

Effect of Various Alcohols and Reaction Time on the Properties of Hydroxyl Terminated Natural Rubber Synthesized via Oxidative Degradation

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The oxidative degradation of deproteinized natural rubber (DPNR) using cobalt bis(acetyl acetonate) in the presence of different alcohols and various reaction time; followed by reduction with sodium borohydride (NaBH₄) for the synthesis of hydroxyl terminated liquid natural rubbers (HTNRs) was carried out. The synthesis of HTNRs from natural rubber is particularly important as an alternative to hydroxyl terminated polybutadiene (HTPB); one of the current leading synthetic rubber for the production of rubber binders for composite solid propellants. Four different alcohols (i.e. methanol, ethanol, propanol and hexanol) were investigated in order to achieve degraded DPNR with lowest molecular weight. The structure of the obtained HTNRs were analysed using gel permeation chromatography (GPC) and fourier transform infrared (FTIR). Based on GPC analysis, it was found that the use of ethanol at 1 h reaction time resulted in lowest molecular weight of approximately 6,690 g/mol. Analysis of chain scission of the HTNRs were consistent with the molecular weight attained. FTIR analysis, on the other hand confirmed the presence of hydroxyl functional group in the synthesized HTNRs with the highest amount of hydroxyl group presence in the HTNR prepared using ethanol. Overall, the properties of synthesized HTNRs (molecular weight and functional groups) displays a potential material for the production of propellant binder and are comparable to the properties of commercially available HTPB.

1. Introduction

Natural rubber (NR) which obtained from *Hevea brasiliensis* tree is an important material in rubber industry due to its excellent properties i.e. high elasticity, high tensile strength and low heat build-up (Eng and Ong, 2001). Despite the increase in research on synthetic rubbers, natural rubber remains a practically irreplaceable material. The fact that NR comes from a renewable resource, coupled with the good properties signifies that it is an important elastomeric material especially for the production of tyre, latex products as well as engineering products which require high elasticity and flexibility. Despite its advantages, NR also displays some undesirable properties such as low heat and abrasion resistance, poor ageing property as well as low oil resistance. Thus, various researches comprising physical (Sionkowska, 2011) and chemical (Kenji et al., 2014) modification have been conducted in order to overcome these drawbacks.

Recently, the transformation of high molecular weight NR into low molecular weight liquid rubber *via* various process i.e. mastication, ozonolysis (Mohd Nor and Ebdon, 2000), oxidative degradation (Kargazadeh et al., 2015) or combination of physical and chemical degradation (Gupta et al., 1985) has gained significant interest. Compared to dried NR, liquid NR ($M_n < 20,000$ g/mol) with the presence of terminal reactive groups is an alternative way of converting NR into useful products as it is capable of undergo further chain extension or crosslinking. Liquid NR is particularly important for the synthesis of tailor made polymeric structures such as NR based elastomers, block segmented copolymers and NR based thermoplastics and interpenetrating networks (Mohd Nor and Ebdon, 1998). Unlike liquid synthetic rubbers, liquid NR is still not widely explored even though

the introduction of liquid NR was started in early 1970s. Bromine-terminated polybutadiene (BTBD), hydroxyterminated polybutadiene (HTBD), hydroxyl-terminated acrylonitrile-butadiene rubber (HTNBR) are among the commercially available liquid synthetic rubbers. To date, various functional groups have been investigated for liquid NR such as hydroxyl, carbonyl, amine, epoxy etc (Ibrahim et al., 2014). Functional groups are commonly generated at the NR chain end and the type of functional groups formed is determined by the method and reducing agent used in the reaction. Various reducing agents that are widely used for the insertion of reactive terminal groups in the liquid rubber are potassium persulphate, phenylhydrazine-ferrous chloride, periodic acid, sodium borohydride etc.

