

Non Energetic Binder Application for RDBP Propellant Based Large Caliber Munition (MKB)

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Abstract : Double base propellant (DB) to support high-speed rocket experienced problems DB propellant industry is not yet available in Indonesia. DB propellant material in Indonesia is propellant for large caliber munitions (MKB) that are different shapes and specifications. This research aims to convert large-caliber munitions (MKB) to a rocket RDBP propellant by reshaping and adding binders to MKB. RDBP propellant made by mixing MKB with a binding agent (binder), then casted to propellant RDBD with a diameter of 5mm. Propellant RDBP then measured the burning rate, specific impulse (Isp), and its mechanical properties. The research variables are the type of binder used (polyethylene, polyvinyl chloride) and its molecular weight. The results showed that the molecular weight binders positively effect on the mechanical properties of the propellant RDBP. Polyethylene (PE) and polyvinyl chloride (PVC) qualify as a binder (binder) to make RDBP propellant, wherein the propellant mechanical properties produced excellent (above 32 MPa), but RDBP propellant based PVC can not pass the ballistic requirement. The burning rate of RDBP propellant can reach a speed of 1.0 cm per second (above the threshold burning rate as required) by using the binder 5-10%.

Key Words: propellant, burning rate, mechanical properties, burning rate, double base

Nomenclature

| | |
|-------|----------------------------|
| x | : number of fractions |
| m | : molecular weight |
| Mn | : average molecular weight |
| cp | : heat capacity |
| dH | : enthalpy |
| TS | : tensile strength |
| E | : elongation |
| H | : hardness |
| g_o | : gravity acceleration |
| P | : pressure |
| a,n | : burning rate constant |
| r | : burning rate |
| Isp | : specific impulse |

Subscripts

| | |
|-----|------------|
| i | :component |
| A | :material |

1. Introduction

Development of double base propellant (DB) is required for the development of a rocket defense that require high speed and reduced smoke. DB propellant has a high burn rate advantages and smokeless. Development of a high-speed rocket in Indonesia have constraints unavailability of DB propellant industry or institution that can produce propellant DB. National defense industry has a propellant raw materials for large caliber munitions (MKB) which is actually a DB propellant but the specifications are different propellants with propellants for rockets^{1,2)}.

However, manufacturers of large caliber munitions (MKB) as PT PINDAD have DB propellant material which is ready to use commonly used for MKB stuffing materials in large quantities. The propellant material shaped pieces of thin and small (chips). Meanwhile, to the needs of the manufacturing rocket propellant required certain grain shaped according to the shape and size of the

rocket in question. Problems in the provision of DB propellant for rocket development can be completed if it can convert from MKB propellant into the rocket propellant^{2,3}. The problem that arises is how to form a propellant of different sizes and shapes, as well as maintaining a specification in order not to decrease. Under these conditions, the purpose of the research is desirable created DB propellant for rocket propellant MKB using existing or propellant called the RDB.

To accommodate the needs of DB propellant, a research manufacture rocket propellant using propellant RDBP for the MKB. RDBP desired propellant required to have excellent mechanical properties (tensile strength above 30 MPa), the burning rate is greater than or equal to 1.0 cm/sec, impulse kind of above 180 seconds. MKB Propellant from PT PINDAD has a burning rate of 1.5 cm/sec with specific impulse 190 seconds¹. The re-establishment of the propellant shaped propellant grain chips into other forms, can be done in several ways, namely by using a solvent or adding a binding agent (binder). The use of solvents to reshape the difficulties faced obstacles propellant to expel solvent trapped in the propellant solidified perfectly, so often the burning propellant experiencing intermittent combustion (chavung)^{1,4}. MKB Propellant can be converse to RDBP propellant using binder. The binder is suitable thermoplastic types, such as poly vinyl chloride, polyethylene, and others. DB propellant can be reshaped with a size and shape larger by the use of a binder thermoplastic. Thermoplastic materials that can be used are polyethylene (PE), polyvinylchloride (PVC) and others. Based on the characteristics of resistance to strong acids and softening point, the selected PE and PVC which allows processed with process temperatures below 120°C (critical temperature of RDBP propellant). By using a binder thermoplastic, it is expected that mechanical properties can be maintained as propellant DB expected. Binder used must also meet the requirements of high burn rate and great energy, therefore the selection of the binder becomes a key factor in getting a DB propellant that meets the requirements. Selection of binders must be flammable and have good mechanical properties. This research will develop a binder to make propellant RDBP of propellant MKB thus meeting the requirements for high-speed rocket propellants. The focus of research is the type of polymer used and the average molecular weight. Output of research are combustion energy, specific impulse, burn rate and mechanical properties.

