Full paper

Development of Solid Rocket Propellant based on Isophorone Diisocyanate – Hydroxyl Terminated Natural Rubber Binder

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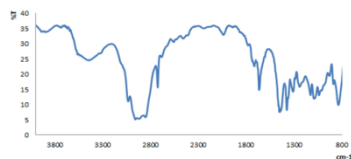
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Abstract

In this work, a novelty solid propellant based on Isophorone Diisocyanate (IPDI) with Hydroxyl Terminated Natural Rubber (HTNR) binder network was successfully developed. The preparation of Liquid Natural Rubber (LNR) by chemical degradation Deprotenized Natural Rubber (DPNR) using cobaltous was carried out. From the FTIR spectroscopy, a broad hydroxyl group peak at 3444cm^{-1} was obtained from HTNR. Rubber network depict a strong carbonyl group C=O at 1714cm^{-1} and amine group N-H at 3433cm^{-1}. NMR analysis also proves that there was hydroxyl group presence in the sample where broad peak at range 1-3 ppm and 3.5 ppm peak for -HOC$\underline{H}_2$CH$_2$CH$_2$-. Four different mol ratio of HTNR with IPDI was carried out to find the best formulation with good properties as propellant. Flory-Rehner equation depict that only slightly increasing occur with higher IPDI mol ratio but mixing with Ammonium Perchlorate (AP) and Aluminium Powder (AL) significantly improve the crosslink density. Melting point for HTNR is near to room temperature and it increase abruptly after crosslink with IPDI up to range of 148-150 °C. For all formulation, cross section morphology showed occurrence of porosity and brittle type of failure however HTNR has good contact with AL and AP. 2 : 1 molar ratio depict the best burning rate but the combustion characteristic shows less energy and spark compared to HTPB binder.

Keywords: HTNR; rubber network; propellant

■1.0 INTRODUCTION

Propellants can be defined as combustible materials which contain the oxygen needed for adiabatic combustion. It simply burns and does not generally detonate or explode. Propellants are used to impart motion to a projectile in guns, missiles, bullets as well as rockets and are termed as gun propellants or rocket propellants accordingly [1]. A rocket is a device that uses the expulsion of internally generated gases as a source of motive power. The gases used for propelling the rocket are generated by chemical reaction of rocket propellant with a mixture of fuel and oxidizer [2]. Rocket propellant is an explosive material that burns slowly in a controlled manner resulting in a large volume of hot gases [1]. Major ingredients for solid rocket propellant are binder, oxidizer and metallic fuel. Others ingredients such as plasticizer, bonding agent, catalyst and stabilizer are another options depends on the desired combustion characteristic to tailor the performance [3]. To behave as ideal solid rocket propellants, it must possess several properties such as a high specific impulse. In order to produce reliability performance, composites propellant must have dimensional stability as well as rubber like properties. Recently, rocket development already had been established and broadening all around the world. In 1898, the first theoretical idea to develop a rocket was started by Konstantin Tsiolkovsky from Russian and 15

years later he come out with the first liquid rocket propellant. On 1974, Japan started a development of an extruded double base propellant which was applied to the missile during World War II. Whereas India introduced their Nike-Apache Rocket in 1963. Another example is from Vikram Sarabhai Space centre, India where they successfully develop composites rocket propellants by using hydroxyterminated polybutadiene (HTPB) as binder and crystalline aluminium perchlorate plus with fine aluminium powder as oxidizer and metallic fuel [4]. Polyurethanes are a broad group of elastomers that may contain just one common element, a urethane linkage. The mechanical properties of such polyurethanes depend largely on the degree of crosslinking, which in turn is dependent on the NCO/OH ratio [5]. There are a number of solid rocket binders such as polyesters, epoxies, polysulphides, polyurethanes which have been reported as binders for composite propellants and plastic bonded explosives (PBXs). The most common binder systems in current years are polyurethane due to compatibility, shelf life stability, flexibility and reproducible mechanical properties to propellants [1, 6]. Energetic composites contain an elastomeric matrix to encapsulate the high energy solid particles. HTPB based PU is amongst the group of these elastomeric materials commonly used in thermosetting energetic composites [7]. Whereas HTNR based was only started by Ravindran *et al*. in 1985 [8]. The functional groups from HTNR