The work presented here aims to synthesize HTNRs from DPNR with the insertion of hydroxyl groups *via* oxidative method in the presence of cobalt bis (acetyl acetonate) (CAA) followed by reduction using sodium borohydride (NaBH_4). Four different alcohols as well as different reaction time (1, 2, 5 and 8 h) will be investigated during the synthesis in order to determine the condition that produce HTNR with low molecular weight ranging from 2,000 – 10,000 g/mol). Attaining HTNRs with low molecular weight (in this work; number average molecular weight (M_n)) is crucial to facilitate the addition of hydroxyl group in the structure. The presence of hydroxyl groups as reactive terminal groups will enable the prepared HTNRs to undergo further chain extension or crosslinking depending on their future applications.

2. Experiment

2.1 Preparation of Degradation of DPNR in the Presence of Alcohol

10 g of purified DPNR was dissolved in toluene (1 L) under stirring for 16 hours to give a rubber solution of 1 % (w/v). After that, 90 mL of the prepared rubber solution was placed into four bottles (for 1, 2, 5 and 8 h reaction) and 10 mL of methanol was added drop wisely into each of sample bottles, followed by addition of 5 % (w/v dry rubber content) of cobalt(II) acetyl acetonate to give a homogeneous solution. The four sets of solution prepared were heated in a thermostat water bath shaker at 60 °C with the shaking rate of 150 rpm. Each of the bottles was taken periodically from the thermostat water bath shaker at one, two, five and eight hours for the subsequent reaction. The same procedure was repeated using different alcohols (ethanol / propanol / hexanol) to give 16 sets of solution.

2.2 Production of HTNR in the Presence of Sodium Borohydride

50 % (v/v) aqueous methanol was prepared by diluting 50 mL methanol in 50 mL distilled water. Then, 2.6 g of sodium borohydride was added into 100 mL aqueous methanol prepared under stirring (Please note that four sets of this solution were prepared for 1, 2, 5 and 8 h reaction). The same procedure was repeated using different alcohols (ethanol / propanol / hexanol).

The samples (16 sets) prepared in Sec 2.1 were stirred vigorously at 700 rpm at 25 °C. Then, the prepared sodium borohydride solution was added drop wisely into the samples within 15 minutes according to the alcohols used. Subsequently, the solutions were heated at 52 °C for two hours and then were left overnight at room temperature.

Next, each of the samples were acidified using 100 mL of aqueous sulphuric acid (10 % v/v) to remove unreacted sodium borohydride followed by washing with distilled water (3 times) to remove residual sulphuric acid. Then the samples were dried overnight on anhydrous magnesium sulphate to remove residual water. The samples were then recovered using rotary evaporator model IKA RV-10 at 60 °C and speed of 140 rpm. An amount of methanol were added to the recovered samples (regardless of alcohol used) to give a precipitate of viscous liquids, termed as HTNRs. The prepared HTNRs (pale yellowish in color) were left in fume cupboard for 2 hours to remove excess methanol and subsequently stored in desiccator. GPC analysis will be conducted to determine the molecular weight of the prepared HTNRs while the presence of hydroxyl groups in the structure will be confirmed using FTIR analysis.

3. Result and Discussion

3.1 Determination of Molecular Weight and Chain Scission

Oxidative degradation reaction of DPNR was carried out in four different alcohols in order to investigate the most efficient alcohols for the reaction. The formulation for the oxidative degradation reaction of DPNR is shown in Table 1. The amount of CAA is fixed at 5 % as the preliminary result revealed with the increase of CAA (above 5 %), the molecular weight increased accordingly.

Table 1: Formulation for the synthesis of HTNR from using DPNR as starting material using 5 % CAA in the presence of different alcohols; ethanol, propanol, methanol and hexanol at 60 °C.