2. Literature

2.1. DB propellant property

DB propellant is propellant with the main component of nitrocellulose and nitroglycerine. DB propellant has elastic properties such as thermoplastic, can be soft in hot conditions, soluble in acetone and squeezed back to dry. Tensile strength of 32MPa to 100 MPa. DB propellant known to have a high burn rate (1.0-1.5 cm per second) and burns reduced smoke. These properties are widely used for high-speed rocket as close and medium range missiles. DB propellant is good at least have good mechanical properties (greater than or equal to 32 MPa, has a glass transition temperature of less than -50°C), high burn rate (1.0-1.5 cm per second). DB propellant has specific impulse 180-190 seconds. DB propellant there are two types of its designation, the propellants for munitions and rockets. Propellants for munitions such as large caliber munitions (MKB) used for stuffing mortar, small spherical shape or flattened (chips). These propellants are usually coated with glazing and given additional graphite powder to stabilizer. DB propellant for both large caliber munitions has the form of a thin chips with a size of 1-2 mm and 0.1 mm thick. Propellants for rockets generally tubular shaped propellant grain with all sorts such as hollow, stars, and so forth. DB propellant is usually applied to military rockets that require high-speed rockets and reduced smoke⁴.

2.2. Energetic property

The most important characteristic of propellant is the propellant specific impulse (Isp), which shows the performance of an energy conversion machine. Isp propellant varies from 180-270 seconds in the normal combustion chamber pressure of 7 MPa (100 psi). high value of specific impulse indicated by the high isobaric combustion temperature and mostly combustion gases with a low molecular weight. A propellant combustion energy is the energy released when a propellant burning. Propellant combustion energy can be represented by a representative with the enthalpy of combustion (dH_C).

Enthalpy of combustion of the propellant constituent can be obtained from the data JANAF or the other not include for polymers. Enthalpy of combustion of polymers of different molecular weights can be approximated by using the group contribution theory developed by Gmehling and Wibowo, calculated based on the number and type of functional groups contained in the polymer^{2,5}.

To determine the temperature of combustion, heat of combustion, and specific impulse type of propellant it can be used a combination of theory of thermodynamics and thermochemical burning propellant. For the purposes of measurement of combustion is assumed to be ideal, occurs and adiabatic process conditions. In normal conditions, for a period of steady state combustion is achieved, then the pressure is relatively unchanged. The calculation is performed with steady state condition, the pressure out of the nozzle is considered equal to atmospheric pressure. If the propellant material is burned it will produce chemicals to combustion products of smaller molecular weight (m_i) by the number of fractions x_i . Heat of combustion (q) the adiabatic condition will be equal to the amount of the heat capacity of each component of combustion (cp_i) as shown in Eq. (1). In addition, heat of combustion will be equal in value to enthalpy at adiabatic combustion conditions, as shown in Eq. (2).

$$q = \sum m_i c_{p,i} dT \quad (1.)$$

$$q = dH \quad (2.)$$

Gas velocity is expressed by Eq. (3). Specific impulse of the propellant produced can be calculated from the formulation speed combustion gases exit the nozzle divided by the earth's gravity acceleration (g_o) as shown in Eq. (4), where $g_o = 980.665 \text{ cm}\cdot\text{sec}^{-2}$, H_i = individual gas enthalpy, J =mechanical equivalent of heat (426.64 gm/cal), m_i = the molecular weight of each component, P = pressure.