which is hydroxyl will undergo stoichiometric urethane reaction with isocyanates to form the polyurethane network which becomes a matrix for the metallic fuel and inorganic oxidizer ingredients and provides superior mechanical properties to the propellant [9]. Ingredient which is an oxidizing material for combustion process of solid rocket propellant is known as oxidizer. Example types of oxidizer are ammonium nitrate (AN), potassium nitrate (KNO_3), sodium nitrate ($NaNO_3$), potassium perchlorate ($KCIO_4$), ammonium perchlorate/ AP (NH_4 CIO_4) and lithium perchlorate ($LiCIO_4$) [10]. In this study, ammonium perchlorate (AP) will be used for oxidizing constituent of the PU composite propellants. AP is stable in room temperature and obtains in a white crystalline solid with chemical formula NH_4ClO_4 which is a compound of the perchloric acid and salt of ammonia. The combustion of AP used with HTPB binder propellants yields a hot flame, higher than that heat produce during the thermal decomposition of HTPB. This high temperature produces low molecular weight hydrocarbon species, e.g. acetylene (C_2H_2), as against to the higher molecular weight hydrocarbons associated with the decomposition of pure HTPB [11]. Metal fuel is the major ingredients in making solid propellant. It will enhance the rocket performance by increasing the combustion temperature [12]. Aluminium powder consists of around 5-25% of the propellant weight and act as metallic fuel and additives in energetic formulations to enhance the performance of the rocket propellant [13].

■2.0 EXPERIMENTAL

2.1 Materials

For synthesizing HTNR, the materials used were Deproteinized Natural Rubber (ESO) purified with solvent, Cobalt Acetyl Acetonate, Methanol and n-Hexane, Ethanol, Sodium Borohydride Glycerine and Sulphuric Acid. For the rubber network and propellant, Dibutyltin Dilaurate (DBTL) and Isophorone Diisocyanate (IPDI), Ammonium Perchlorate, Aluminium Powder and Toluene was used as received. For characterization, Deuterated chloroform was used for NMR, Chloroform was used for FTIR and Toluene was used for crosslink density test.

2.2 Synthesis of HTNR

DPNR was diluted with n-Hexane and purified with Methanol and dried until becoming clear color. 1% (w/v) rubber solution was prepared by using toluene and 0.5% cobalt acetonate as catalyst. Ethanol was drop wisely and stirred for one hour at 80 °C. Then, Sodium Borohydride solution was prepared by stirring aqeos ethanol with Sodium Borohydride. While stirring the liquid natural rubber solution Sodium Borohydride solution was drop slowly at 60 °C within 30 minutes. After two hours, the solution was left overnight at room temperature. HTNR was synthesized through hydroxylation process at Propellant Laboratory, UTM. The yields from the reaction were washed using one time sulphuric acid solution to remove excess sodium borohydride and deionise water for 4 times in separation funnel to remove excess sulphuric acid until the pH was 7. Samples were dried using magnesium sulphate anhydrous and left overnight to remove residual water. The sample was left at dark place in room temperature until it change into clear colour and filtered paper was used to remove residual magnesium sulphate anhydrous. Toluene was evaporated from the samples using rotational evaporator at 60°C in vacuum condition. HTNR was added in methanol for double purification and dried in vacuum desiccators at room temperature. FTIR and NMR test were done to measure the functionality of HTNR.