Solvents (10 ml)	CAA (wt % per dry rubber)	NaBH ₄ (g)	DPNR solution; ml (1 g rubber in 100 ml toluene)	Reaction time (hour)	Molecular weight (g/mol)	Chain scission
Methanol	5	2.6	90 ml	1	104, 000	1.35
Methanol	5	2.6	90 ml	2	119, 000	1.05
Methanol	5	2.6	90 ml	5	155, 000	0.58
Methanol	5	2.6	90 ml	8	185, 000	0.32
Ethanol	5	2.6	90 ml	1	6, 690	35.61
Ethanol	5	2.6	90 ml	2	8, 030	29.49
Ethanol	5	2.6	90 ml	5	9, 820	23.95
Ethanol	5	2.6	90 ml	8	9, 980	23.54
Propanol	5	2.6	90 ml	1	14, 000	16.55
Propanol	5	2.6	90 ml	2	17, 400	13.08
Propanol	5	2.6	90 ml	5	20, 800	10.79
Propanol	5	2.6	90 ml	8	93, 400	1.62
Hexanol	5	2.6	90 ml	1	*	*
Hexanol	5	2.6	90 ml	2	*	*
Hexanol	5	2.6	90 ml	5	*	*
Hexanol	5	2.6	90 ml	8	*	*

*No measurement available due to solubility problem

Based on Table 1, the use of ethanol in the reaction resulted in the lowest molecular weight at 1 hour reaction in comparison to other alcohols; methanol, propanol and hexanol. Increasing the reaction time to 2, 5 and 8 h led to the increase of molecular weight slightly to 8,030 g/mol, 9,820 g/mol and 9,980 g/mol, respectively. Similar trend was also observed for propanol whereby 1 h reaction gave molecular weight of 14,000 g/mol and increasing the reaction time again increase the molecular weight to 17,400, 20,800 and 93,400 g/mol. In the presence of methanol, the molecular weight attained at 1 h reaction was 104,000 g/mol, followed by 119,000, 155,000 and 185,000 g/mol for 2, 5 and 8 h. The molecular weight attained in the presence of methanol at all reaction times were too high as opposed to ethanol and propanol.

However, in the presence of hexanol, the separation of rubber part was not achieved due to the partial solubility of hexanol in water. It was observed that rubber, toluene and hexanol were in one phase while the other phase consisted of water. Comparing to other alcohols (methanol, ethanol and propanol) which completely dissolved in water, hexanol has highest number of carbon (six) and according to alcohol solubility chart as shown in Table 2; the higher the number of carbon, the lower the alcohol solubility. Thus the insolubility issues of hexanol in water explained the separation observed. Therefore, no further analysis will involve HTNRs sample prepared using hexanol.

It was observed that increasing the reaction time will increase the molecular weight and it is true for all alcohols used. The lowest molecular weight was achieved at 1 hour reaction and increasing the reaction time increase the molecular weight accordingly. The increase of the molecular weight at longer reaction time might due to the presence of aldol condensation (recombination) in the system. Similar observation was reported by Sadaka et al. (2012), during oxidative cleavage of carbonyl telechelic cis-1,4-oligoisoprene (CTNR) by periodic acid. However, in the case of ethanol, the recombination reaction occurred at much slower rate as opposed to propanol and methanol. According to Mohd Nor et al. (1998), during oxidative degradation involving ethanol, the formation of ketone and aldehyde (unstable terminal groups) is reduced as both terminal groups further react to form hemiacetal (ethoxy I and ethoxy II end groups) which later in the presence of sodium borohydride will be reduced to alcohols and become HTNR as shown in Figure 1. These hemiacetal groups which are more stable minimize the aldol condensation process. Similar observation was also reported by the same group in controlled ozonolysis of natural rubber in chloroform in the presence of ethanol to yield HTNR.

Another parameter, which can be used to examine the effectiveness of degradation reaction is chain scission. Chain scission is defined as the degradation of polymeric material. The higher the chain scission value, the shorter the chain. From Table 1, it can be seen that ethanol obtained the highest chain scission of 35.61 (at 1 h reaction), followed by propanol (16.55) and methanol (1.35) and this findings are consistent with the molecular weight values discussed earlier. Higher chain scission value observed indicated higher reactive sites presence in the structure.