$$v_e = (2g_o J(dH))^{1/2} \quad (3.)$$

$$Isp = v_e / g_o \quad (4.)$$

2.3. The burning rate of propellant

The propellant burning rate (r) is defined as the burning rate in the axial direction of the propellant. The burning rate in the rocket system is a function of the combustion chamber pressure (P) as shown in Eq. (5) with a and n is the burning rate constant. For the purposes of testing without the use of rocket motors, burning of propellant (1 atm), so take the value of n is one^{4,6,14}.

$$r = ap^n \quad (5.)$$

Value a is the value characteristics of a propellant burn rate without being influenced by the model of the motor fuel and pressure. When used assumptions combustion is constant, only one directions, adiabatic, the burning rate of propellant is the reaction rate loss of propellant materials such (dn/dt) in units of cross-sectional area (A) as shown in Eq. (6), with a constant speed of reaction is k and the concentration is C . The rate of combustion reaction ($-r_A$) can be determined from existing data, while the value of the reaction rate constants will be comparable to the coefficient of polymer activity concerned. Activity coefficient values of different polymer molecular structure and length can be determined using the group contribution theory.

$$r = (-r_A) \cdot A = kC_A \quad (6.)$$

2.4. Mechanical Properties

A solid propellant must have a high flexibility in a wide operating temperature range. The cracks should be avoided during handling to reduce the occurrence of thermal cycling during storage or during combustion. In some cases, the deformation of grain cultivated there. In general, the mechanical properties represented by the value of tensile strength, elongation and hardness. Propellant must have good hardness and flexibility are balanced so that no cracks in the composite matrix. Crack will make the direction of combustion unfocused and cause an explosion. Therefore, the mechanical properties at the operating temperature of the rocket must be maintained. The mechanical properties of the propellant

is a combination of the properties of its components. In accordance with the law on composite mixing, the tensile strength (TS) of the composite is a combination of tensile strength of each component (TS_i) as shown in Eq. (7).

$$TS = \sum x_i TS_i \quad (7.)$$

3. Methodology

Materials used propellant is MKB propellant with the basic composition of nitroglycerine and nitrocellulose, produce by PT PINDAD. Propellant MKB has specifications : burn rate $1.5 \text{ cm}\cdot\text{sec}^{-1}$, specific impulse 190 second, tensile strength 42 MPa, has a deformation resistance to a temperature of -50°C , soluble in acetone. Binders used are PE and PVC with different average molecular weight. Anti-retardant material used is calcium powder (1%). Binder material that is used 4-12%. The ingredients are mixed, stirred in a vessel at temperature $60\text{-}120^\circ\text{C}$ (softening point of binder). The material is then molded into a mold grain shape of propellant. Standard grain shape is tubular (rod) with 5 mm diameter. The research variables are the type of polymer used and the average molecular weight. Mechanical properties (tensile strength and elongation) is determined with tensilemeter. Combustion temperature and specific impulse are determined numerically using propellant program¹⁾. Burning rate of propellant is determined base on kinetic combustion reaction where the data on the heat capacity of each polymer used Gmehling group contribution method²⁾.

4. Results and Discussion

Raw materials RDBP propellant is MKB propellant production PT PINDAD, form chips with size 1-2 mm as shown in Fig. 4.1. The resulting propellant is propellant with a grain size of 5mm with a solid tube is shown in Fig. 4.2. It turns propellant produced quite hard, it can be printed and formed according to the desired grain with a smooth surface. By using a binder PE and PVC, then with the propellant grain can be made tubular base on MKB propellant. Binder PVC requires temperatures above to melt, while PE requires temperatures above $70\text{-}90^\circ\text{C}$ to melt. Based on the characteristics of the softening point, the PE and PVC great as propellant binder RDB given the nature of the explosive propellant.



