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Enhancing the propulsion characteristics of rockets by adding the energetic Nitro-hydroxyl-terminated polybutadiene (NHTPB) in the propellant compositions

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Abstract: Replacing the inert binder by an energetic one could increase the specific impulse of the propellants and enhance the propulsion characteristics of rockets. In this study, Nitro-hydroxyl-terminated polybutadiene (NHTPB) was prepared by a simple method. The prepared NHTPB in addition to HTPB binder were characterized. FTIR spectra of both HTPB and NHTPB was determined and compared. The thermal behavior of the prepared NHTPB was studied using DSC technique at heating rate 5 degree/min. A composite propellant based on AP/NHTPB was prepared and the specific impulse was measured for AP/NHTPB using two inch motor. It was concluded that the energetic nitro-hydroxyl-terminated polybutadiene has a clear max. exothermic peak at 203 °C with heat release of 323 J/g. By comparing the results, the prepared propellant AP/NHTPB has specific impulse higher than the traditional AP/HTPB propellant. NHTPB is a promising binder for the application of rocket propellants and needs more tests for its approval.

1. Introduction

The technology used for the production of composite solid rocket propellants (CSRPs) is based on preparing a liquid laquer (binder system) where the solid powders, ammonium perchlorate (AP) and aluminum, are usually added into [1, 2]. The most usable traditional binder is hydroxyl terminated polybutadiene (HTPB) [1]. Other additives are usually used with the binder such as plasticizers and curing agents [3, 4]. HTPB has been used for several years as the main polymer system applied on explosives and CSRPs [5-7]. The perfect thermal stability of HTPB and its ability to produce CSRPs with good mechanical characteristics recommended its distribution in many countries [8-10]. BUT still the inert characteristics of HTPB is the disadvantage for its application [11, 12]. The new trend in the rocket propellants field is probably looking for highly energetic materials to enhance the energy output of the CSRPs and also enhance the mechanical properties of the produced propellants [13-15]. Several energetic binders were prepared and studied to reach this goal such as glycidyl azide polymer (GAP) [16-18] and 3-nitratomethyl-3-methyloxetane (polyNIMMO) [18, 19]. Several publications discussed the performance of GAP in a propelling charges and other studied the thermal behavior of GAP in heterogeneous compositions [20, 22]. The results proved that these binders have not good compatibility with the most usable oxidizer (AP) in comparison with HTPB binder. Also the cost of these advanced binders is high compared with the HTPB. On the other side, GAP has acceptable results in compositions based on ADN oxidizer [22].

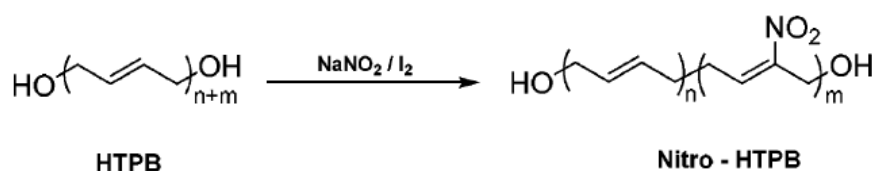


Nitro-hydroxyl-terminated polybutadiene (NHTPB) is a promising binder with energetic characteristics. It is predicted to have a higher performance than traditional used binder (hydroxyl terminated polybutadiene (HTPB)) [23, 24]. It has been published that thermal properties and propulsion characteristics of HTPB propellants are optimum and oblige the companies to use it in filling the rockets [25]. The energetic nitro-group of NHTPB is the main source of increasing the energy output of NHTPB in comparison with the inert HTPB. Few studies were carried out on the preparation of the energetic nitro-HTPB and reported that the characteristics of nitro-HTPB are suitable for its application as a binder for CSRP [26]. It was reported that nitro-HTPB has low viscosity and several isocyanates (aromatic or aliphatic) could be used as curing agent for it. The glass transition temperature of nitro-HTPB is higher than that of HTPB and also NHTPB is compatible with energetic plasticizers [27]. In this study, NHTPB was prepared using a simple method of production. The thermal behavior of NHTPB was checked using DSC technique. The FTIR spectra of both NHTPB and HTPB was obtained and compared with each other to check the presence of energetic group in NHTPB. A propellant based on NHTPB was produced and tested using two inch motor in comparison with CSRP based on the inert HTPB.

