR) backbone can be divided into two ways which are photochemical and chemical routes. Some methods that can be used to produce TLNRs have been developed and can be summarized that there are three main methods photochemical, redox, and oxidation at high pressure and temperature¹⁻⁵.

Telechelic liquid natural rubbers (TLNRs) are very useful in the synthesis of tailor made polymeric structures such as NR based elastomers, block segmented copolymers, NR based thermoplastics and interpenetrating networks⁶. Moreover, these liquid rubbers can also be used as a photocuring component and binders in rocket propellant. In recent years, productions of LNR more focus on tires, rubber gloves, wiring, tube and others.

Basically, the polymeric binders used in the propellant have been transformed starting with traditional polyvinyl chloride (PVC), to polybutadiene acrylic acid acrylonitrile terpolymer (PBAN), then carboxyl terminated polybutadiene (CTPB) and lastly come out with hydroxyl terminated polybutadiene (HTPB)⁷. Many previous researchers reported about the use of HTPB as a rubber binder. Maruizumi et al., (1988) in research entitled development of HTPB binder for solid propellant reported the production of HTPB by free radical polymerization⁸. Then, they examined the characteristic of produced HTPB by studying the performance of the propellant. Muthiah et al., (1993) studied on the rheology of HTPB propellant and examined the effect of mixing speed and mixing time⁹.

HTNR have been used as a rubber based binder for development of fuel rich propellant as reported by Thomas et al., (1992)¹⁰. Moreover, hydrocarbon-based composite solid propellant binders have an advantage due to the potential for mass production (lower the cost of manufacturing material). They reported HTNR have an advantage over HTPB in their highest H/C ratio which are 1.6 and 1.5 respectively and lowest decomposition temperature (initial 250 and 350°C and peak 390 and 485°C respectively)¹⁰. Therefore, it is commercially and strategically attractive to carry out an intensive research to work on the uses of HTNR and to explore new applications of NR.

The objective of this work is to synthesize HTNR with Mn value below 10 000 gmol⁻¹ by using oxidative degradation at 60°C and also study the effect of Cobalt percentage in the reaction. The best formulation was applied to produce HTNR as binder for solid propellant that comparable to HTPB binder solid propellant.

Experimental

Materials. The main material used in this study is DPNR, supplied by Malaysian Rubber Board (MRB) (Selangor, Malaysia). The materials were stored and experimented at Propulsion Laboratory, Faculty of Mechanical Engineering, UTM.

Synthesis of HTNR. All solution of DPNR in toluene employed in this work had concentrations of 1% w/v. 90 ml of the DPNR solution was stirred and 10 ml ethanol was added dropwisely followed by 1, 3, 5, 10% (w/v dry rubber content) Cobalt (II) acetyl acetonate to give a homogeneous solution. The solutions were heated in a thermostat water bath shaker at 60°C and 150 rpm. At every one, two, five, and eight hours the respective solution were withdrawn. After reaction, the sample solutions were cooled down to 25°C meanwhile 50% (v/v) aqueous alcohols was prepared. Then, Sodium borohydride solution was prepared by stirring 100 ml aqueous ethanol with 2.6g Sodium borohydride. As soon as the sample solution reached 25°C, Sodium borohydride solution was dropped slowly while stirring the sample solutions. Then, sample solutions were heated and maintained at 52°C for two hours reaction. After two hours, the solutions were left overnight at room temperature. Next, 10% v/v sulphuric acid solution was prepared by adding 10.53 ml sulphuric acid and 89.47 ml distilled water to remove unreacted Sodium borohydride. The sample solutions were washed with acid solution followed by washing with distilled water three times to remove residual sulphuric acid. Then, the sample solutions were dried overnight with anhydrous Magnesium sulphate to remove residual water. The solutions were recovered by rotary evaporator model IKA RV-10 at 60°C and 140 rpm to give viscous liquids. This viscous liquid called HTNR were used in making the propellant.

Material Characterization. The molecular weight and molecular weight distribution of DPNR and HTNR were investigated by Gel Permeation Chromatography (GPC, model Waters 1500 Series HPLC Pump) manual injector with refractive index detector model Waters 2410. The column was calibrated using the polystyrene standards. The solvent flow rate is 1 ml per minute and chloroform as a mobile phase. Molecular structure was analysed by Fourier Transform Infrared (FTIR, Perkin Elmer spectrum 2000) by using a thin film on a KBR cell.

Preparation of solid rocket propellant. Preparation was started with mixing the samples with IPDI using a glass stirring rod in an agitating and swirling motion until the mixture become homogeneous. Next, Al powder were added and stirred together until all Al were coated with the binder. Then AP was added to get the propellant mixture. The same procedure was applied to HTPB samples following the desired formulation.

Burning rate measurement. The burning rate measurement was carried out with a strand burner. The propellant strand was fixed vertically into the head of a modified 5mm low carbon steel nut acting as the strand holder. Wire technique was used to measure the burning rate.