Fig. 4.1. MKB propellant



Fig. 4.2. RDBP propellant

In the manufacturing process, reaction temperature is follow the softening point of binder. For binder PE used in accordance $70\text{-}120^\circ\text{C}$, while the PVC has a softening point at 70°C ⁷⁾. Several other thermoplastic like polyisobuthylene, polyester and polypropylene have properties of good flexibility and strength, but has a high softening point (above 200°C) so harmful in the manufacturing process due to risk of explosion^{8,9)}. Polyethylene is soft, transparent and flexible, have impact strength and good tear strength. With heating will become soft and melts at $70\text{-}120^\circ\text{C}$. Polyethylene has properties: appearance varies, from transparent to cloudy, malleable, limp and easily drawn, southwest high range with no rips, resistant to acids, bases, alcohols and detergents, can be used to store the material at freezing temperatures up to -50°C , water-resistant and water vapor. Polyethylene in the market generally is LDPE (low density polyethylene) and HDPE (high density polyethylene). HDPE has a lower softening point, as well as other properties are higher than LDPE. LDPE is generally stronger than LDPE, but other properties similar to LDPE¹⁰⁾.

Polystyrene (PS) has a high permeability to water and gas. PS has general properties as follows: bending and not easily torn, a melting point of 88°C, will be softened at a temperature of 90-95°C, resistant to acids and bases, except oxidizing acids, will decompose with esters, ketones, aromatic hydrocarbons, chlorine and alcohol with a high concentration¹¹⁾. The nature of low resistance to oxidizing makes PS susceptible to propellant nitrocellulose and nitroglycerin because the material has a high acid content so that it can function as a strong oxidizing agent. Thus, the PS will not be durable to bind the propellant RDBP. PVC is resistant to oils and has a low permeability to water and gas. Other properties of PVC, namely: invisibility, although there also has a turbid surface, not easily torn and has a high tensile strength. This makes the nature of PVC is resistant to acids of nitrocellulose and nitroglycerin. Polypropylene is very similar to polyethylene and properties of its use are similar. Polypropylene is stronger and lighter with low vapor permeability, good resistance to grease, stable to high temperatures and quite shiny¹²⁾. However, soft temperatures above 150°C so it is not fit for use as a propellant binder RDBP. Polycarbonate (PC), are not suitable because although strong and heat-resistant and strong acids, but it will be decomposed by alkali, amines, ketones, esters aromatic hydrocarbons, and some alcohol. Nylon material does not qualify for the acid-soluble and is not impermeable to water or water vapor that can occur entrapment of water into the propellant. Methyl cellulose resistant to vegetable and animal oils, but this material when in direct contact with water will dissolve, the higher the temperature it will be more and more soluble. Cellulose acetate has the sensitive nature of the water, will decompose if strong acids, strong bases, alcohols and esters that are not suitable for propellant RDBP the very high acidity¹³⁾.

4.1. Mechanical Properties of RDBP Propellant

Mechanical properties testing of propellant RDBP base PE and PVC binder conducted to determine the characteristics of the mechanical properties of the binder. Binder PS is not used because of easy oxidation properties that will damage nitrocellulose and nitroglycerin because it decomposes into nitric acid or nitro gas. For the purposes of testing the mechanical properties of used PE and PVC with some average molecular weight. Testing of mechanical properties of propellant carried out by measuring the tensile strength, elongation and hardness of the RDBP propellant with binder material PE with a molecular weight of 10000, 50000, 100000, and 500000. PVC binder used for the molecular weight of 10000, 50000, and 100000.