2. Results and discussion

2.1. Preparation of NHTPB

NHTPB has been prepared by the following steps; ethyl acetate was used to dissolve the HTPB sample. A mixture of water and ethylene glycol was used to dissolve sodium nitrite then this solution was added to the HTPB solution under continuous stirring. The temperature was decreased to 0 °C then iodine was poured to the mixture and left under continuous stirring for 4 days at 25 °C. The mixture was placed in separating funnel followed by separation of the organic layer and washing it with sodium thiosulphate then neutralized by sodium bicarbonate. The yield was washed by methanol to get rid of the impurities where a viscous liquid of NHTPB was obtained. Scheme 1 clarify the introducing of Nitro group to the polybutadiene chain. A photo of the separation step of NHTPB from the mixture is presented on Fig. 1.



Scheme 1: NHTPB preparation reaction



Fig. 1 NHTPB separation step.

2.2. FTIR spectra

The spectra of both the prepared NHTPB and the raw material HTPB were determined using SHIMADZU 8400 FTIR spectrometer obtained from Japan. The range of the spectra were 400–4000 cm^{-1} , with 40 scans using the methodology of KBr pellet. Figure 2 includes The spectra of NHTPB in comparison with HTPB. It was observed that NHTPB has nearly the same stretching frequency as the original sample (HTPB) with only two more peaks appeared at 1521 cm^{-1} and 1336 cm^{-1} . These two peaks represent the NO_2 symmetric stretch and asymmetric stretch which did not appear in the spectrum of HTPB. These results confirm the the presence of nitro-group in the sample obtained after the preparation method.

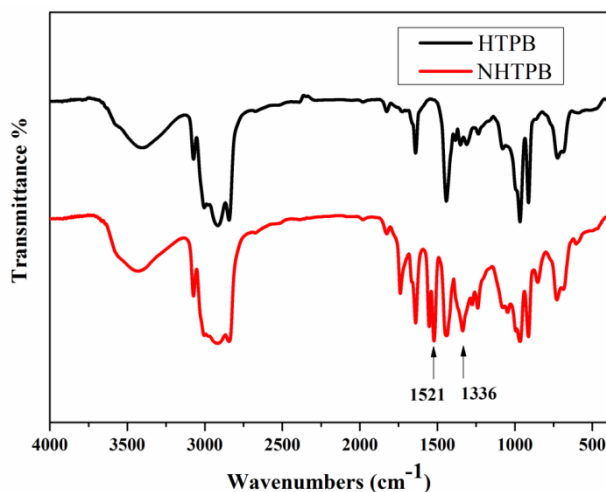


Fig. 2 The FTIR spectra of NHTPB in comparison with HTPB

2.3. DSC measurement

The measurement process is based on obtaining the heat flow at different temperatures for the studied sample. The prepared NHTPB sample was measured using DSC-Q200 of TA instruments. The sample weight was 2 mg placed on Al pan and the non-isothermal technique was used at heating rate of 5 $^{\circ}\text{C}/\text{min}$.

A typical NHTPB thermogram is presented in Fig 3. The measurements started at 25 $^{\circ}\text{C}$ with heating rate 5 $^{\circ}\text{C}/\text{min}$. A decomposition peak of the sample started at onset decomposition temperature of 176 $^{\circ}\text{C}$ and the maximum decomposition peak was observed at 203 $^{\circ}\text{C}$. The end peak of the decomposition process was at 246 $^{\circ}\text{C}$. The heat release due to the exothermic decomposition of NHTPB was 323 J/g. This exothermic peak represents the decomposition of the energetic NHTPB. This result confirms the high exothermicity of NHTPB and gives clear idea about the ability of NHTPB to energy out put to composition on its base.