2.3 Preparation of Propellant Strands

IPDI as cross linker was added with HTNR with four different mole ratios 0.5:1, 1:1, 1.5:1 and 2:1 and were mix with 1% of DBTL. FTIR was used to characterize the reaction between IPDI and HTNR. Crosslink density test was carried out to prove the formation of rubber network. AP and AL were dried inside oven for 24 hours at 60°C to remove moisture. Before mixed with binder, it was filtered and added with toluene. The ingredients were mix homogenously by using stirring rod. Next, it was loaded and casted into the soda straws and cured for 14 days. Using needle, around 20 small holes was made to ensure the trapped air was removed out when applying compression force. The performance was tested out by Differential Scanning Calorimetry (DSC), Crosslink Density, Scanning Electron Microscopy (SEM) and Burning Test.

2.4 Testing and Characterization Procedures

2.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

The assessment was carried out according to ASTM E 1252 using Perkin Elmer Spectrum 2000 Explorer. The sample was placed on a potassium bromide (KBr) disk and dries under 100 watt lamps to remove any solvent. All samples were run with scan 16 times at a resolution of 5 cm^{-1} and the wavelength range is between 600-4000 cm^{-1}.

2.4.2 Nuclear Magnetic Resonance (NMR)

The instrument use is a NMR BRUKER AVNCE II 400 MHz Ultrashield. FT-NMR Spectrometer operating at strength 400 MHz was employed to measure proton ^1HNMR spectra of the samples. Samples were recorded from 5 hours solutions of 10% w/v concentration in deuterated chloroform. Measurement was made using a 5 mm probe PABBO BB-1H/D Z-GRD. Probe was used to hold the sample, transmit radio frequency signals which excite the sample and receive the emitted response.

2.4.3 Differential Scanning Calorimetry (DSC)

The test was carried out by using a differential scanning calorimeter (Mettler-Toledo 822). The samples were first heated at the rate of 10 ^{0}C minute from 50 ^{0}C to 200 ^{0}C. Then, the samples were cooled back from 200 ^{0}C to 50 ^{0}C at the rate of 10 ^{0}C/ min. DSC study was carried out according to ASTM D 3418-82 and calorimeter was calibrated with indium reference. Sample in size range of 8.0-12.0 mg was placed in a sealed aluminium pan and an empty aluminium pan was used as a reference. The DSC data was presented as heat flow against temperature plot.

2.4.4 Crosslink Density Test

Solvent swelling measurement was carried out to determine the number of crosslink per gram (moles crosslink/g). Sample was immersed in toluene for 72 hours at room temperature. The Flory-Rehner equation was used for determination of crosslinking density [14]:

$$-[\ln(1-\Phi_r)+\Phi_r+x1\Phi_r 2] = V_0 n / (\Phi_r 1/3 - \Phi_r/2)$$

Where:
n = Crosslink density or effective number of chains in a real network per unit volume or number of crosslink per gram (moles crosslink / g)
X_1= Flory Huggins polymer solvent interaction parameter of toluene solvent (0.391)
V_o = Molar volume of toluene solvent (106.2)

Φ_r = Volume fraction of polymer in a swollen mass and calculated by the expression:

$$\Phi_r = \frac{W_i\text{-}W_w}{(W_i\text{-}W_w) + [(W_s\text{-}W_i)/ \rho_s]}$$

Where:
W_i = Weight of dry rubber in air
W_s = Weight of the rubber sample in swollen
W_w= Weight of rubber immersed in water
ρ_s = Density of toluene ; 0.87 g/cm^3

In the case of composite propellant, the volume fraction of the filler is obtained from:

$$\Phi_f = \frac{(W_i\text{-}W_w) - W_i - a}{b\rho_f}$$

Where:
a = PHR of filler in the formulation (75.46)
b = Total weight of the compound (100)
ρ_f = Density of filler (2.9 g/cm^3 for Al and 1.95 g/cm^3 for AP)

2.4.5 Scanning Electron Microscopy (SEM)

Morphology of propellant cross section was observed by using scanning electron microscopy (SEM). All specimens were coated with platinum using auto fine coater before examination. The fracture surface was examined using SEM instrument JEOL JSM-6390LL Scanning Electron Microscopy. Magnification x5000, x200, x40 and electron beam with accelerating voltage of 5 kV was used.