The test results of mechanical properties such as tensile strength, elongation and hardness are shown respectively in fig. 4.1.1, 4.1.2, and 4.1.3. Based on test results shows that the tensile strength of PE binder, the higher the molecular weight PE, the tensile strength increases linearly. According to Flory polymer growth theory, the higher the molecular weight of the polymer, the longer the chain length and molecular size become larger, so that the hardness and tensile strength increases. Polymers such as PE will become increasingly powerful (tensile strength) and a hard line with the increase in molecular weight. This is a basic characteristic of the polymer. In the process of mixing the propellant, so if other components held constant, the mechanical properties of propellant is only affected by the binder alone^{1,2,14)}. If the binder component has a high tensile strength, then the system propellant mixture with other components remain, then the mechanical properties change depending on the type and amount of binder used. This follows the theory engaging in theory blending component and composite, in which the mechanical characteristics of a mixture of unreacted (TS) will be the total fraction of the component (x_i) the mechanical parameters of each components, as shown in Eq. (7). Thus, the higher the molecular weight of the polymer binder is used, the higher the stronger tensile and hardness, on the contrary will decrease this elongation. When following Eq. (7), then the change will follow the changes in the mechanical properties of polymer molecular weight linear manner. This can be shown in fig. 4.1.1, 4.1.2, and 4.1.3 wherein the polymer molecular weight change would provide propellant mechanical properties change linearly. The influence of linearly binder holds true also for PVC binder. Linear regression analysis of the influence of the molecular weight of the PVC binder obtained tensile strength $TS=1.1E-5M_n+31.671$, a linear regression against the influence of molecular weight binder obtained elongation $E=-2.2E-05M_n+31.671$, and linear regression influence of molecular weight binder obtained against violence $H=2.1E-05+31.671$. It is interesting to observe that the influence of PVC with PE on mechanical properties of propellant is almost the same approach. Based on its

mechanical properties, PVC has a strong tensile strength 25-40 MPa, while PE has a strong strong tensile 20-40 MPa. Thus, the strong mechanical characteristics of PE with PVC is adjacent.