Results and Discussion

Characterization of HTNR.

Number average molecular weight (Mn) was determined for DPNR, HTPB and HTNR at different degradation time and percentage (%) of Cobalt. Table 1 gives the number and weight average molecular weights also polydispersity indices (PDI, Mw/Mn) of the samples. There was a drastically decreased of Mn in the first hour of reaction and then increased gradually over the 8 hours reaction. It can be clearly seen as shown in Figure 1. From the graph, the same trend was showed for different % Co used. These values suggested that at one hour of reaction with 5% Co used gives the lowest Mn, at 6691 gmol^{-1} . For 10% Co used the Mn decreased rapidly after one hour reaction and then increased more progressively compared to 1, 3 and 5% Co. It concludes that 5% Co used is the optimum value for this reaction to achieve the lowest molecular weight of HTNR. The addition of metallic catalyst (Cobalt (II) acetyl acetonate) has been reported that from 1-5% by weight is the best amount to work on¹¹. If below the specified range the rate of air oxidation is too low and not practical whereas if exceed the range, it causes difficulties such as catalyst removal after the reaction. In this research, the lowest molecular weight and comparable to HTPB has been chosen for the next reaction. HTNR yielded from one hour reaction using 5% Co with Mn=6691 (PDI=4.12) were found to be chosen which comparable with HTPB with 7708 (PDI=3.23). The molecular weight distribution values for HTNR showed a relatively large dispersion range compared to HTPB. The GPC chromatograms of the samples given in Figure 2, 3 and 4 showed clearly behavior of the samples. As retention time increased, the molecular weight of the sample decreased.

Table 1: Molecular weights of DPNR, HTPB and HTNR samples

%Co	Time (h)	Mn	Mw	PDI
DPNR	0	244951	802335	3.28
HTPB		7708	24922	3.23
1% Co	1	10449	80714	7.72
	2	15350	86630	5.64
	5	21905	95471	4.36
3% Co	1	8650	56251	6.50
	2	11349	78607	6.93
5% Co	5	10520	55754	5.30
	8	11009	71434	6.49
	1	6691	27560	4.12
	2	8033	76792	9.56
10% Co	5	9816	55270	5.63
	8	9983	50727	5.08
	1	11381	70290	6.18
	2	11880	89287	7.52
5% Co	5	29214	75541	2.59
	8	35434	84444	2.38

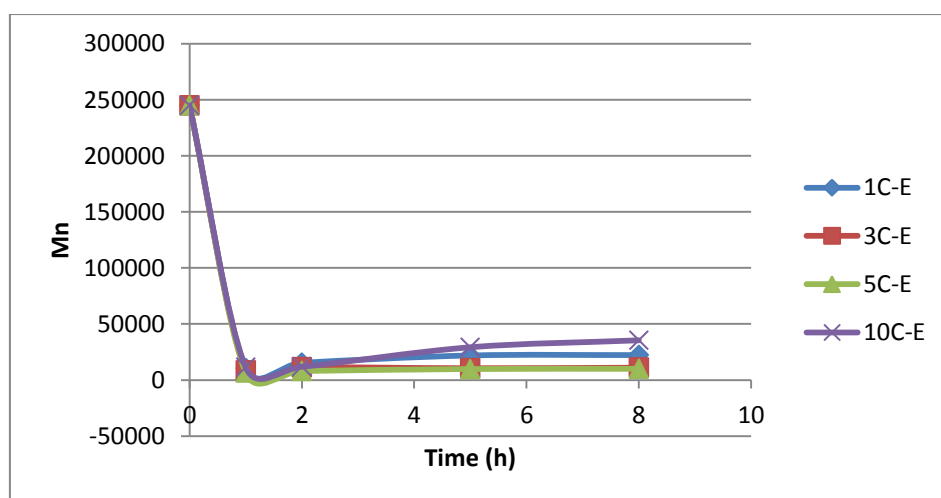


Figure 1: Effect of reaction time on Mn for oxidative degradation of DPNR (60°C) using 1, 3, 5 and 10% Co in ethanol

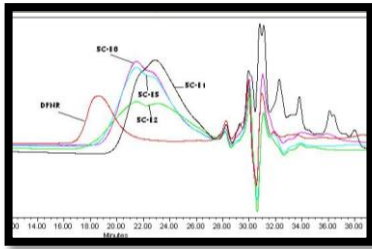


Figure 2: GPC chromatogram of DPNR and HTNR using 5% Co at various reaction times

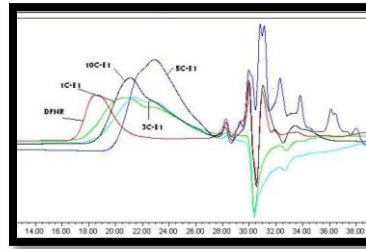


Figure 3: GPC chromatogram of DPNR and HTNR using various percentages Co (1%, 3%, 5%, and 10%) at 1 hour reaction