2.4.6 Burning Rate

Wire technique was used to measure the burning rate. Three small holes were placed accurately along the strand length using a needle. An igniter and two fuse wires were passed through these holes and connected to a power supply and electronic timer respectively. The burning time was measured using an electronic timer. Burning rate was determined from the period it takes for both fuses separated at a distance of 50 mm apart to cut off. From the recorded timing, the burning rate was calculated by specific propellant length (mm) divided with burning time from recorded data (s).

■3.0 RESULTS AND DISCUSSION

DPNR is primarily cis-1,4-polyisoprene consisting of repeat units containing unsymmetrically substituted carbon-carbon double bonds. The assignment of IR peaks for NR occur at 2960 cm^{-1}, 2915cm^{-1}, 2853cm^{-1}, 1664cm^{-1}, 1447cm^{-1}, 1375cm^{-1}, and 834cm^{-1} [15]. According from Figure 1, the spectrum exhibit three new main peaks compared to that of NR such as at 3300-3600 cm^{-1}, 1038 cm^{-1} and broader 1720-1660 cm^{-1}. Peak at 3444 cm^{-1} may arise from hydroperoxide (-OOH) or alcoholic hydroxyl (-OH). The broad peak in the region 3600 to 2300cm^{-1} reveals the presence of hydroxyl group OH in the HTNR. The second new major peak is a strong band at 1715 cm^{-1} which become broader and assigned to carbonyl groups. Thirdly is 1038 cm^{-1} which assign for C-O stretch. The double bond for HTNR still occurs at 1666 cm^{-1} and C-H aliphatic bond at peak 2960cm^{-1}. The peaks at 1127cm^{-1} (a shoulder) is normally indicative of C-O stretch 3600-3000 cm^{-1} which are the range of broad band that show the presence of hydroxyl groups in HTNR. Other small peaks at the range of 1309-930 cm^{-1} also show the presence of hydroxyl groups. The characteristics of natural rubber are still present in HTNR showed by the peaks of 2960, 2726, 1666, 1446, 1375 and 836 cm^{-1}.
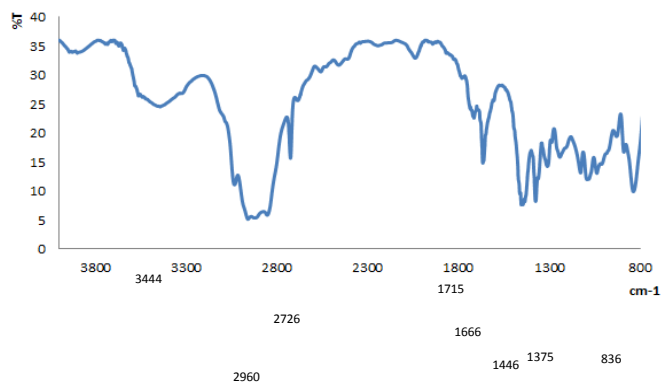

Figure 1 FTIR spectrum for HTNR

IPDI carried out NCO functionalities and the strong peaks occur at 2261 cm^{-1}. Also, at 3433 cm^{-1} broad N-H peak from amide group was observed. The peak at 2261 cm^{-1} (isocyanate) disappear and peak at 3444 cm^{-1} become broaden during the curing process at 50 ºC shows the reaction was occurred to form urethane -NCOH-linkage. New strong carbonyl C=O peak after crosslink process occur at 1710-1720 cm^{-1} has proved that HTNR has reacted with IPDI. From the rubber network Figure 2, after mixing the HTNR with IPDI, all the isocyanate at peak 2260 cm^{-1} had been reacted and excess N-H or remaining hydroxyl is still in PU system. It can be observed that absorbance at peak 2918 cm^{-1},
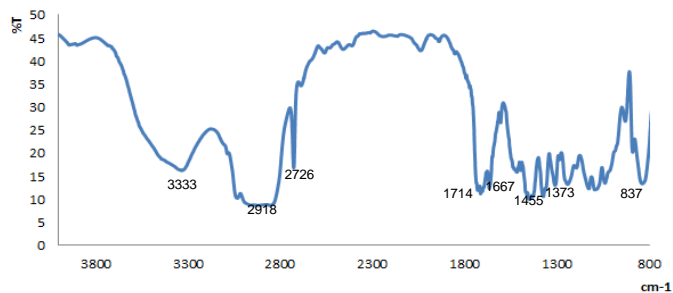