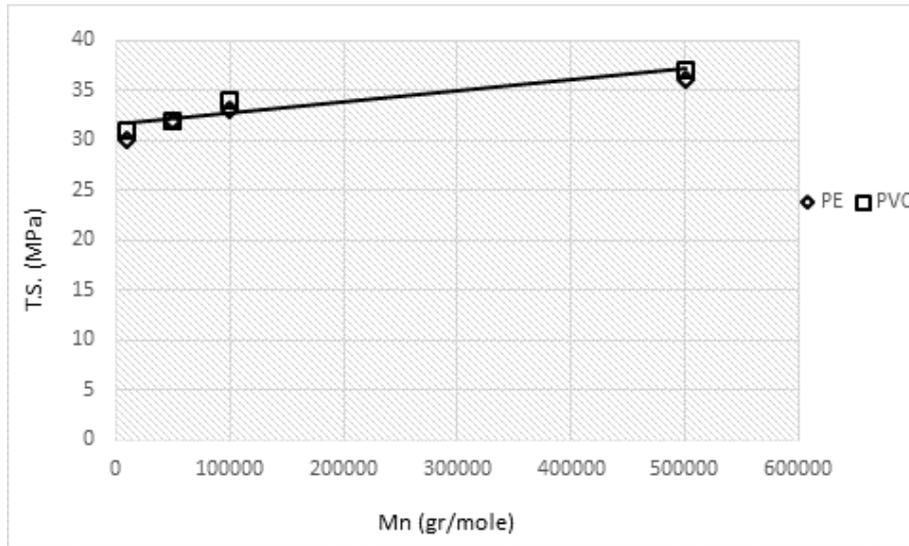


Fig. 4.1.1. Effect molecular weight to tensile strength of RDB propellant

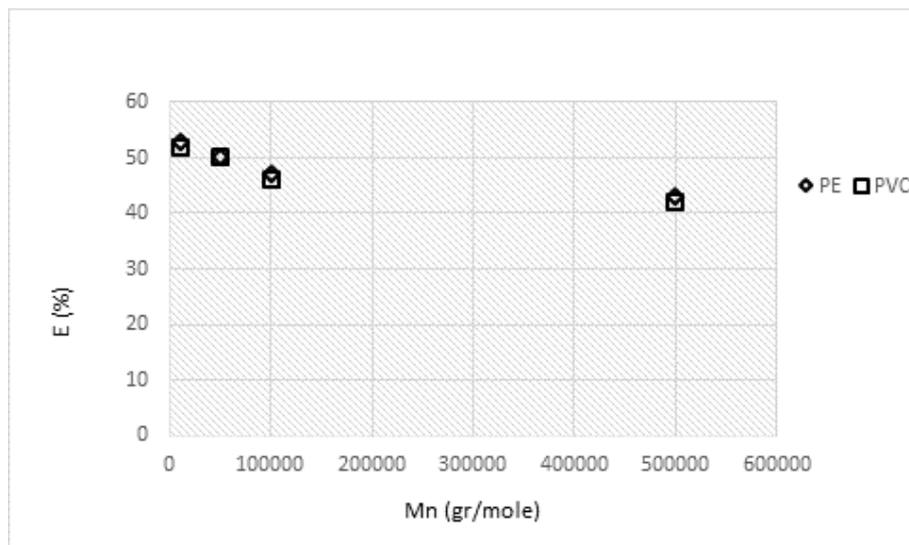


Fig. 4.1.2. Effect molecular weight of binder to propellant elongation

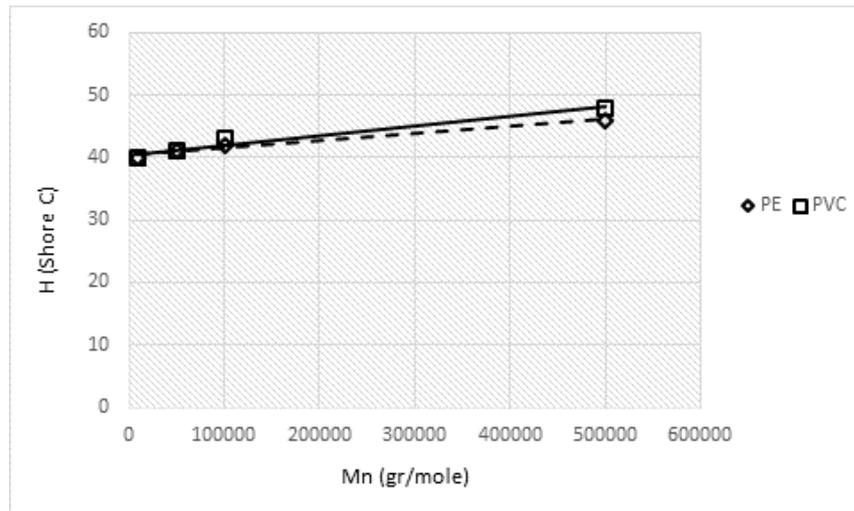


Fig. 4.1.3. Effect molecular weight to hardness of RDB propellant

Strong influence on mechanical propellant binder RDBP also studied using different binder compositions, i.e. in the range of 5-10%. Intake of these ranges for binder below 5% resulting mixture cannot be evenly distributed, while the binder composition above 10% make a lot of empty space that is not filled with propellant material. The observation is shown in Fig. 4.1.4, where the higher levels of binder, then strong mechanical (tensile strength) will increase. This value is consistent with the theory of unreacted polymer blending or composite, where the addition of a component that has higher mechanical strong will enhance the strong mechanical mixtures according to the Eq. (7). In accordance with the mixing theory of composite, then the strong rise tensile strength of propellant is linear with the concentration of binder used^{2,15}.