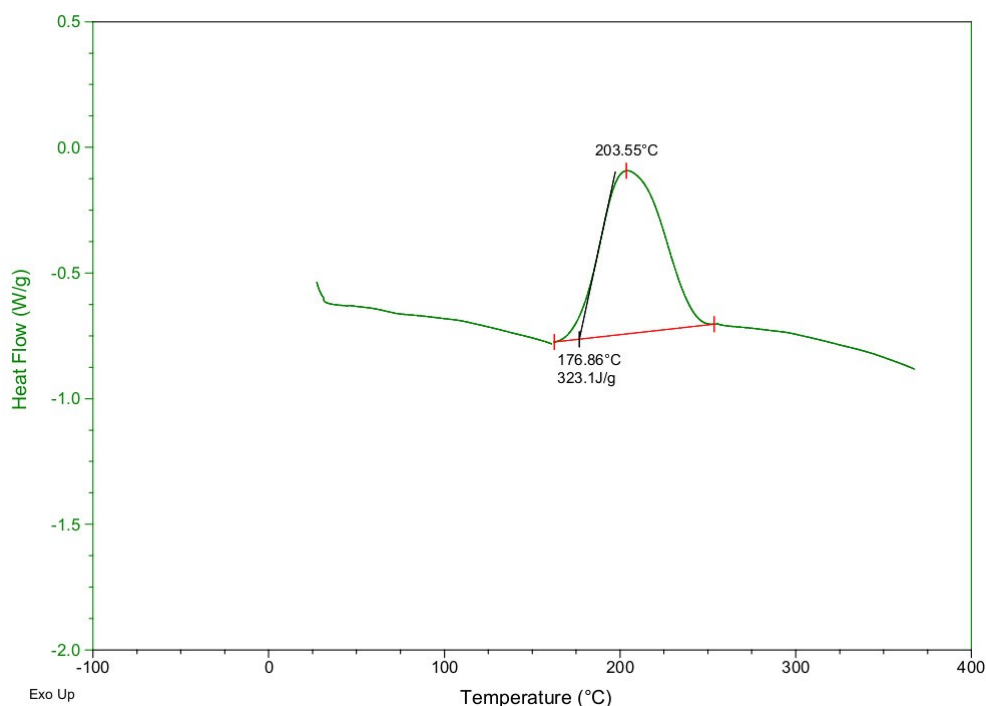


Fig. 3 typical NHTPB thermogram obtained by DSC

2.4. NHTPB composite propellant preparation

NHTPB-CSRP was prepared using 3 gallon mixer. The prepared NHTPB, dioctyl adipate (DOA) and MAPO were placed on the mixer and mixed for 10 min. at 60 °C, and then the solid phase (Ammonium perchlorate and Aluminum) was added in four portions, each portion takes 10 min. Finally the curing agent (HMDI) was added at 40 °C to the mixture during the stirring.

The prepared NHTPB-CSRP was casted and cured for two weeks. Two inch rocket motors were prepared to measure the ballistic performance of the prepared sample. The curing ratio of NHTPB-CSRP (NCO/OH) was 0.7.

2.5. Ballistic performance of NHTPB-CSRP

As mentioned in the preparation part, the prepared NHTPB-CSRP was casted and cured in selected steel cylinders. Two inch rocket motor was used to determine the ballistic characteristics (specific impulse, operating pressure and burning rate) of the prepared sample. The tests were performed using nozzle of 7 mm. In order to compare the results, a traditional HTPB-CSRP was tested under the same conditions used for NHTPB-CSRP. Typical charts of the pressure-time curve of both NHTPB-CSRP and HTPB-CSRP are shown in Fig. 4 and Fig. 5 respectively. Also the ballistic characteristics of both NHTPB-CSRP and traditional propellant are reported in table 1.

Table 1 The ballistic characteristics of the tested samples

Formulations	Pressure (bar)	Burning rate (mm/sec)	Specific impulse I_{sp} (sec)
HTPB-CSRP	109.2	9.86	243.6

NHTPB-CSRP	126.4	10.12	248.4
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It is clear that the NHTPB-CSRP has higher operating pressure than the traditional propellant tested in this study. The burning rate of NHTPB-CSRP has slight increase in comparison with HTPB-CSRP while the specific impulse was significantly increased. These results confirm that the addition of NHTPB instead of HTPB caused a significant enhancement on the ballistic performance of the propellants which should lead to increase on the propulsion characteristics of the rockets.