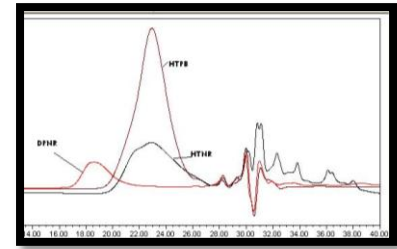


Figure 4: GPC chromatogram of DPNR, HTPB and HTNR using 5% Co at 1h reaction

The HTNR yielded was yellow, viscous liquid. Figure 5 shows the combination FTIR spectra of DPNR and HTNR at various reaction times with 1% Co. The same figure with different percentage Cobalt bis(acetyl acetonate) (3%, 5% and 10%) shows in Figure 6, 7 and 8 respectively. The existence of absorption bands at 3400 cm^{-1} and 1720 cm^{-1} indicates the hydroxyl and carbonyl groups on the HTNR chain after the reaction with reduction agent, Sodium borohydride. From the graphs, generally at 1 hour reaction the intensities peak of hydroxyl and carbonyl groups is the highest compared to the following 2, 5 and 8 hours reaction. This result proves the previous data from GPC which was the lowest molecular weight has the highest hydroxyl group in the HTNR chain. As the DPNR underwent oxidative degradation reaction, the chain scission occurred and followed by hydroxylation process.

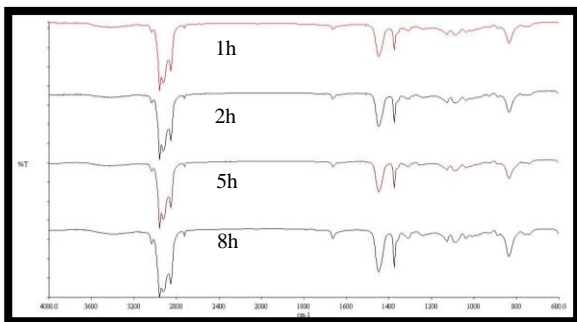


Figure 5: IR spectra of HTNR using 1% Co at various reaction times

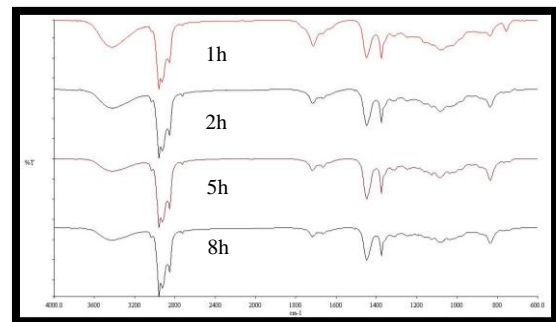


Figure 7: IR spectra of HTNR using 5% Co at various reaction times

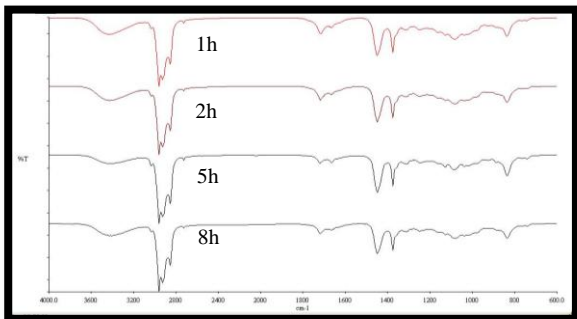


Figure 6: IR spectra of HTNR using 3% Co at various reaction times

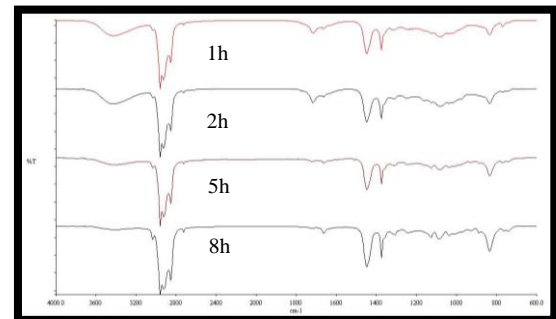


Figure 8: IR spectra of HTNR using 10% Co at various reaction times

Burning rate test.

The burning rate of propellant strand from HTPB samples and HTNR samples was measured at 1 atm, and was calculated with the cut-off period of the two fuses wire separated at a distance of 50mm. Burning rate were calculated as $r = L_p/t_b$ where, L_p = Specific propellant length, (mm) and t_b

= Burning time from recorded data, (sec). Average burning rate were calculated using at least 4 samples of propellant. HTPB give slightly highest than HTNR which is 2.95 mms^{-1} and 2.79 mms^{-1} respectively. It prove that HTNR can be used as a binder in solid propellant and comparable to HTPB.

Conclusion

A new route of reaction has been developed in synthesizing HTNR by oxidative degradation reaction of DPNR. HTNR obtained was used as binder in rocket propellant and comparable to HTPB where has been used worldwide.

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