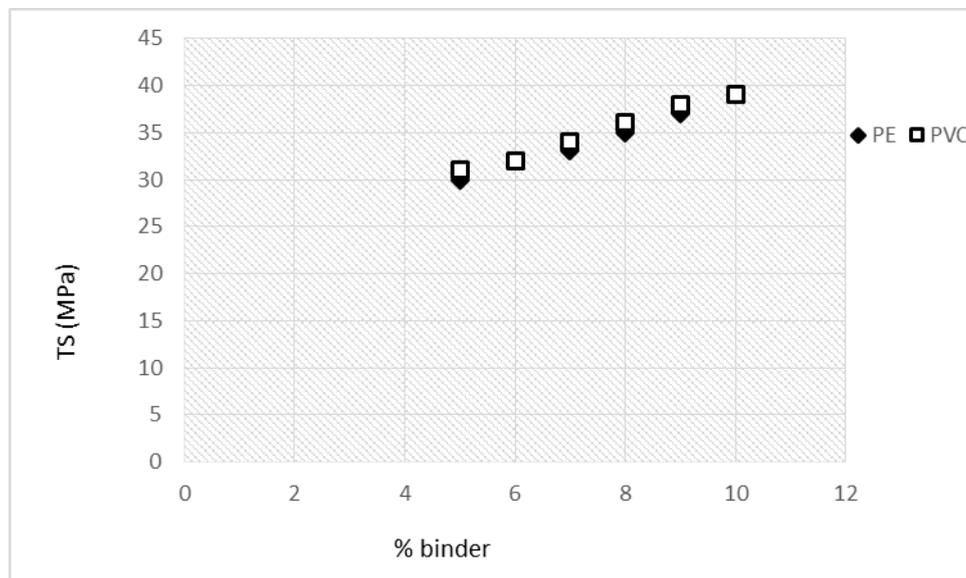


Fig. 4.1.4. Effect binder concentration to tensile strength of RDBP propellant

4.2. Ballistic properties of RDBP propellant

Characteristic ballistic properties include the temperature of combustion, combustion energy and specific impulse and determining the program was studied using the thermodynamic and thermochemical expressed in Eq. (1) - (6). The measurement results presented in table 4.2.1. Based on energy combustion, hence increasing the molecular weight of the binder lowers the combustion energy and specific impulse. In the theory of combustion, combustion is if a fuel-burning turned into

compounds which are the smallest in size so large combustion enthalpy. The smaller the size of the molecule, then chances are burned into components smaller size more. The use of polymers with a molecular weight of 10,000 provide combustion energy that is far greater than the use of polymers with a molecular weight of 50,000. By using Eq. (3), whose molecular weight used is the total molecular weight fractions of the components of combustion, it is seen that the more components of low molecular weight compounds will provide high-energy combustion. This is because the total compounds with low molecular weight gives much less gas enthalpy higher than compounds with a molecular weight greater. However, the rise of the combustion energy is not significant with the increase in molecular weight, and even tends to say negligible. This is because, although different in molecular weight or the size of the molecule, but the total chemical elements that make up one unit of weight does not very much. The increase combustion energy also experienced the impulse rise is small, between 185-190 seconds. These changes are not much different from the propellant MKB which has specific impulse just 190 seconds.

Table 4.2.1. Combustion characteristic of RDBP Propellant

| Molecular weight (Mn, gr/mole) | BINDER PE | | | BINDER PVC | | |
|-----------------------------------|--------------------------------|-------------------------------|--------------------------|----------------------------------|-------------------------------|--------------------------|
| | Combustion energy (kJ/mole) | Combustion temperature (K) | I _{sp} (sec) | Combustion energy (kcal/mole) | Combustion temperature (K) | I _{sp} (sec) |
| 10000 | 34 | 1700 | 187 | 34 | 1725 | 185 |
| 50000 | 34 | 1700 | 187 | 35 | 1730 | 185 |
| 100000 | 35 | 1725 | 188 | 36 | 1730 | 186 |
| 500000 | 37 | 1725 | 190 | 37 | 1730 | 189 |

With high energy combustion, the specific impulse will be high, as indicated that increased combustion energy will be followed by an increase in specific impulse. The influence of the molecular weight of the binder both PE and PVC against combustion energy and specific impulse are relatively small. Similarly, the combustion temperature, whereby the combustion temperature does not change significantly from the MKB propellant 1700 K, with the addition of binder did not change significantly.