Figure 2 FTIR spectrum for rubber network (HTNR + IPDI at 2:1 mol ratio)

2726 cm^{-1}, 1714 cm^{-1}, 1667 cm^{-1}, 1455 cm^{-1}, and 1373 cm^{-1} which are the characteristics of NR elastomer is still present. N-H group modes were assigned at 3340-3300 cm^{-1} they appear at lower frequencies than those expected for the free amine group (3422 and 3318 cm^{-1}) due to the presence of the hydrogen bonds indeed observed in the crystalline package of these molecules. 2918 cm^{-1} depict band for C-H asymmetrical stretching CH$_2$. 1714 cm^{-1} shows the presence of carbonyl C=O group, 1446 cm^{-1} peak shows the CH$_2$ scissoring, 2855 cm^{-1} shows the CH$_2$ asymmetric stretch.
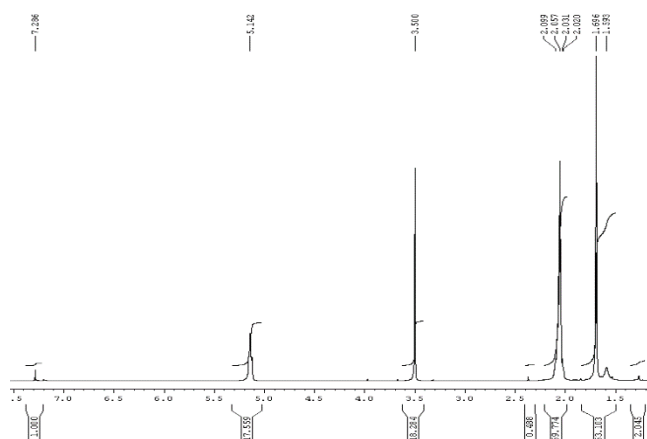
Figure 3 400 MHZ ^{1}HNMR for HTNR

The prediction structure ^{1}H chemical shifts are shown in Figure 4. It can be seen that the strong peaks in the ^{1}H NMR spectrum at 5.149 ppm, 2.064 ppm and 1.703 ppm which correspond to methane protonand methylene protons respectively.

Table 1 ^{1}H NMR of HTNR peak structure

Structure	δH (ppm)
-CH$_2$C(CH$_3$)C**H**CH$_2$-	5.149
-C**H**$_2$C(CH$_3$)CHCH$_2$-	2.064
-HOC**H**$_2$CH$_2$CH$_2$-	3.5
-CH$_2$C(C**H**$_3$)CHCH$_2$-	1.703

Table 1 and Figure 3 depicts the assignment of proton types for every peak. The resonances at 2.064 (H$_1$ and H$_4$), 1.703 (H$_3$) and 5.149 ppm (H$_2$) are characteristic of isoprene units. H$_1$ and H$_3$ indicate the presence of methylene protons. The methyl protons in the isoprene units (H$_3$) are confirmed by the peak at 1.703 ppm. H$_2$ at peak 5.149 ppm shows the presence of olefinic hydrogen. Peak 3.5 ppm depict the H attached to -HOC**H**$_2$CH$_2$CH$_2$- proved the occurrence of hydroxyl group. Besides, the range between 1-3 ppm exists as a broad peak which is the structure contain hydroxyl group mainly at broad peak between 1.5-1.8 ppm.
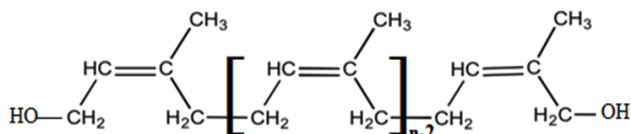