Table 2: Solubility data of alcohols in water.

Alcohols	Solubility in water (g/L) at 20 °C
Methanol	Miscible
Ethanol	Miscible
<i>n</i> -Propanol	Miscible
<i>n</i> -butanol	77.00
<i>n</i> -pentanol	22.00
<i>n</i> -hexanol	5.9
<i>n</i> -heptanol	1.0
<i>n</i> -octanol	0.0

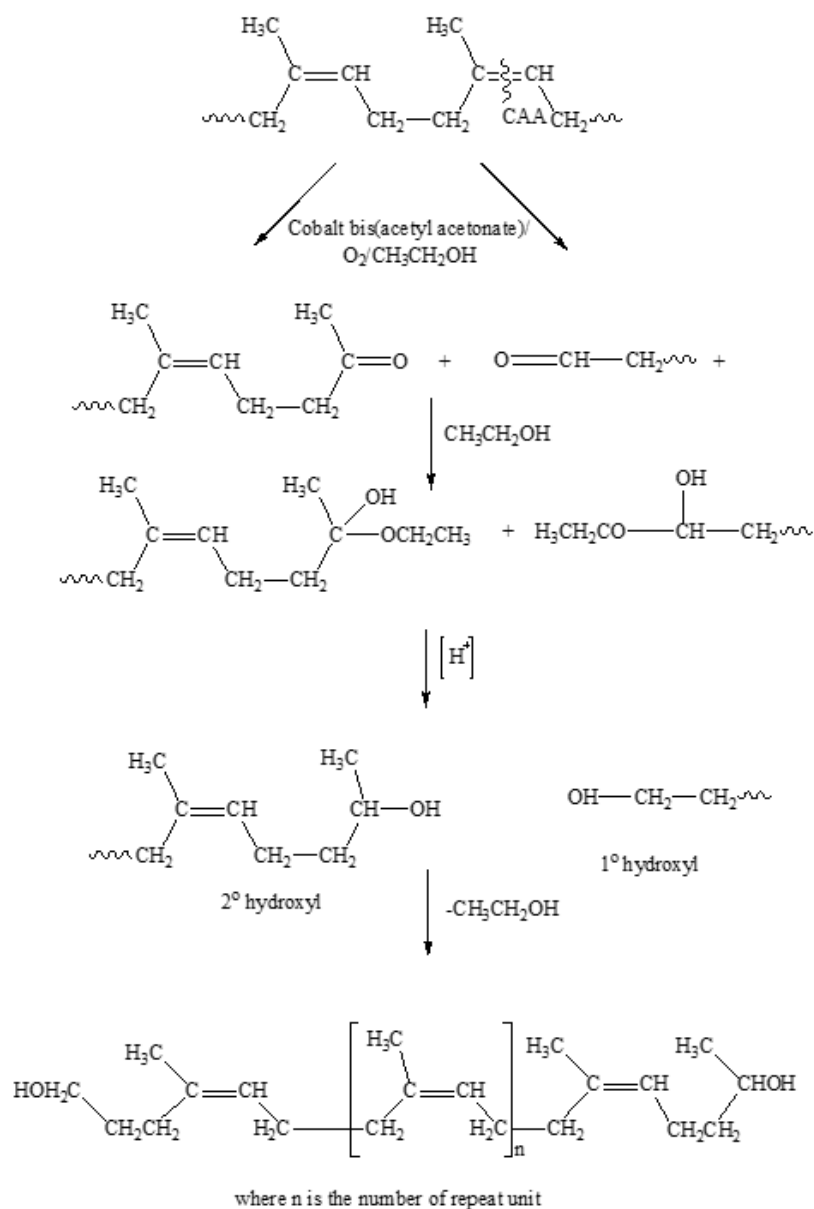


Figure 1: Proposed reaction mechanism of oxidative degradation of DPNR

3.2 FTIR Analysis

FTIR analysis was also conducted to examine the presence of hydroxyl groups for all HTRNs samples. Figure 2 shows the FTIR spectra of DPNR (starting material prior to oxidative degradation reaction) and HTNRs prepared in the presence of ethanol, propanol and methanol at 1 hour reaction (1 h is chosen due to lowest