4.3. Characteristics of the burning rate

Burn rate testing can be done by using a strain gauge burner. However, this tool cannot be used to measure the propellant is very short, so testing is done by using a conversion rate of the combustion reaction into the burning rate according to the Eq. (6). Value burning rate (r) in the atmospheric condition is equal to a, comparable to the rate of propellant combustion reaction divided by the cross sectional area of the propellant. Propellants, uses cross-sectional area is 1 cm², then the value of the rate of combustion is equal to the rate of the combustion reaction. Combustion reaction rate (r_A) can be predicted using the principle polymer combustion reaction rate prediction of Gmehling and Wibowo¹⁾. Testing the burning rate is used to determine whether the propellant burn quickly, so the rate of rocket becomes high, so that used for high-speed rocket. DB propellant has a high burn rate, namely 1.0 to 1.5 cm per second for a 15 to 40G acceleration. Meanwhile, the composite propellant fueled rockets can produce burning rate is low (0.5-0.8 cm per second at atmospheric conditions) making it suitable for large-size rocket. RDBP propellant testing results shown in table 4.3.1. Table 4.3.1, it appeared that the propellant burn rate does not go down significantly, meaning that with the addition of binders

PE as much as 5%, then there is no significant decrease in the rate of fuel which is only down about 2%. If the MKB propellant has a burning rate of 1.2 centimeters per second RDBP propellant then using PE binder produces burning rate of 1.1 cm per second. On the use of binders of 10% will reduce the burning rate into 1 cm per second. Thus the use of binder threshold recommended is a maximum of 10%, but effective at levels of 5%.

A significant change occurred in using PVC binder, wherein the binder usage by 5% will decrease the burning rate to 7.5%. By using PVC binder 5%, then the RDBP propellant burn rate be less than 1.0 cm per second so it does not qualify as high-speed propellant. The different outcomes resulting polyethylene easier to decompose during the burning gases into small propellant burn at a temperature (1700K) than PVC. Binder PVC despite having good mechanical properties, but has a burn rate that is lower than the PE so cannot be used as a binder for RDBP propellant. RDBP propellant at a binder concentration of 5% is the best because it meets all the elements of the characteristics required for high-speed propellant.

Table 4.3.1. Burning rate of RDBP propellant with binder 5%

| M _n | Burning rate (cm/sec) | |
|----------------|-----------------------|------------|
| | Binder PE | Binder PVC |
| 10000 | 1,2 | 1,0 |
| 50000 | 1,1 | 0,9 |
| 100000 | 1,1 | 0,9 |
| 500000 | 1,0 | 0,8 |

Furthermore, it can be seen the effect of molecular size on the burning rate of propellant. It turned out that the higher the molecular weight of the polymer, the burning rate of decline despite the relatively small. The decline in the burning rate is applicable for PE and PVC binders. Binder with a higher molecular weight will be denser and harder to burn compared with a binder that is lighter, so that the propellant composition will affect the overall burn rate. Binder has a good burn rate is the binder PE where all molecular weight has a burning rate at least equal to 1.0 cm per second. The observation of the effect of binder content shown in Table 4.3.2, where more and more binder used will provide a lower burning rate. In observation of Table 4.3.2, the binder with a molecular weight above 100000, with increased levels of above 5% binder provides burning rate of less than 1.0 cm per second. Thus, the threshold used is the best PE binder that molecular weight 10000-50000 with grade 5-10%, or 100000 levels with a maximum of 5% level.

Table 4.3.2. Effect binder concentration to burning rate of RDBP propellant

| M _n | Burning rate (cm/sec) | | | |
|----------------|-----------------------|-----------|-----------|------------|
| | 5% binder | 6% binder | 8% binder | 10% binder |
| 10000 | 1,2 | 1,1 | 1,1 | 1,0 |
| 50000 | 1,1 | 1,1 | 1,1 | 1,0 |
| 100000 | 1,1 | 1,0 | 0,9 | 0,9 |
| 500000 | 1,0 | 0,9 | 0,8 | 0,8 |

5. Conclusion

Based on the analysis, it is evident that the polyethylene is the most suitable binder for RDBP propellant manufacturing process. The influence of the molecular weight is very real to the strong mechanical and propellant burn rate, but did not significantly affect the specific impulse and combustion temperature. RDBP propellant has a burn rate above 1.0 cm per second and has a good mechanical powerful at 32 MPa so as to enable use as a replacement material for DB propellant rockets high speed. Levels suggested binder is 5% because it provides the burning rate above 1.0 cm per second for all molecular weight of polyethylene.

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