Figure 4 Expected HTNR structure where n is number of repeating unit

For DSC result, increasing of melting point from 35.7 °C which is before crosslink (HTNR) and after crosslink the melting increase up to range 148-150 °C was observed. It shows that equimolar amount of isocyanate and hydroxyl molecules were used to get maximum molecular weight leading to entanglements or physical crosslinking points so that physical interactions would prevent melting of urethane network. Even the HTNR networks prepared by reaction with different mol of IPDI show a similar melting behaviour. Substantial depression of the melting temperature with increasing amounts of crosslinking was observed for networks formed from randomly coiled chains irrespective of the method by which the crosslinks were introduced. It is also found that the melting temperatures of networks formed from

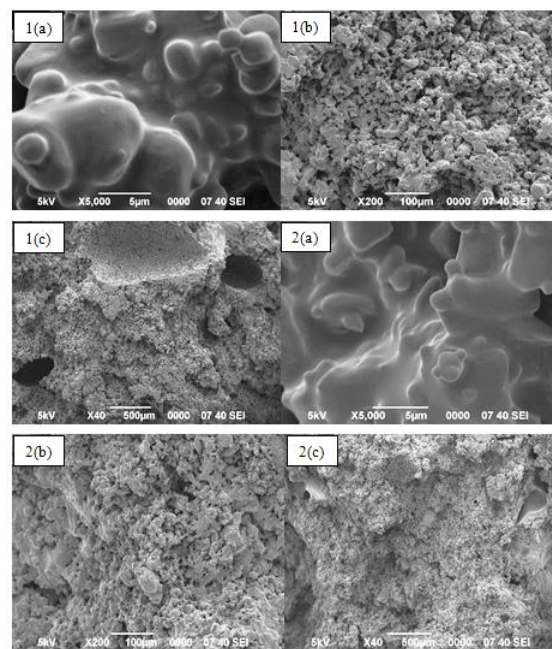highly ordered chains are substantially higher than those of corresponding networks formed from random chains.

Figure 5 Propellant cross section morphologies 1(a) 0.5:1 mol x 5000 magnifies, 1(b) 0.5:1 mol x 200 magnifies, 1(c) 0.5:1 mol x 40 magnifies, 2(a) 1:1 mol x 5000 magnifies, 2(b) 1:1 mol x 200 magnifies, 2(c) 1:1 mol x 40 magnifies

Morphology testing was further carried out to study the dispersion of powder and characteristic of the propellant. From Figure 5 and Figure 6, there is no differences observe by varies amount of crosslinker added. Micropicture of propellant cross section shows occurrences of pores significantly at magnificent x 200 for all formulations. The uniform micro pores are needed to have efficient burning where it needs more oxygen to react with carbon to produce fire. Propellant which has highly cellular structures will be easily ignitable and highly flammable. Flames can spreads very fast because it can diffuse into the propellant strands and provide a high burning rate. However the sizes of the pores and uniformity need to be control to produce uniform burning rate. At magnificent x 40, it figured that brittle failure has occurred at the cross instead of ductile failure. High filler loading is responsible for this brittleness. The big bubbles also occur and will lead to unhomogenizes combustion. However, the dispersion and distribution was good since no agglomeration is found and all the powders were distributed well. It can be proving from the magnificent x 5000 where all powder has good interaction with the rubber matrix. The main future is it tackiness characteristics of the HTNR and the compatibility between the ingredients enhance the interaction between the filler.
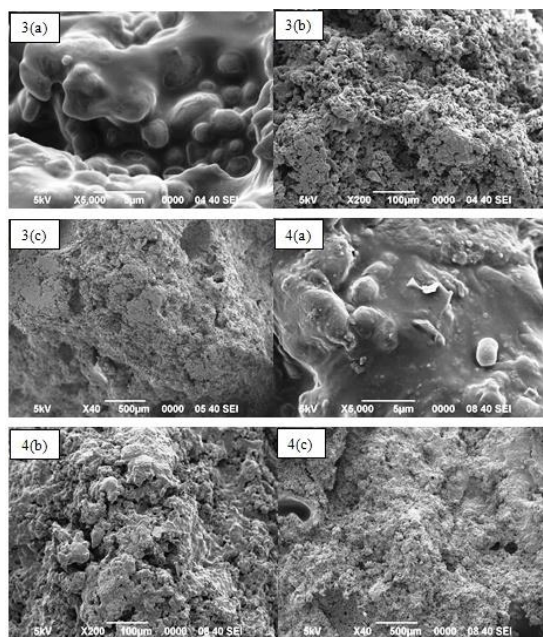
Figure 6 Propellant cross section morphologies 3(a) 1.5:1 mol x 5000 magnifies, 3(b) 1.5:1 mol x 200 magnifies, 3(c) 1.5:1 mol x 40 magnifies, 4(a) 2:1 mol x 5000 magnifies, 4(b) 2:1 mol x 200 magnifies and 4(c) 2:1 mol x 40 magnifies