molecular weight attained for all HTNRs). FTIR spectrum of DPNR (Figure 2 (a)) displays several peaks which represent the characteristics of natural rubber (Isa et al., 2007). The three significant peaks observed at $2,961\text{ cm}^{-1}$, $2,919\text{ cm}^{-1}$ and $2,855\text{ cm}^{-1}$ were attributed to the presence of C-H asymmetric stretching in CH_3 , C-H symmetric stretching in $-\text{CH}_2-$ and C-H symmetric stretching in $-\text{CH}_2-$ and CH_3 , respectively. Another peak observed at $1,664\text{ cm}^{-1}$ was assigned to $\text{C}=\text{C}$ stretching while two sharp peaks at $1,447\text{ cm}^{-1}$ and $1,376\text{ cm}^{-1}$ were assigned to C-H asymmetric bending in $-\text{CH}_2-$ and $-\text{CH}_3$, respectively.

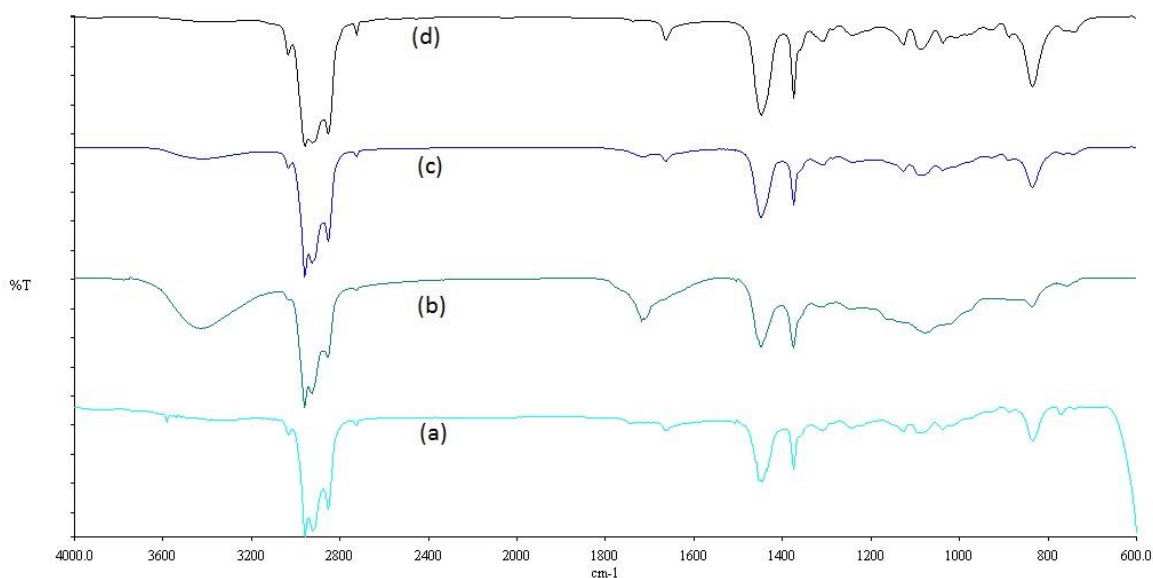


Figure 2: FTIR spectra of (a) DPNR (starting material prior to oxidative degradation reaction) and HTNRs prepared in the presence of (b) ethanol, (c) propanol and (d) methanol.