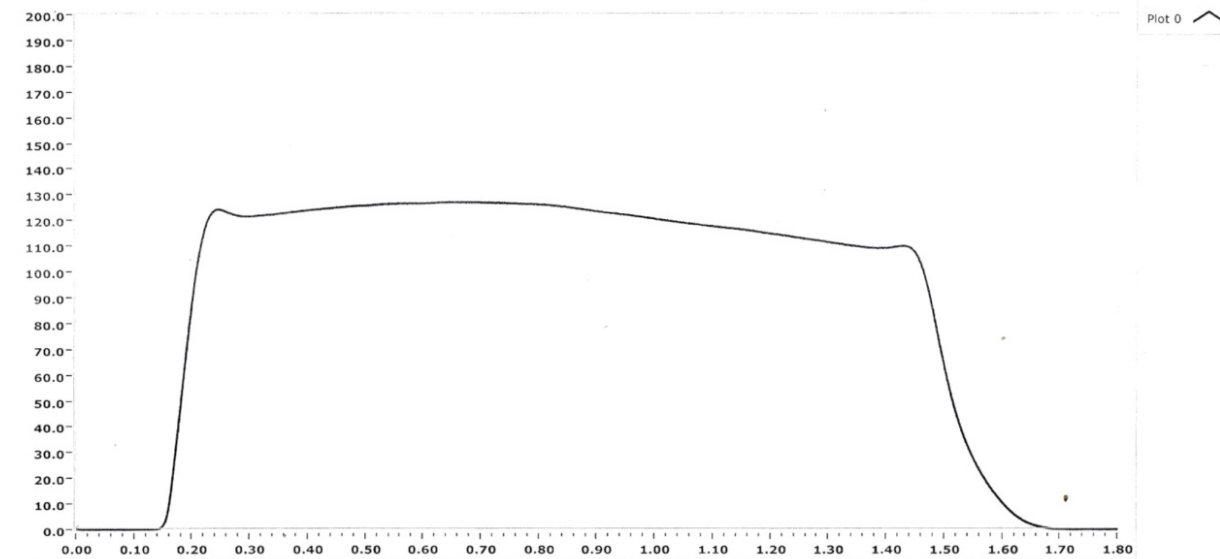


Fig. 4 Pressure-time curve of NHTPB-CSRP

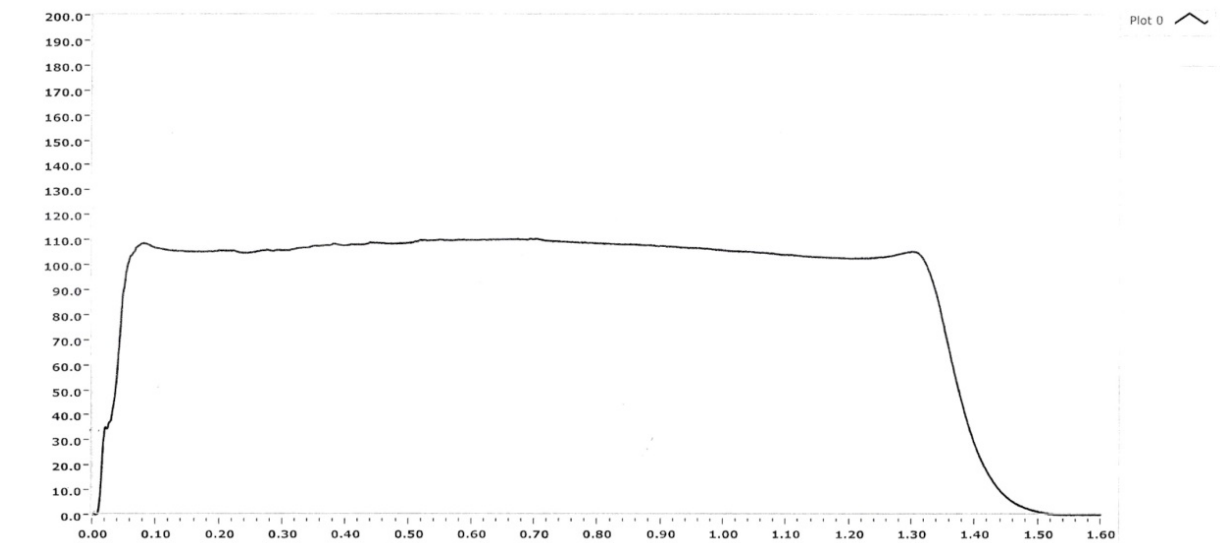


Fig. 5 Pressure-time curve of HTPB-CSRP

3. Conclusion

Nitro-HTPB was prepared successfully on our laboratories. The FTIR spectra confirmed the presence of nitro group on the building units of HTPB after the nitration. On the other side, the high energetic characteristics of the prepared NHTPB was observed as a result of the exothermicity of the decomposition peak of NHTPB. The prepared CSRP based on NHTPB (NHTPB-CSRP) has higher performance than the traditional CSRP based on the inert HTPB; the operating pressure and the specific impulse was significantly increased, while a slight increase on the burning rate was observed in case of NHTPB-CSRP. NHTPB is a candidate to replace HTPB in the composite solid rocket propellants and it is recommended to be under more studies in the near future.

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