Table 2 Volume fraction for rubber network (Φr), fiber fraction for propellant (Φf), crosslink density (n) for rubber network and propellant composite

Ratio	Φ_r (cm³)	Φ_f (cm³)	Rubber Network, (n)	Propellant Composite, (n)
0.5:1	0.207	0.582	1.567×10^{-4}	2.735×10^{-3}
1:1	0.214	0.542	1.690×10^{-4}	2.146×10^{-3}
1.5:1	0.294	0.602	3.817×10^{-4}	3.076×10^{-3}
2:1	0.288	0.612	3.467×10^{-4}	3.260×10^{-3}

As depicted in Table 2, crosslink density increase slightly by increasing mol ratio and powder ingredients. If the polarity and hydrogen bonding with rubber is near, it will easily mix and dissolve the rubber. Toluene is a strong solvent and has good dissolving power towards rubber. The compatibility between the ingredients and good interaction between binder and powder hold the constituents from dissolved by the toluene solvent. The amount of IPDI in polyurethane system could contribute higher density of crosslink when higher isocyanate is reacted to the hydroxyl in HTNR. Also the density of the powder is very high, where aluminium is 2.7 g/cm³ and ammonium perchlorate is 1.95 g/cm³ make it difficult to penetrate the highly pack structures of the sphere powders.

Table 3 Burning rate data for propellant

Sample	Burning rate (mm/s)
HTPB	4.04
0.5 : 1 mol	-
1 : 1 mol	4.54
1.5 : 1 mol	5.05
2 : 1 mol	5.23

From Table 3, the burning length is constant at 50 mm, only the speed of burning is different for every propellant. A good propellant must have high burning rate and high energy of combustion for a good repulsion. High combustion energy is needed to provide high specific impulse which is needed for a rocket to repulse. HTNR have its own strength where it can burn very fast compared to HTPB but the energy produce is low. 2 : 1 mol depict the fastest burning rate which is 5.23 sec. HTPB depict the slowest burning rate but provide a very high energy combustion with a shower of spark. Data for 0.5 : 1 show an error because there was only dark smoke was occur instead of flame therefore no result can be collected.

■4.0 CONCLUSION

The production of novelty HTNR binder was successfully carried out via chemical depolymerization of deprotenized natural rubber (DPNR). The high density of AP and AL, compatibility between the ingredients and good interaction between binder and powder hold the constituents from dissolved by the toluene. For melting temperature, it can be relate with crosslink density where more energy heat is needed to break the crosslinked chain compared to uncrosslink chain. Morphology study figured good dispersion and contact of AP and AL powder towards HTNR binder. Burning rate results prove the HTNR has better burning characteristic compared to current HTPB binder. Overall, formulation of IPDI-HTNR network which is 2 : 1 mol ratio depict the best characteristic as rubber network binder for the solid propellant. In conclusion, HTNR has a big potential in replacing imported binder which is HTPB. This research is a small step for Malaysia to be growing up as a best competitor in aerospace industries in the future.

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