As for HTNRs samples, regardless of the alcohols used, the characteristics of DPNR as discussed above were still remained unchanged. After undergone oxidative degradation reaction, a few new peaks were observed. In the case of HTNR prepared in the presence of ethanol (Figure 2 (b)) a significant broad peak at $3,600 - 3,200\text{ cm}^{-1}$ which indicate a substantial amount of hydroxyl groups presence in the structure was observed. In addition, another sharp peaks at $1,124\text{ cm}^{-1}$, $1,092\text{ cm}^{-1}$ and $1,036\text{ cm}^{-1}$ were also detected. Those peaks were assigned to the C-OH stretching, C-O stretching primary alcohol and OH deflection in primary and secondary alcohol, respectively. Those newly formed peaks were possibly due to the reduction reaction from sodium borohydride. The same findings were observed by Yang et al. (2010) in the ozonolysis of butadiene rubber in the presence of ethanol. The significant amount of hydroxyl groups presence in HTNR prepared using ethanol might due to the lower molecular weight attained by the sample. At low molecular weight, the chain scission is dominant thus higher number of reactive sites in the chains will react with hydrogen from sodium borohydride to form hydroxyl groups at the terminal chains.

As for HTNR using propanol (Figure 2 (c)), similar peak at $3,600 - 3,200\text{ cm}^{-1}$ was also observed with slight lower in the intensity as opposed to HTNR with ethanol. In addition, another peak appeared at $1,721\text{ cm}^{-1}$ which attributed to characteristic of carbonyl group (aldehyde; $\text{C}=\text{O}$). Similar finding was reported by Ibrahim et al. (2014) whereby their group investigated the effect of pH on the formation of functional groups that occurred in liquid natural rubber prepared *via* oxidative degradation using hydrogen peroxide (H_2O_2) and sodium nitrite (NaNO_2). They found that LNR prepared in neutral and slightly alkaline media showed a small band at $1,721\text{ cm}^{-1}$ suggesting the presence of carbonyl groups. The presence of aldehyde group in the HTNR prepared in the presence of propanol confirmed by FTIR is consistent with the aldol reaction discussed in the previous section. HTNR prepared in the presence of methanol (Figure 2 (d)) on the other hand shows a small peak at the same region ($3,600 - 3,200\text{ cm}^{-1}$) indicating the presence of small amount of hydroxyl groups in the sample as opposed to HTNRs prepared using propanol and ethanol. This observation is as expected as the molecular weight attained by the sample was considerably high $\sim 104,000\text{ g/mol}$ (at 1 h). Higher molecular weight indicated lower chain scission which resulted in the less hydroxyl groups formed in the HTNR sample as less reactive sites presence.

4. Conclusions

It can be concluded that the use of ethanol in the oxidative degradation of DPNR at 1 hour reaction time has yielded the lowest molecular weight as compared to methanol and propanol. Regardless of the alcohols used, increasing the reaction time resulted in the increase of molecular weight and decreasing the chain scission of the prepared HTNRs. As discussed, this observation occurs probably due to the presence of aldol reaction (recombination) which occur significantly at higher reaction time. FTIR analysis, on the other hand shows the preservation of existing DPNR peaks for all HTNRs samples. A new peak which confirmed the presence of hydroxyl functional group was observed with the highest amount of hydroxyl groups occurrence in the HTNRs prepared in presence of ethanol. Hydroxyl group peak was also observed for HTNRs prepared using propanol and methanol. However the amount of hydroxyl groups were much lower as opposed to HTNR using ethanol. The presence of significant amount of hydroxyl groups observed in the ethanol is due to the lower molecular weight and higher chain scission which provide higher reactive sites for reaction. The formation of hydroxyl groups in the HTNRs structure is particularly essential to create rubber network which important for various applications such as tyre, smart materials, solid propellant and many more.

Acknowledgement

The authors would like to thank the Universiti Teknologi Malaysia (UTM) and Ministry of Education (MOE) in providing the research funds (Vote No. Q.J130000.2744.01K88 and Q.J130000.2746.02K29).

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